Application of the Ultra High Resolution, Low Voltage Scanning Electron Microscopy in the Materials Science

A thesis submitted to the University of Manchester for the degree of Doctor of Philosophy in the Faculty of Engineering and Physical Sciences

2012

Kayoko Kawano

School of Materials

Corrosion and Protection Centre
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Abstract

The University of Manchester

Kayoko Kawano

Doctor of Philosophy in the Faculty of Engineering and Physical Science

Application of the Ultra High Resolution, Low Voltage Scanning Electron Microscopy in the Materials Science

2012

The efficiency of low voltage scanning electron microscopy, which presents near-surface information, has been well known for a long time. However, it is not widely known that the high resolution capability can only be achieved when the surface reveals the original characteristics of the materials without any deterioration due contamination. Therefore, initial attention in this study is directed at clarifying the efficient use of the ultra high resolution, low voltage SEM (UHRLV SEM), (Ultra55, Zeiss). The SEM images and the selected electrons for detection, and damage that occurs through UHRVL SEM observation are also researched. Subsequently, the most efficient specimen preparation technique, which is appropriate for the characteristics of the individual materials, is investigated for galvanized steel, ultrasonically welded alloys of Al6111 and AZ31 alloy, Ti6Al4V alloy honeycomb structure and a ceramic sensor. The outcomes of appropriate specimen preparation technique and use of the extremely Low-Voltage below 2.0 kV, are presented in the results section. The study also presented the challenge of improving the low compositional contrast for the dissimilar materials of aluminium and magnesium, and to reduce charging effects in an insulating material comprising a ceramic sensor. As an application of the surface prepared by the process in this study, 3D tomography is also introduced.
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Acknowledgements

I would like to express my sincere gratitude to my supervisor, Prof. George. E. Thompson and Prof. Kenich Shimizu for providing me this precious study opportunity as a PhD student in The University of Manchester.

I am heartily grateful to Prof. Michael Preuss, Prof. Peter Skeldon, Prof. Phil Prangnell and Dr. Xiaorong Zhou for their elaborated guidance and support during the PhD study.

I would like to acknowledge Dr. Heiner Jaksch and Mr. Patric Chapon for their insightful comments and suggestions with the “state-of-the-art” SEM and GDOES operation respectively.

I would like to express my gratitude to Mr. Akira Fujimoto, Mr. Hiroyuki Oshikawa, Mr. Shigeaki Tachibana, Dr. Takeshi Hanada and Mr. Tomoaki Mitani for their elaborated guidance and considerable encouragement that make my research of great achievement and my study life unforgettable.

I thank to Mr. Gary Harrison, Dr. John Walton, Mr. Paul Jordan, Ms. Shirley Zhong and Mr. Teruo Hashimoto for their valuable support for my experiments. I also thank to the LATEST and LATEST 2 for making my PhD study possible by the financial support.

I would particularly like to thank my personal tutors, Anna, Endzhe and Michele, and my friends, Aleksandra, Cacia, Carlos, Diana, Fabien, Fabio, Francesca, Francisco, Fred, Loreto, Marialuisa, Masakazu, Mirnaly, Nick, Nicolas, Olwen, Raul, Sandra, Simon, Steve, Susan, Yang Wen and Yin for their friendship and companionship during my PhD life in Manchester.

I am indebted to Ayako, Katsuko, Masako, Melek, Nami, Naoko, Tomoko, Zuigaku, my sister Yukako, father, grandma, auntie and most importantly my wonderful husband Michiharu for their understanding, endless patience and encouragement when it was most required.

To the memory of my beloved mother
Chapter 1. Introduction

The technology associated with microscopy has evolved over many years, with ever increasing sophistication. The wide range of microscopy includes, for example, optical microscopy, electron microscopy and atomic force microscopy. Most notably, the recently developed helium ion microscopy may be one of the most leading-edge microscopes (Carl Zeiss, Orion). It is neither scanning electron microscopy (SEM) nor transmission electron microscopy (TEM); it provides resolution of 0.24 nm, which generally can only be achieved by TEM.

In this study, the primary focus has been directed largely to scanning electron microscopy (SEM). Essentially, SEM has advantages compared with TEM. Its observation area is more extensive than TEM; it is also particularly easy to locate the region of interest, for instance, a corroded area. Further, SEM continues to markedly improve the resolution available; it is now equivalent to that of TEM by use of the ultra high resolution, low voltage (UHRLV) SEM (Carl Zeiss, Ultr55).

In general, SEM images result from a combination of secondary electrons and backscattered electrons. The major advantage in the use of the UHRLV SEM is the ability to provide surface sensitive information, using low energy primary electrons which penetrate only the near-surface regions. Because of the sensitivity, the UHRLV SEM image can reveal the original structures of the surfaces, which are difficult to observe by conventional SEM. Thus, sufficient knowledge and comprehension of the UHRLV SEM is required to understand the UHRLV SEM images. The first aspect of this study is to define the mechanism of operation of the UHRLV SEM, including the detector systems, electrons employed, and effects of different acceleration voltages for high resolution imaging. Problems, e.g., charging and beam irradiation damage, and an approach to their solution are also discussed. Several analytical instruments associated with the UHRLV SEM, including energy dispersive X-ray analysis (EDX), electron backscattered diffractions (EBSD) and X-ray diffractions (XRD) are also considered for their functions and efficient usage.
As described, the UHRLV SEM is able to provide surface-sensitive information of the materials. However, the resolution performance of the UHRLV SEM is controlled by the quality of the specimen surface, rather than the SEM. High resolution images can only be achieved when the original structures of the specimen appear on a flat surface without damage and contamination; the previsions is termed and SEM friendly surface (SFS). In order to obtain the SFS, two processes are necessary, surface preparation with general techniques and surface finishing using glow discharge optical emission spectroscopy (GDOES, Horiba Jobin Yvon).

Importantly, appropriate SFS preparation methods were considered for the following materials; galvanized steel, and a joint of Al6111/AZ31 alloys prepared by ultrasonic welding, a Ti6Al4V alloy honeycomb structure and a ceramic sensor. The individual materials were provided by TaTa steel and Professor Prangnell and Ms. Pantel at the University of Manchester, Rolls & Royce and Michell Instruments Ltd respectively.

For the initial preparation process, three different instruments are used depending on their physical and mechanical properties, ultramicrotome (Leica), a mechanical polishing facility (Presi) and a pen-shaped diamond knife. Subsequently, GDOES surface finishing was undertaken for each surface.

The Experimental findings are shown in the Result sections respectively. The microstructures of the surfaces are revealed, including deformation and corrosion propagation. In order to assist further understanding, analytical approaches using EDX and XRD were also undertaken for each material as appropriate. This study also considered the challenging research of improving the issues for high-resolution imaging, e.g., low resolution of the compositional images (ESB images) in dissimilar joint of Al6111 alloy and AZ31 alloy, and charging effects in insulating materials, i.e., a ceramic sensor. An application of SFS to 3D tomography is also considered.

In the final part of the thesis, further UHRLV SEM images are presented in the Appendix. The similar SFS processes, which are described in Section 4.4.2, “Specimen preparation for SFS”, were undertaken on the following materials:

- Commercial stainless steel 304
- stress corrosion cracking stainless steel 304
• proton irradiated stainless steel
• Al10%Zn cold splay carbon steel and Al50% Zn mild steel
• aluminium alloys (Al4%Cu, Al1901, Al2024, Al2025 and Al7075)
• magnesium WE43 alloy and corrosion tested WE43 alloy in 3.5% NaCl solution for 1h
• CPU / Central processing unit of computer
• sea cultured pearl

The details of individual SFS processes are also explained with the images. Accordingly, it is revealed that the SFS preparation and the UHRLV SEM can be used effectively for surface observation of various types of materials.
Chapter 2. Literature Survey

2.1. Introduction

In order to understand the UHRLV SEM images, it is necessary to clearly appreciate the operation of the UHRLV SEM, including the importance of the Low-Voltage primary electrons and generated electrons. This is because the UHRLV SEM image can show extreme surface sensitive information compared with conventional SEM. In this study, the following instrument and associated facilities were used to provide the required understanding, Ultra55 (UHRLV SEM, Carl Zeiss), INCA (EDX, Oxford instruments) and Channel 5 (EBSD, Oxford instruments). Monte Carlo simulation (Casino) was frequently used to research the relations between the primary electron energy and trajectory in the solid target. Further, appropriate specimen preparation methods with GDOES surface finishing are introduced in this section. Problems and damage during UHRLV SEM observation and their solutions are also considered.

2.2. SEM and Low-Voltage SEM

The fundamental scanning electron microscope (SEM) was established in 1935 by Knoll. Three decades later in 1965, the initial commercial SEMs were developed by Cambridge Scientific Instruments and JEOL [1, 2]. A range of acceleration voltages of 10.0 kV to 20.0 kV was generally used for imaging at that time; the resolution was usually stated as 50 nm. Since then, the technology has made enormous progress, especially with the development and introduction of field-emission electron guns. Importantly, the UHRLV SEM may now achieve equivalent results to TEM in terms of resolution, which is 1.7 nm of at an acceleration voltage of 1.0 kV.

SEM is a type of electron microscope for observing material surfaces and cross-sections by scanning an electron beam. The SEM comprises an electron gun, a filament,
electrostatic/electromagnetic lenses, scan coils and detector systems. The detector systems recognize two types of electrons, namely secondary electrons and backscattered electrons.

In general, an SEM using electron energies in the range of 0.5 to 5.0 keV is termed a Low-Voltage SEM [3]. A relatively short working distance between the specimen and the final lens is frequently used; the working distance is less than 5.0 mm in the Low-Voltage SEM.

Previous studies have demonstrated that the Low-Voltage SEM is capable of revealing surface sensitive information as a result of the low penetration depth of primary electrons, which reduces charging effects and increases secondary electron yield [2-12].

The surface sensitivity in the Low-Voltage SEM can be explained using Monte Carlo simulation [13-15]. For instance, according to the simulation, comparing the acceleration voltages of 0.5 kV and 15.0 kV, the penetration depths of primary electrons reaches the levels of 8 nm and 2 μm from the surface respectively; the area is similar to the area of secondary electrons generation (Figure 2.1). Further, backscattered electrons are generated in a region from within 4 nm of the surface at 0.5 kV, but the region expands to 500 nm from the surface at 15.0 kV (Figure 2.1). Thus, in a simple comparison of the simulation results, it is apparent that an acceleration voltage of 0.5 kV can be used to show surface sensitive information.

As described, a Low-Voltage is also an effective technique for the minimizing charging effects. Thus, this technique is frequently used for examining insulating materials, such as semiconductors and biological tissues [16]. The mechanism of charging and reduction of its effect are also described in Section 2.5, “Damage”.

2.3. Electrons

After the incident primary electrons reach the surface, elastic and inelastic scattering occurs in the material. As a result of elastic scattering, secondary electrons and characteristic X-rays are generated with loss of electron energies. Backscattered electrons are generated with high energies after inelastic scattering without loss of energy. These generated electrons are detected
in individual detectors depending on the type of electrons; characteristic X-rays are detected by EDX, which allows identification of the elements.

### 2.3.1. Secondary Electrons

Multiple secondary electrons will be generated as a result of elastic scattering after the incident primary electrons reaches the specimen surface (Figure 2.2). However, the generation of secondary electrons is not directly related to the atomic numbers. Thus, unlike backscattered electrons, it is difficult to discuss material composition using secondary electrons.

Secondary electrons 1 (SE1) are generated from the centre area of the incident primary electron beam. Secondary electrons 2 (SE2) are generated at greater distances from the centre spot after multiple scattering events. Secondary electrons 3 (SE3) are generated by backscattered electrons after hitting the SEM chamber and the specimen itself (Figure 2.2). Among those secondary electrons, SE1 and SE2 are the only valid signals for UHRLV SEM imaging.

### 2.3.2. Backscattered Electrons

Backscattered electrons are generated after inelastic scattering without loss of electron energy. The elements have individual electron energies which are in the order of atomic number. Therefore, the image using backscattered electrons can present compositional information of the surface; the contrast of the elements becomes brighter with increasing atomic number.

The backscattered coefficient, which is the ratio of the generated backscattered electrons yield to the primary electrons yield, is affected by an acceleration voltage. It may be related to the resolution ability of the backscattered electrons.

According to a previous study [3], for elements of atomic number below 30, the highest ratio of the backscattering coefficients can be obtained at an acceleration voltage of 0.5 kV and incident angle of 0 ° (Figure 2.3). The coefficients decrease with increasing acceleration voltages, with
the lowest ratio obtained at an acceleration voltage of 5.0 kV. In this study, the backscattered coefficients were also calculated in aluminium and magnesium at acceleration voltages between 0.5 kV and 15.0 kV using Monte Carlo simulation (Table 2.1). According to this, the backscattering coefficient decreases with increasing acceleration voltage, which corresponds to the previous study. In other words, it is clear that increasing the primary electron yield can not increase the backscattered electron yield. Further, it is also revealed that the backscattering coefficient is increased when the incident angle increases (Table 2.2 and Figure 2.4). For instance, at the incident angle of 70°, the backscattering coefficient has increased twice that at an incident angle at 0° at an acceleration voltage of 0.5 kV; it increases approximately four times at 5.0 kV.

As described, backscattering coefficients are affected by the primary electron energies and the incident angle. Thus, it is necessary to consider the impact of the backscattering coefficient on the backscattered electrons image resolution capabilities, at varied acceleration voltages and incident angles. It is one of the important studies, especially for the USW joint of Al6111 / AZ31 alloys in this study. This is because the alloys include dissimilar materials of aluminium and magnesium; it may be difficult to present both alloys independently in high contrast backscattered electron images.

2.3.3. Mott Scattering Electrons

Mott scattering electrons are generated from about 10 nm below the surface at relatively high acceleration voltage. They provide to depth information as well as the crystallographic orientation of the surface. Differences in Mott scattering electron yields on the surface is termed as channelling contrast, which consists of the AsB image (Section 2.4.4, “AsB Detector”)[17].
2.4. Ultra High Resolution, Low Voltage (UHRLV) SEM

The detector systems of the Ultra 55 are presented in Figure 2.5 [18]. In order to clarify differences of the individual detectors, the cross-sectional image of aluminium 4% copper alloy is presented in Figure 2.6 and Figure 2.7.

2.4.1. In-lens detector

The In-lens detector, which can detect secondary electrons 1 (SE1) and secondary electrons 2 (SE2), is located above the magnetic lens (Figure 2.5). Secondary electrons are not directly related to the atomic number orders; the In-lens image shows the surface potential mapping using the yield of generated secondary electrons from the surface without compositional information. Thus, the In-lens image is often affected by edge effects and charging effects. For instance, edge and negatively charged areas on the surface are often presenting brighter contrast than other areas (Figure 2.6.a). The mechanism of charging is described in Section 2.5.2, “Charging”.

2.4.2. SE2 Detector

The SE2 detector is located below the magnetic lens (Figure 2.5). Combinations of secondary and backscattered electrons are used for the SE2 imaging. Unlike the In-lens detector, charging is not often evident in the SE2 image. This is because the SE2 detector uses backscattered electrons, which are less affected by charging and edge effects, and include depth information. Thus, it is possible to understand surface topography and roughness using the SE2 image (Figure 2.6.b).
2.4.3. **ESB Detector and the Filtering Grid**

The ESB (energy and angle selected backscattered electrons) detector is located above the In-lens detector and the filtering grid (Figure 2.5); the surface sensitive compositional information enables to be obtained (Figure 2.7.a).

The filtering grid voltage, which can generate an electric field above the In-lens detector, is absolutely imperative for high resolution ESB imaging. This is because the filtering grid can avoid low-energy secondary electrons, which overlap with backscattered electrons (Figure 2.8) [18]. This is the major difference from the conventional backscattered electrons detector (BSD); a BSD will show compositional information along with crystallographic contrast because the detector can not separate backscattered electrons and low-energy secondary electrons.

The filtering grid voltage is able to select voltages in the range from 0 V to 1500V. It is necessary to select an appropriate voltage at which the high-energy backscattered electrons can only reach the ESB detector. Using the Monte Carlo simulation, backscattered electrons energies are able to be simulated at each acceleration voltage (Figure 2.9). According to the simulation in aluminium and magnesium, the filtering grid voltage is able to select the range from 250 V to 300 V, at an acceleration voltage of 0.5 kV. Similarly, the energy range from 750 V to 800 V may be suitable at an acceleration voltage of 1.5 kV; that of 1500 V may also be suitable at an acceleration voltage above 2.5 kV.

As described in Section, 2.3.2, “Backscattered Electrons”, it is required to consider the effect of the primary electron energies and or the incident angles to the backscattered electron image. In addition to that, it is also required to consider the effect of the filtering grid voltages in obtaining the high resolution ESB image, especially for aluminium and magnesium in this study.

2.4.4. **AsB Detector**

The AsB detector is located below the magnetic lens (Figure 2.5). It can show the channelling contrast of the materials using Mott-backscattering electrons, which include crystallographic
information and compositional information from approximately 10 nm below the surface (Figure 2.7.b). Although the AsB detector generally requires a high acceleration voltage, it is useful to employ when crystallographic information is required from an extensive area. The reason is that the Low-Voltage ESB observation requires a relatively short working distance (Section 2.2, “SEM and Low-Voltage SEM”), which is not suitable condition to observe a wide area.

2.5. Damage

Damage may be evident on the specimen surface from the commencement of specimen preparation to the completion of SEM observation; it interferes with the high-resolution imaging process. In this section, damage including contamination, charging and beam irradiation damages, are considered in order to understand their mechanisms and individual solutions.

2.5.1. Contamination

It is necessary to minimize contamination, but it is difficult to avoid it completely eliminate it from the surface because specimen preparation is generally undertaken in the air. Thus, in most cases, contamination includes insulating dust and hydrocarbons. Insulating contamination often induces charging on the surface, and it contributes to the electron beam instability. Further, during the SEM observation, hydrocarbons on the surface increase the thickness which will degrade the surface sensitivity (Section 2.5.3, “Beam Irradiation Damage”). The mechanism of charging and the approach for minimizing contamination are discussed in Section 2.5.2, “Charging” and Section 2.7.3, “GDOES Surface Finishing” respectively.
2.5.2. Charging

Charging is caused by the differences in the yields of accumulated electrons in the specimen, and secondary and backscattered electrons which are emitted from the surface. Depending on the balance of the electron yield, charging is namely categorized as positive charge and negative charge.

For insulating specimens, the charging and the total electron yields are presented in Figure 2.10; the secondary electron yield and the backscattered coefficient are represented as \( \sigma \) and \( \eta \) respectively [3]. Positive charge occurs when the incident electron energy, \( E \), is \( E_1 \leq E \leq E_2 \) (\( E_1 \) and \( E_2 \) are the critical energies for charging). This is because the yield of electrons emitted as secondary electrons and backscattered electron are greater than the electrons accumulated in the specimen. Thus, the positively charged area usually presents a dark contrast in the In-lens image. On the other hand, negative charge occurs when the electron energy, \( E \), is \( E \leq E_1 \) and \( E \geq E_2 \). Compared with the electrons accumulated inside the specimen, fewer secondary electrons and backscattered electrons are generated. As a result, the negatively charged area presents a bright contrast in the In-lens image.

Using a similar principle, charging in the conducting specimen can be explained; it often occurs when insulating contamination is present on the conductive material surface (Figure 2.11.a). Further, previous studies revealed that charging is affected by the acceleration voltages and electron beam scanning speed [3]. For instance, when a slow scan speed is selected at an acceleration voltage of 15 kV, an insulating contamination on the surface is negatively charged but the surface beneath contamination is positively charged. This is because the electron probe slowly passes through a point of the surface; more electrons are accumulated in contamination, more secondary and backscattered electrons leave from the surface below contamination. Thus, insulating contamination is shown in strong bright contrast and the surface beneath that contamination is shown in dark contrast (Figure 2.11.b). Charging contrast slightly reduces when a scanning speed increased at the same acceleration voltage; however, the positive charge beneath contamination expands the area (Figure 2.11.c). In both cases, it makes it difficult to discuss what the original feature of the surface is in both cases. In contrast, when the surface is scanned slowly at an acceleration voltage of 1 kV, the negative charge of an insulating
contamination changes to the positive charge. Further, charging is not evident on the surface (Figure 2.11.d). Therefore, it is clear that the Low-Voltage technique enables reduction of the charging effect; thus it can be useful for insulating materials, i.e., for a ceramic sensor in this study.

Additionally, a conductive coating is commonly used to coat the insulating specimen surfaces in order to avoid the charge on the surface. However, in this study, surface observation in the ceramic sensor was undertaken without any conductive coating. As the previous studies of the author has been involved, that contamination and charging van be minimized by appropriate specimen preparation and Low-Voltage observation without the need for the conductive coating. This is because previous studies, which involved the author, proved that contamination and charging are able to be minimized by appropriate specimen preparation and Low-Voltage observation without a conductive coating [19-24]. The conductive coatings may produce gas which increase hydrocarbons inside the chamber; it may interrupt the surface sensitive imaging in the high resolution.

2.5.3. Beam Irradiation Damage

Hydrocarbon deposition is a form of contamination, which is difficult to avoid during SEM observation (Figure 2.18). Hydrocarbon molecules generally exist on the specimen surface and also in the SEM chamber because specimen preparation is generally undertaken in air, and the vacuum system of an SEM generally uses an oil diffusion pump [25]. Beam irradiation damage occurs because hydrocarbons increase in thickness by primary electron beam irradiation, and, eventually, a relatively thick layer of hydrocarbons can interrupt sufficient detection of secondary and backscattered electrons by the SEM detector [26-28].

In recent years, plasma cleaning has been developed to remove hydrocarbons [29]. This newly in developed plasma cleaner is generally located in the SEM chamber; thus, it is possible to use the cleaner shortly after surface observation. In this study, glow discharge optical emission spectroscopy (GDOES, Horiba Jobin Yvon) was employed instead of a plasma cleaner. It is located outside in the UHRLV SEM. However, by using a gentle argon ion plasma, it is possible
to remove hydrocarbons without significant damage. The mechanism of GDOES is described in Section 2.7.3, “GDOES surface finishing”.

2.6. Corresponding Analytical Instruments and Applications

2.6.1. Energy Dispersive X-Ray Analysis

Energy dispersive X-ray spectroscopy is known as EDX. The detector for EDX is generally located in the SEM chamber. Thus, it enables in-situ elemental analysis detection after observation. The analytical range of elements is generally from boron to uranium.

The EDX detector can discriminate the elements and approximate their quantities using characteristic X-rays [30]. Characteristic X-rays are generated when the transition occurs after primary electrons collide with atoms and remove an electron from the inner shell (Figure 2.12.a and Figure 2.12.b). The vacancy in the inner shell is filled with an outer electron. The characteristic X-rays are classified depending on the distance of the electron jump. For instance, when a vacancy is filled by an electron from an adjacent shell, it is termed as $\alpha$ X-rays. Similarly, depending on the length of the electron jump distance, the characteristic X-rays are also termed as $\beta$ X-rays and $\gamma$ X-rays respectively (Figure 2.12.c).

In recent years, two comparable EDX detectors have become available, which are the Si (Li) detector and the Silicon Drift Detector (SDD) [31]. Table 2.3 presents the contrasting features of the Si (Li) and the SDD. In this study, EDX analyses were undertaken using the Si (Li) detector because it was located in the UHRLV SEM.

The Si (Li) detector uses lithium. Lithium can be mobile at room temperature, and easily diffuses into silicon at a high temperature during EDX analysis. Therefore, cooling with liquid nitrogen is necessary to prevent lithium diffusion, but it may bring vibration problems during analysis [32]. Further, the Si (Li) detector generally requires a longer analysis time than the SDD.

According to recent studies [32-35], it appears that the SDD detector has greater energy resolution compared with the Si (Li) detector; it can clearly distinguish light elements such as
boron, carbon, nitrogen, oxygen using the SDD tip. This is because the energy resolution of the SDD tip is relatively high compared with the Si (Li) detector. Further, it is a nitrogen-free instrument, so there is no need to consider vibration problem. It appears that the SDD detector may be suitable for surface sensitive EDX analysis; however, further verification is required.

A further consideration for achieving surface sensitive EDX analysis is the acceleration voltage. In general, in order to increase the yields of characteristic X-rays, high acceleration voltages and a large aperture are required for EDX analysis compared with surface observation. Further, it is also generally considered that more accurate data are obtained after sufficiently long analysis times. However, compared to acceleration voltages of 2.0 kV and 15.0 kV, the X-rays are apparently generated from the more extended area at an acceleration voltage of 15.0 kV (Figure 2.13). Further, due to use of a large aperture, the broad incident electron beam may overlap on the surface and electron beams may drift during a long analysis time. Overall, EDX analysis at a high-acceleration voltage can not provide surface sensitive information. Therefore, low acceleration voltage is also preferable for the EDX.

The advantage of the Low-Voltage EDX is able to emit the low energy X-ray from near the surface region. For example, Figure 2.14 shows the peak position of the K and L lines X-rays for major elements, including the elements required in this study at an acceleration voltage of 2.0 kV. According to this, the peaks are separated in most elements; thus, theoretically, it is possible to provide surface sensitive information at an extremely low acceleration voltage of 2.0 kV.

Therefore, in order to obtain surface sensitive EDX analysis, the sensitive EDX detector and low acceleration voltage may be necessary.

Additionally, beam irradiation damage is often present on the surface after EDX analysis. Although, the accumulated hydrocarbons can be removed by the GDOES (Section 2.7.3, “GDOES surface finishing”), it is recommended to perform EDX analysis after the observation, rather than before, in order to improve efficiency of the research.
2.6.2. Electron Backscattering Diffraction

Electron backscattering diffraction (EBSD) is an instrument that is employed to analyze the crystal orientations using diffraction patterns of backscattered electrons which are generated by diffraction from a crystallographic plane. The widths and strength of the bands always correspond to the lattice constant and crystallographic structure; the intersecting angle and the position of a band differ for each crystallographic orientation. Further, the orientation and numbers of the slip plane are defined depending on the crystallographic structures (Table 2.4). The majority of common metals are represented by three main crystallographic structures, namely the face centre cubic (FCC), body centre cubic (BCC) and hexagonal closed-packed (HCP). Using EBSD, it is possible to identify the characteristics of the materials, e.g., grain size and grain boundaries, crystallographic orientation and deformation, which determine the material behavior [36-38]. For the EBSD analysis, specimen is required to be tilted to 70°. It is related to the fact that high yield backscattered electrons are emitted from the surface at incident angle of 70° (Section 2.3.2, “Backscattered Electron”).

2.6.3. X-Ray Diffraction

Since the discovery of X-rays by Röntgen in 1865[39], X-ray diffraction (XRD) become a major method of identification of materials, i.e. symmetry elements and lattice planes, using X-ray diffraction patterns.

After constant wavelength X-rays are irradiated on the material, dispersion X-rays are generated from an atom in a crystal. Those dispersion X-rays are interfered with each other; accordingly, specific diffraction patterns appear depending on the atoms and molecular sequence of the materials.
2.6.4.  3D Tomography

Three dimensions (3D) imaging is one of the most advanced technologies which is frequently used in recent years. 3D tomography may contribute to the development of materials science because it is possible to compensate for the lack of information by 2D, e.g., the exact location of corrosion, form of the grains and deformation structures.

It is possible to construct 3D tomography with various instruments. For instance, X-Ray tomography has been widely used in recent researches since the discovery of X-rays [39]. The latest X-Ray tomography instrument reaches a resolution of approximately 1μm [40].

Meanwhile, it is also possible to produce 3D tomographic image using TEM and SEM, with resolutions corresponding to the individual instrument capabilities. The images are generally automatically recorded; 3D tomography is obtained after manual reconstruction of the images using special software. However, TEM and SEM are not suitable for all materials. It is difficult to utilize them for materials with high hardness, such as stainless steel. Thus, the leading-edge technology of the focused ion beam (FIB) is frequently used to produce 3D tomography for those hard alloys.

2.7.  Damageless Specimen Preparation

2.7.1.  Introduction of SEM-Friendly Surface (SFS)

The advantage of low voltage SEM, which is able to produce surface sensitive information, was indicated by Shimizu et al. in [11]. In particular, the importance of the achieving an SEM friendly surface (SFS) was revealed in these studies [19, 20]. The SFS is a clean and flat surface with original features of the material presented. It is a prerequisite, especially for the UHRLV SEM observation because when the surface is deformed or contamination and oxide products are present on the surface, the image is modulated by them. Accordingly, this makes it impossible to observe the original features.
The SFS is generally produced using two processes, a general surface preparation and surface finishing using GDOES.

**Figure 2.15** shows the SFS and Non-SFS in stainless steel. It is revealed that the surface finishing process enhanced the original features of the materials, by removing contamination.

### 2.7.2. Specimen Preparation

As an initial step of SFS, it is requires to create a clean, flat and smooth surface rapidly, using, for example, an ultramicrotome or a mechanical polishing facility [11]. The specimen preparation methods may vary depending on the characteristics of the materials in order to avoid generating deformation on the surface. Further, flatness and smoothness of the surface are necessary for GDOES surface finishing. The reason is that contamination and roughness on the surface will induce air leaks and interrupt uniform surface finishing.

After the initial preparation process, GDOES surface finishing is undertaken on the specimen. The initial surface preparations, which are appropriate for individual characteristics of materials, are described in the Experimental procedure.

### 2.7.3. GDOES Surface Finishing

In order to remove contamination, a surface finishing process is generally required after initial surface preparation. Since Low-Voltage electrons reach only the near surface region, contamination and oxide products are present on the surface, obscure the original features of the surface.

A surface finishing technique using GDOES, which is generally used for elemental depth profiling analysis, has been introduced by Shimizu [11]. A GDOES system is specified in **Figure 2.16**. In order to commence GDOES surface finishing, two conditions of GDOES are required. Firstly, the anode should be clean because contamination from the anode will be deposited on the surface during the sputtering process. Secondly, it is also necessary to wait until the inner
pressure is stabilized for homogeneous sputtering. Instability of the inner pressure will cause inhomogeneous sputtering.

After the stabilized condition is reached, the specimen surface is gently sputtered with an argon ion plasma with low ion energy of \(< 50 \text{ eV}\), and low ion current density from \(100 \text{ mA / cm}^2\) [41].

The effect of argon ions on the surface is able to be simulated using SRIM, which is able to calculate the stopping and range of ion (up to 2 GeV/amu) into matter using a quantum mechanical treatment of ion-atom collisions [42]. According to the simulation of the argon ion impact area for bulk aluminium, argon ions are able to reach only the area of 2 nm in diameter (Figure 2.17).

Further, the surface finishing is generally obtained in 10 seconds. Thus, using this specific ability, contamination is removed from the surface and the original structures of the surface may be enhanced without little significant change of the surface. Eventually, the SFS can be produced instantly [20, 21, 23].

Additionally, this unique ability of GDOES can be used for surface cleaning after surface observation, instead of using a plasma cleaner [25]. As described in Section 2.5.3, “Beam irradiation damage”, the specimen surface is contaminated through an electron beam irradiation and associated with hydrocarbon accumulation (Figure 2.18.a). Once a specimen is contaminated by hydrocarbon, it is difficult to observe the same area again. However, the surface can be observed repeatedly after GDOES (Figure 2.18.b), because each individual treatment nearly completely removes hydrocarbon from the cross-section without inflicting any damage.
Tables

**Table 2.1.** Backscattering coefficients of magnesium and aluminium at acceleration voltages between 0.5 kV and 15 kV and incident angle of 0°, calculated by Monte Carlo simulation using electrons of 200,000.

<table>
<thead>
<tr>
<th>Acceleration voltage</th>
<th>Mg (%)</th>
<th>Al (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5 kV</td>
<td>0.227985</td>
<td>0.258005</td>
</tr>
<tr>
<td>1.0 kV</td>
<td>0.199630</td>
<td>0.227340</td>
</tr>
<tr>
<td>1.5 kV</td>
<td>0.187665</td>
<td>0.209690</td>
</tr>
<tr>
<td>2.0 kV</td>
<td>0.174955</td>
<td>0.200455</td>
</tr>
<tr>
<td>2.5 kV</td>
<td>0.170765</td>
<td>0.191770</td>
</tr>
<tr>
<td>3.0 kV</td>
<td>0.165005</td>
<td>0.185460</td>
</tr>
<tr>
<td>3.5 kV</td>
<td>0.159915</td>
<td>0.180645</td>
</tr>
<tr>
<td>4.0 kV</td>
<td>0.156390</td>
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<tr>
<td>4.5 kV</td>
<td>0.153520</td>
<td>0.172425</td>
</tr>
<tr>
<td>5.0 kV</td>
<td>0.145415</td>
<td>0.170720</td>
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<tr>
<td>10.0 kV</td>
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</tr>
<tr>
<td>15.0 kV</td>
<td>0.125075</td>
<td>0.141490</td>
</tr>
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Table 2.2. Backscattered coefficient of magnesium and aluminium at acceleration voltages between 0.5 kV and 5 kV and incident angle of 70°, calculated by Monte Carlo simulation using electrons of 200,000.

<table>
<thead>
<tr>
<th>Acceleration voltage</th>
<th>Mg(%)</th>
<th>Al (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5 kV</td>
<td>0.519110</td>
<td>0.542655</td>
</tr>
<tr>
<td>1.0 kV</td>
<td>0.503815</td>
<td>0.526410</td>
</tr>
<tr>
<td>1.5 kV</td>
<td>0.495180</td>
<td>0.518830</td>
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<tr>
<td>2.0 kV</td>
<td>0.489925</td>
<td>0.510050</td>
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<tr>
<td>2.5 kV</td>
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<td>0.504255</td>
</tr>
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<td>3.0 kV</td>
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<tr>
<td>3.5 kV</td>
<td>0.480995</td>
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<td>5.0 kV</td>
<td>0.474820</td>
<td>0.491140</td>
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Table 2.3. Features of silicon drift EDX detector (SDD) and Si (Li) EDX detectors [31].

<table>
<thead>
<tr>
<th>Features</th>
<th>Detector</th>
<th>SDD</th>
<th>Si(Li)</th>
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<tr>
<td>Resolution</td>
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<td>123 eV</td>
<td>140 eV</td>
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<tr>
<td>N2(refrigeration)</td>
<td></td>
<td>No</td>
<td>Required</td>
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<tr>
<td>Vibration</td>
<td></td>
<td>No</td>
<td>exist</td>
</tr>
<tr>
<td>Analysis time</td>
<td></td>
<td>short</td>
<td>Longer than SDD</td>
</tr>
<tr>
<td>Energy resolution</td>
<td></td>
<td>high</td>
<td>Lower than SDD</td>
</tr>
<tr>
<td>Signal saturation in the High incident X-Ray dosage</td>
<td></td>
<td>No</td>
<td>easy to saturate</td>
</tr>
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Table 2.4. Crystallographic structures and slip systems in major metals [36].

<table>
<thead>
<tr>
<th>Crystal structure</th>
<th>Metals</th>
<th>Slip plane</th>
<th>Slip direction</th>
<th>Number of slip plane</th>
</tr>
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<tr>
<td>FCC</td>
<td>Cu, Al, Ni, Ag, Au</td>
<td>{111}</td>
<td>&lt;110&gt;</td>
<td>12</td>
</tr>
<tr>
<td></td>
<td>α-Fe, W, Mo</td>
<td>{110}</td>
<td>&lt;111&gt;</td>
<td>12</td>
</tr>
<tr>
<td></td>
<td>α-Fe, W</td>
<td>{211}</td>
<td>&lt;111&gt;</td>
<td>12</td>
</tr>
<tr>
<td></td>
<td>α-Fe, K</td>
<td>{321}</td>
<td>&lt;111&gt;</td>
<td>24</td>
</tr>
<tr>
<td>HCP</td>
<td>Cd, Zn, Mg, Ti, Be</td>
<td>{0001}</td>
<td>&lt;1120&gt;</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>Ti, Mg, Zr</td>
<td>{10T0}</td>
<td>&lt;1120&gt;</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>Ti, Mg</td>
<td>{10T1}</td>
<td>&lt;1120&gt;</td>
<td>6</td>
</tr>
</tbody>
</table>
Figure 2.1. (a) Schematic diagrams showing primary electron (blue) and backscattered electron (red) trajectories in aluminium at different primary electron energies and incident angle of 0°, simulated by the Monte Carlo simulation using electrons of 200,000: (a) acceleration voltage of 1.0 kV; (b) that of 15.0 kV. At an acceleration voltage of 0.5 kV, primary electrons penetrate approximately 8.0 nm from the surface and backscattered electrons are generated from 4.0 nm from the surface. Meanwhile, the penetration depth is approximately 2 μm and backscattered electrons are generated beneath from 500 nm the surface when an acceleration voltage is 15.0 kV.
Figure 2.2. Schematic represent showing varieties of electrons, including secondary electrons 1 (SE1), secondary electrons 2(SE2), secondary electrons 3(SE3) and backscattered electrons (BSE). Individual electrons are generated after primary electrons penetrate the specimen surface. For example, SE1 is generated near the spot centre; SE2 is generated at greater distance from the spot centre. SE3 is generated by backscattered electrons after hitting the SEM chamber or specimen surface. BSE is generated after inelastic scattering without loss of electron energy.
Figure 2.3. Schematic diagram showing the backscattering coefficient distributions on atomic number Z at different electron energies E and incident angle $\varphi = 0^\circ$ [3]. In theory, the highest backscattering coefficient is obtained at a primary electron energy of 0.5 keV, if atomic number is below 30.
Figure 2.4. Schematic diagram showing the distribution of the backscattering coefficients in aluminium at different primary electrons energies and the range of incident angles, $\phi$, is $0^\circ$ to $80^\circ$ [3]. At each primary electron energy, with increasing incident angles, backscattering coefficients are gradually increased.
<table>
<thead>
<tr>
<th>Detectors</th>
<th>Electrons</th>
<th>Characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td>ESB</td>
<td>Backscattered electrons</td>
<td>Compositional image</td>
</tr>
<tr>
<td>In-lens</td>
<td>Secondary electrons (SE1, SE2)</td>
<td>Surface mapping using potential difference of SE</td>
</tr>
<tr>
<td>SE2</td>
<td>Secondary electrons and backscattered electrons</td>
<td>Surface topographic image</td>
</tr>
<tr>
<td>ASB</td>
<td>Mott scattering electrons</td>
<td>Channelling contrast image</td>
</tr>
</tbody>
</table>

**Figure 2.5.** Schematic diagrams showing the detector system of UHRLV SEM (Ultra55, Zeiss). Electrons for imaging, and characteristics of individual images are also presented. In order to clarify the difference from the ESB detector, the characteristics of a conventional BSE detector are also shown; it generally presents compositional information including crystallographic contrast.
Figure 2.6. Scanning electron micrographs showing the cross-sectional images of the Al4%Cu alloy after thermal treatment at 180 °C for 24 h. An acceleration voltage of 1.5 kV was used: (a) In-lens image; surface potential map using secondary electron yield differences: (b) SE2 image of (a); topographic image with surface roughness. The individual images show the grain boundaries, second phase particles and precipitates. Edge effects are evident in the In-lens image.
Figure 2.7. Scanning electron micrographs showing the cross-sectional images of the Al4%Cu alloy after thermal treatment at 180 °C for 24h: (a) ESB image at an acceleration voltage of 1.5 kV; (b) AsB image of (a) at an acceleration voltage of 15.0 kV. The ESB image shows the compositional information near the surface region with slight influence of surface roughness. The AsB image shows the channelling contrast, which represents the crystallographic information of the surface and beneath the surface region.
Figure 2.8. Radial distribution of backscattered electrons and secondary electrons, reference from [18]. A region where the low energy BSE and SE overlap is shown. SE may be detected by the ESB detector as BSE [18]. Thus, in order to obtain the compositional image with surface sensitivity, it is necessary to use an appropriate filtering grid voltage to avoid the overlapped region.
Figure 2.9. Schematic diagrams showing the backscattering energy distribution in aluminium and magnesium, calculated by Monte Carlo simulation using electrons of 200,000; the range of acceleration voltage is 0.5 kV to 5.0 kV, with an incident angle of 0°. The black dashed lines indicate the filtering grid voltages which appear to be most appropriate: (a) 250 V at acceleration voltage of 0.5 kV; (b) 750 V at acceleration voltage of 1.5 kV; (c) and (d) 1500 V at acceleration voltages of 2.5 kV and 5.0 kV. The filtering grid voltage can be selected between 0 V and 1500 V. For surface sensitive compositional image, the filtering grid voltage needs to avoid low energy backscattered electrons which overlap with secondary electrons. In addition, at acceleration voltages of 2.5 kV and 5.0 kV, the high backscattered electrons energies exceed 1500 V; thus, 1500 V may be the appropriate filtering grid voltage for obtaining the surface sensitive ESB image at 2.5 kV and 5.0 kV.
Figure 2.10. Schematic diagrams showing energy distribution of charging of a bulk insulating material: (a) total electron yield ($\sigma$) = backscattered coefficient ($\eta$) + secondary electron yield; (b) surface potential of (a) [3]. $E$ representes incident electrons and $E_1$ and $E_2$ are critical energies for charging. When the electron energy $E$ is at the condition $E_1 < E < E_2$, a large number of secondary electrons, which is more than the incident electrons, are emitted. Further, a relatively constant yield of backscattered electrons is also emitted. Thus, the total electron yield is high; the surface potential become positive. Meanwhile, when the condition is $E < E_1$ or $E > E_2$, the yield of emitted backscattered electrons is still constant, but the secondary electrons emitted are less than the yield of incident electrons (a) which means electrons are accumulated in the specimen. Therefore, the surface potential is termed as negative.
Figure 2.11. (a) Schematic diagrams showing the concept of charging. Metal surface is positively charged when an insulating particle is negatively charged [3]; (b) scanning electron micrographs showing an insulating particle on the metal surface at an acceleration voltage of 15 kV and slow scan speed; (c) same acceleration voltage of (b) and fast scan speed; (d) acceleration voltage of 1.0 kV and slow scan of (b). Positive charge of an insulating particle at an acceleration voltage of 15kV is reduced when the scanning speed increased. An insulating particle is positively charged when the acceleration voltage is reduced to 1kV, the charging effect revealing dark contrast on the metal surface is not present.
Figure 2.12. (a) Schematic diagrams showing the models of basic electron shells; (b) the generation of characteristic X-rays. Characteristic X-rays are generated due to the electron jump which fills a vacancy in the shell when an electron is pushed out from the shell by primary electrons; (c) Classification of characteristic X-rays after the electron transition. Characteristic X-rays are categorized depending on the electron jump distance and vacancy shell which is filled. For example, when an electron jumps from N line to fill the vacancy of K line, it is termed as γ X-ray in K line.
Figure 2.13. Schematic diagrams showing the radius distribution of K line X-rays in aluminium, simulated by Monte Carlo simulation using electrons of 200,000: (a) most of X-rays are generated within 10 nm from the surface at acceleration voltage of 2.0 kV; (b) The area of X-ray distribution is expanded with increased of acceleration voltage to 15 kV.
Figure 2.14. Schematic diagram showing the X-ray peak positions in K line (V, Mn, F, Na, Ga, Ge) and L line for the major elements which are excited at an acceleration voltage of 2.0 kV. The peak position is presented separately. Thus, it is theoretically possible to distinguish individual elements by EDX at an acceleration voltage of 2.0 kV. However, a high detection capability is necessary.
Figure 2.15. Scanning micrographs showing the stainless steel surface after mirror finishing, in the In-lens image at an acceleration voltage of 0.95 kV; (a) Non-SFS, before GDOES surface finishing; (b) SFS, after GDOES surface finishing. After GDOES surface finishing, contamination is absent from the surface; the original structures of the surface is enhanced.
Figure 2.16. Schematic diagram showing specification of GDOES and its system. The GDOES treatment area is 4 mm. However, the dimension of specimen minimal is 10.0 square mm at least, which includes the distance to the O-ring in order to promote uniform sputtering.
Figure 2.17. Schematic diagrams showing argon iron trajectory in aluminium at 50 eV and incident angle of 0°. The simulated iron energy and incident angle are similar to GDOES: (a) XY direction; (b) XZ direction, calculated by the software of Stopping and Range of Iron in Matter (SRIM). Accordingly, the argon ion impact area is of diameter within 2 nm only.
Figure 2.18. Scanning electron micrographs showing the cross-sectional images of the Al4%Cu alloy; (a) beam irradiation damage; (b) after GDOES surface cleaning for the area (a). Beam irradiation damage, which includes hydrocarbon deposition, is evident on the cross-section after several UHRLV SEM observations. However, after GDOES surface cleaning, hydrocarbon are removed from the cross-section without significant damage. Accordingly, it is possible to observe repeatedly the similar area of (a).
Chapter 3. Introduction to the Present Work

Characterisation of a myriad of materials, minerals, inorganic, organic etc, is often the starting point to understand and develop materials property and performance relationships. In order to assist this, the original structures of material surfaces, which are difficult to observe by conventional SEM, have been identified in this study using the UHRLV SEM.

In order to observe the of original structures a variety of differing materials, galvanized steel, and a metal joint of Al6111 alloy and AZ31 alloy (USW joint of Al6111/AZ31 alloys), a Ti6Al4V honeycomb construction and a ceramic sensor, were selected as representative materials. These materials have interesting features, including complicated microstructures and defects; however, these were previously not investigated in detail at very high resolution. This is because each material has specific requirements to enable effective use of the UHRLV SEM.

The individual materials have different mechanical and physical properties; thus, it is expected that an appropriate surface preparation process should be different for the individual materials. Therefore, the first area of this study focused on understanding the characteristics of individual materials, as described in Section 4.1, “Materials”.

In order to characterise the materials, the research has focused on investigating the most appropriate specimen preparation technique for individual materials. It is essential to obtain a clean, flat and damage-free surface that also revealed important original structures of the materials, which is termed the SEM friendly surface (SFS). The SFS is obtained after surface preparation with the general techniques and GDOES surface finishing (Chapter 2, Literature survey, 7.3, “Damageless specimen preparation”). For the surface preparation, three instruments were used individually in this study; ultramicrotomy (Leica) for galvanized steel, mechanical polishing machine (Presi) for the USW joint of Al6111/AZ31 alloys and Ti6Al4V alloy honeycomb, and a diamond pen-shaped knife for the ceramic sensor (Section 4.2, “Specimen Preparation for SFS”).

After initial preparation, GDOES was employed for each surface in order to obtain the SFS. The effects of SFS preparation techniques for the UHRLV SEM images are presented for individual
materials in Chapters 5 to 8, Sections “Results”, which includes analytical findings using EDX and XRD.

Subsequently, an approach to improve resolution of the compositional image (the ESB image) in the dissimilar materials of the USW joint of Al6111/AZ31 alloys was developed. Considering that the contrast of the ESB image depends on atomic number, the low contrast resolution is an issue if there is an only small difference in atomic number. In order to improve the contrast, the following conditions in the UHRLV SEM were examined; a range of acceleration voltages from 0.5 kV to 5.0 kV, and a range of the filtering grid voltages s from 0 V to 1500 V. Further, the impact of different incident angles to the ESB images was also investigated at 0˚ and 70˚. The experimental findings are presented in Section 6, “USW Joint of Al6111/AZ31 alloys”.

For the insulating material, i.e., the ceramic sensor, it is necessary to observe the structure at high resolution without being affected by charging effects. The challenge was undertaken using a significantly low acceleration voltage below 2.0 kV, and without use of any conductive coatings. The revealed structures of the ceramic sensor, and the low acceleration voltage effect on the imaging are presented in Chapter 8, “Ceramic sensor”.

For the final topic in this study, the further application of the SFS was considered. This SFS is showing the original structure of the materials, thus, it has a potential to create 3D tomography using e.g. SEM, focused ion beam (FIB) and X-Ray tomography. A further possibility to improve understanding of the materials using 3D tomography was also discussed in Chapter 9, “3D Tomography, Application of the SFS and Additional Possible Approaches”.

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Chapter 4. Experimental Procedure

The first section “Materials” introduces the characteristics of individual materials including galvanized steel, the ultrasonically welded (USW) joint of Al6111/AZ31 alloys, a Ti6Al4V alloy honeycomb structure and a ceramic sensor. The SFS (SEM friendly surface) preparation methods for the individual materials are described in the following section “Specimen preparation for SFS”. The experimental parameters used for the UHRLV SEM are discussed in the final section in this Chapter.

4.1. Materials

4.1.1. Galvanized Steel

The galvanizing technique is a relatively popular and effective coating process for steel. Consequently, galvanized steel is one of the high demand materials for various industrial sectors, including automotive, building and electrical products because of its significant corrosion resistance.

Historically, pure zinc had been frequently used for galvanizing until the Zn-55 % Al system (Galvalum) was developed in 1972. Following subsequent improvement of the binary system, the invention of the ternary Zn-Al-Mg system gave rise to a variety of galvanizing processes, including Super zinc and Dymazinc (Figure 4.1)[43, 44]. However, these ternary systems undergo a complicated reaction at the eutectic point, and further investigation is required [45-47].

In this study, the latest Zn-Al-Mg system galvanized steel, Magizinc (MZ350), has been examined. The material was provided by TaTa Steel Europe (formerly Corus Research, Development & Technology) in the Netherlands.

According to Vlot [48], the coating layer of MZ350-Magizinc is generated at both faces of steel plates by immersion in a hot zinc bath which contains 1.6 - 1.8 wt% aluminium and 1.6 - 1.8
wt% magnesium. During the immersion process, Fe-Al precipitates are frequently generated on the interface between the steel plate and the coating layer. After the treatment, the coating thickness is brought to the desired value by jet wiping. The back face of Magizinc is passivated using a commercial chrome-free system.

**Figure 4.2** reveals several defects on the surface of the Magizinc-MZ350 coating [48]. For example, shiny edge lines and angel hair lines are indicated with gray dashed lines and green dashed lines respectively. Dark patterns are indicated with purple circles, and the areas where shiny edge lines and angel hair lines cross are indicated with red circles. C1 and C2 labels indicate areas of different colour with respect to the surroundings. Shiny edge lines and colour differences can be seen by the naked eye.

The generation process and the nature of the defects have not been clarified in the literature. Therefore, this study is intended to understand the structures of the coating layer, and provide further knowledge of these defects using the UHLRV SEM.

### 4.1.2. USW Joint of Al6111/AZ31 Alloys

Aluminium and magnesium alloy welding is nowadays a high priority project in the automotive and aeroplane industries. This is due to the potential reduction of weight and production costs, and to the lower carbon dioxide emissions that an improved welding technique could provide.

The Al 6111 and AZ31 alloy joints investigated in the present work were prepared using an ultrasonic welding (USW) process. The Chemical compositions, thermal and physical properties of individual alloys are presented in Table 4.1 and Table 4.2. A schematic diagram of the setup employed for USW is shown in **Figure 4.3**. In the USW process, ultrasonic acoustic vibrations are locally applied to the selected alloys, which are held together by high pressures thereby avoiding the formation of contamination and the growth of oxide layers in the welding zone. During welding, the workpieces are kept below the eutectic temperature, which makes USW suitable for the bonding of metals with low melting points, e.g. aluminium and magnesium because it avoids the formation of eutectic products that are potentially detrimental for the
interface strength [49-56]. Furthermore, USW is a low energy, low cost and high reproducibility technique (Table 4.3). It is suitable for thin foils, although it is not recommended for bulk metal joints and for workpieces with complicated shapes.

The USW joint of Al6111/AZ31 alloys investigated in the present work was prepared using a USW process designed by Pantel and Prangnell [57] (Figure 4.3). At first, the AZ31 alloy surface was coated with a pure aluminium layer of 50 µm thickness using a cold spray process in order to improve the interface strength. Subsequently, the Al6111 and AZ31 alloys were welded using the USW process, applying 600 J for 0.4 seconds. The final thickness of the joined materials by the welding process was approximately 2.5 mm.

As stated previously, one of the advantages of the USW process is its suitability for dissimilar materials. However, it may cause the formation of defects at the interface. For instance, in the case of joints between aluminium and magnesium alloy, there is a potential risk of generating brittle Al$_{12}$Mg$_{17}$ intermetallics at the interface (Figure 4.4) [14]. The formation of Al$_{12}$Mg$_{17}$ intermetallics takes place at low temperatures and it is a common issue in the welding of aluminium / magnesium alloys (Table 4.3) [50, 57].

A systematic study of the welded zone, including characterization of intermetallics, has not been reported yet. This may be due to the difficulties typically encountered during specimen preparation and to the low resolution of the conventional SEM imaging.

The tendency to be quickly oxidized by exposure to air and the relatively low hardness make aluminium and magnesium alloys specimens difficult to prepare for SEM observations. This may be the major reason why chemical etching has been undertaken by most research groups, rather than mechanical polishing. However, chemical etching generally creates surface roughness and causes formation of by-products [58] that are responsible for hindering surface sensitive imaging.

The compositional image using the UHRLV SEM is made even more difficult by the low contrast between the Al6111 and AZ31 alloys, due to the fact that they consist mainly of elements with close atomic numbers, 12 and 13 for magnesium and aluminium respectively.
In this study, the SFS preparation method involving mechanical polishing is used to reveal the welded zone, thus providing the most suitable, damage-free surface to achieve a high contrast UHRLV SEM imaging.

### 4.1.3. Ti6Al4V Alloy Honeycomb

Titanium alloys are widely employed in several industries because of their strength and high corrosion resistance. Importantly, in the aerospace industries, titanium alloys are essential materials for producing the aeroengine [59]. The wide chord fan blade (Figure 4.5.a), which is one of the important components of the aeroengine, has been developed from the need for the parts that meet the criteria of design, aerodynamical efficiency, low weight, and also excellent corrosion and fatigue resistance.

In the present study, two variations of the fan blade components have been provided by Rolls-Royce [60]. The fan blade component generally consists of two Ti6Al4V alloy plates, and CP titanium, which is moulded in the shape of a honeycomb structure and placed between the Ti6Al4V alloy plates (Figure 4.5.b). In order to increase the interface strength, filler metal is generally placed between the metal faces; the materials are joined using the diffusion bonding technique. The components successfully bonded is termed the Ti6Al4V alloy honeycomb structure.

The difference between the two Ti6Al4V alloy honeycombs is that a modified surface layer (MSL) of approximately 30 μm thickness exists above the transformed layer on a Ti6Al4V alloy plate surface; thick and short acicular α phases, and β phases which is filled the gap between the α phases, are present in the MSL layer (Figure 4.6). In contrast, the MSL does not exist on another Ti6Al4V honeycomb surface, which is termed the Non-MSL [60] (Figure 4.7).

As described, the copper-nickel alloy was used as the filler material, although detailed composition of both metals have not been identified. For reference, the general compositions of a Ti6Al4V alloy and CP titanium are presented in Table 4.4.
Considering the elements contained in the Ti6Al4V honeycomb, the CP titanium and the copper-nickel filler metal, the individual elements are classified as \(\alpha\) stabilizers and \(\beta\) stabilizers, which have varying functions during the bonding process (Table 4.4 and Figure 4.8). For example, nitrogen and oxygen contained in general in the Ti6Al4V alloy and CP titanium are categorized as the \(\alpha\) stabilizers; these elements increase the \(\beta\) transus temperature in order to promote a further transformation. Aluminium contained in the Ti6Al4V alloy, which is classified as the \(\alpha\) stabilizer, assists in stabilizing the \(\alpha\) phase because it dissolves uniformly into the \(\alpha\) phase and the \(\beta\) phase. Meanwhile, iron and vanadium in the alloy are also known as \(\beta\) stabilizers; these are categorized as the \(\beta\) eutectoid and the \(\beta\) isomorphous respectively (Figure 4.8). Iron stabilizes the \(\beta\) phase by eutectoid transformation which decreases the the \(\beta\) transus temperature. Vanadium is miscible in the \(\beta\) phase which also reduces the \(\beta\) transus temperature. The final elements, copper and nickel in the filler metal, are also categorized as \(\beta\) eutectoid stabilizers, which work to stabilize the \(\beta\) phase [61-63].

The \(\beta\) transus temperature, which was mentioned above, is one of the important factors in order to understand the microstructures of the Ti6Al4V alloy honeycomb. The reason is that the CP titanium and the Ti6Al4V alloy change their microstructures significantly at or near the \(\beta\) transus temperature, depending on the thermal treatment and cooling process.

For instance, the microstructure of the CP titanium is a hexagonal close-packed (hcp) structure at the room temperature, but it is transformed to the \(\beta\) phase which has a body-centered cubic (bcc) structure at 888 °C [61]. The final grain dimensions and shape will change in response to cooling processes. In addition, tensile and yield strengths of the CP titanium are approximately quarter or half of the Ti6Al4V alloy (Table 4.4)

Meanwhile, the Ti6Al4V alloy is categorized as an \(\alpha+\beta\) alloy (Figure 4.9). The transformed temperature (\(\beta\) transus temperature) of the Ti6Al4V alloy is generally considered near 980 °C. The microstructures and properties are developed by cooling from the \(\beta\) region or \(\alpha-\beta\) region, or subsequent low temperature aging to decompose martensite which is formed during quenching [61, 64].

For example, above the \(\beta\) transus temperature in the \(\beta\) region, the microstructure of the Ti6Al4V consists of the \(\alpha\) plates and the \(\beta\) phases; the bright lines are presented as the \(\alpha\) and, the dark
contrast areas between the lines are presented as the β phases in Figure 4.10.a. When the α phases are slowly cooled below the β transus temperature, these α-line-phases commence forming in the plates, which are parallel to one specific plane of β (Figure 4.10.b).

The α phases slowly increase the thickness perpendicular to the planes, but grow rapidly along the planes. The reasons are that α forms the nucleus, and atoms in close proximity to that planes are matching along this plane (Figure 4.10.c). The final microstructure consisted of parallel α plate, and the β phases which are retained between the α plates; the previous constitute are termed the Widmanstten microstructure (Figure 4.10 and Figure 4.11.a).

However, the microstructure appears to the different on the Ti6Al4V alloy if the thermal treatment is performed at different temperatures from the β region or α+β region, and the cooling is different. When the thermal treatment and furnace cooling are commenced near the β transus temperature, the primary α phase generally forms the equiaxed structure in the transformed β matrix, that are of plate-shaped structure (Figure 4.11.b).

After thermal treatment at on near the β transus temperature and subsequent aging, a mixture of the equiaxed and the acicular structures is generally formed, that is termed a bimodal structure (Figure 4.11.c). Meanwhile, after thermal treatment and aging commenced at below the β transus temperature, the microstructure consists of the primary α, the acicular α and the β phases (Figure 4.11.d).

The more significant transformation occurs differently if cooling is rapid to room temperature of 25°C; the microstructure of the α+β titanium alloy commence a martensite transformation, which is a diffusionless and nonequilibrium transformation. In general, the β phase is decomposed in to the α+β phases by martensite transformation during quenching or aging at temperatures between Ms and Mf , which are indicated in the binary titanium phase diagram in Figure 4.9 and Figure 4.11.

During the martensite transformation, the crystal structure changes along with deformation of the matrix phases. Martensite alpha prime (α') and alpha double prime (α'') are developed from the β phase; however, these α' and α'' phases are decomposed to the α phase and the β phase during an aging process on cooling.
The α' phase has a hexagonal crystal lattice structure, and the α" phase is a supersaturated orthorhombic phase. The microstructure of the α' phase is an acicular structure similar to the primary acicular α phase; however, it is difficult to distinguish each phase by the UHRLV SEM. As a proposed solution, EBSD may be able to reveal the primary α phase and the α' phase, which is transformed from the β phases. According to Obashi [65] and previous research [66], it is expected that the transformation occurs only according to the Burgers crystallographic relationship of {110}β // {0002}α and <111>β // <1120>α, which suggests that a bcc crystal is able to transform to 12 hexagonal variations which have different orientations with depending on the parent β crystal. Initially, it is required to obtain the β location and orientation map, including high angle grain boundaries, with the use of EBSD. Subsequently, the β map is able to convert to the α map based the Burgers relationship which was mentioned above. Compared with the original β map and the converted α map, it is possible to determine the location of the β transformation.

From the above, it is clear that the α+β alloys consisted of the variant α phases and the β phases; each α phase appeared differently depending on the thermal treatment temperature and cooling process. Further, individual α phases have different functions in each form (Table 4.5) [17]. The equiaxed structure has excellent yield strength, tensile strength, high stress and corrosion resistance; creep strength and fracture toughness are inherent in the acicular structure. Therefore, in other words, it is possible to control the generation of α phases by the thermal treatment temperature, the cooling process and additional aging, depending on the function required in the titanium alloy.

For example, Table 4.6 shows the tensile and yield strengths of the Ti6Al4V alloy and the microstructure formation with different thermal treatment and cooling processes. In both temperatures, the water quenched Ti6Al4V alloy shows higher strength than the alloy cooled in a furnace; the highest tensile and yield strengths are obtained at 955°C, which is a common condition in the industry. Comparing with the microstructures of the Ti6Al4V alloys quenched in water from 900 °C and 955 °C, 60 % of the primary α phases have been contained in the alloy at 900°C, however, that has declined to 50 % in the alloy quenched at 955 °C. Similarly, 40 % of mixture of the transformed α phases and the remaining β phases have been contained in the alloy quenched at 900° C; that have increased to 50 % in the alloy of 955°C. In contrast, the
microstructures of the furnace cooled alloys contained 90% of the alpha phases, and 10% of the 
β phases which may be decomposed from transformed alpha phases. As a result, it is clear that 
the transformed α phase is essential in order to increase strength. Further, it is also clear that 
additional aging can increase those strength more because it may increase the transformed α 
phases (Table 4.7).

The final factor needed to understand the Ti6Al4V Alloy honeycomb structures is the diffusion 
bonding process. At the present time, a transient liquid phase bonding (TLP) process is 
commonly used in order to produce the Ti6Al4V alloy honeycomb structure [67]. The TLP 
bonding is able to join metal faces intimately in contact without high bonding pressure at below 
the melting temperatures.

In a general TLP process, the metals are heated above the eutectic temperature in a sufficient 
period of time; the components interdiffuse to a eutectic composition. As a result, the gaps in the 
interface are filled with the eutectic liquid, which can enhance the diffusion of components. The 
temperature is maintained while the liquid solute elements diffuse into the titanium component. 
After continuing this solute diffusion, the components become a titanium-enriched solution by 
isothermal solidification. Accordingly, the melting temperature increases. By extending the time 
at the same temperature, it is possible to enhance the strength more because it accelerates a 
further solid-state diffusion. After the bonding process, the joint material is slowly cooled in the 
vacuum furnace [67, 68].

As an application of the diffusion bonding process, the activated diffusion bonding (ADB) 
process has was developed in Rolls-Royce in 1988 [69], for producing the wide chord fan blade. 
Briefly, the following steps are required for the ADB process. Firstly, none of the elements 
contained in the components are transformed to liquid at the bonding temperature. Therefore, 
during the heating cycle, a prior solid-state interdiffusion is necessary between the Ti6Al4V 
alloy, the CP titanium and the Cu-Ni filler metal, which is intended to provide a Ti-Cu-Ni 
composition for the melt at the diffusion bonding temperature with elimination of the original 
joint surface. Subsequently, rapid isothermal solidification occurs at the diffusion bonding 
temperature, and the joint is produced. Finally, additional solid-state diffusion at the same 
temperature develops a strong joint which is comparative to the Ti6Al4V alloy. However, the 
presence of the MSL is not clear in that study.
Consequently, the Ti6Al4V alloy honeycomb is produced through the complicated bonding process. The generation mechanism of the MSL layer still requires further research at the present moment, although one idea about the MSL layer is proposed by Rolls-Royce. According to their current research, it is expected that some effects of the Cu-Ni filler metal may exist in the MSL layer because the filler metal may relate to the generation of the MSL. Therefore, in this study, attention was directed to understanding the difference between the MSL and the non MSL honeycomb, and to reveal the effect of the Cu-Ni filler metal in the MSL.

4.1.4. Ceramic Sensor

A porous aluminium-oxide humidity sensor, which consists of a sensor zone and an alumina ceramic substrate, is frequently used in various areas because of its high sensitivity and high reaction speed. Thus, researches on the mechanism of operation of the ceramic sensor, including humidity detection system and performance degradation, have been widely undertaken.

In particular, sensor drift is one of the degradations that has revealed in recent years. The alumina ceramic sensors in this study, which have been provided by Michell Ltd (Ely, UK), are also facing to a similar drifting issue; it await full understanding of the reasons of drifting, and the solutions for it.

In order to understand the drift mechanism, it is essential to understand the structure of the alumina ceramic sensor. Figure 4.12 shows a digital micrograph of the alumina ceramic sensor in this study. The dimensions of the ceramic sensor are approximately 6.0 mm × 50.0 mm × 0.63 mm; three sensors are presented in Figure 4.12.a. The gold coating layer is presented in dark contrast on the front face (Figure 4.12.a); the silver coating layers, which provide conductivity to the sensor, exist on the back face of the sensor (Figure 4.12.b).

The alumina ceramic sensor was produced by the following processes [70].

- An alumina layer of approximately 10 μm thickness was sputtered on an alumina substrate surface
• Anodizing was undertaken to form a porous alumina film an approximately 1 μm thickness using an oxalic electrolyte
• Immersion of the film in boiling water to undertake hydrothermal sealing
• Passivating in a phosphate solution
• Gold coating on the front surface, which is the sensor zone, Silver coating on the back surface to give conductivity.

Figure 4.13 shows the expected structure of the sensor, which generated from the processes presented above. According to past study, the structure may consist of the close-packed alumina oxide columnar hexagonal cells with elongated pores which pass perpendicular to the alumina substrate; the cell is enveloped by the pore. Further, the interface between the cells and the substrate are separated by thin barrier film [71].

Considering the electrical resistance of the ceramic, it is possible to explain the mechanism how the humidity is detected by the sensor. The moisture infiltrates through the surface conductive layer in the sensor, and it is adsorbed on the pores. The porous Al₂O₃ film is a dielectric material which has conductivity; thus, the value of its admittance is changed by the amount of moisture content in the pores. As a result, humidity can be revealed by calculating that capacitance [71].

As initially mentioned, the sensor has a drifting issue which is one of degradation factors. According to previous study, drifting occurs under certain conditions by the amount of moisture and exposure time; it becomes more significant at high temperature and high humidity [71]. Figure 4.14 represents the relation between gradation of humidity and moisture diffusion at high humidity. Lateral moisture diffusion may occur in the sensor during exposing to moisture for long time. With increasing humidity, moisture gradually permeates from the pore wall to the internal cell. As a result, the internal cell is wetted; the wetting of the internal cell may be one of the reasons of drift.

The drifting in the ceramic sensor in this study may also occur in a similar condition. Thus, as the initial approach in order to investigate the cause of the drifting, it is necessary to clarify the structure of the sensor using the UHRLV SEM.
In terms of the specimen preparation process, the ceramic sensor is one of the interesting materials. Ceramic is superior in thermal conductivity, heat resistance, strength, high insulation and corrosion resistance, compared with metals and polymers (Table 4.8).

Further, the hardness of alumina ceramic is approximately 10 times higher than that of stainless steel [72, 73], which brings a difficulty to the specimen preparation process. This may be a reason that only few cross-sectional SEM images of the ceramic sensor are available from previous studies (Figure 4.15) [70].

In addition to that difficulty, the alumina ceramic sensor contains the anodized aluminium film; the hardness of anodized aluminium film is significantly inferior compared with the alumina ceramic. Thus, mechanical polishing may destroy the sensor zone (Table 4.9) [74, 75]. Due to the complicated structure and the hardness of the sensor zone, it is not able to polish mechanically, nor to use the ultramicrotome. A focused ion beam (FIB) may be one of the solutions; however, from the image (Figure 4.15), it is predictable that the specimen preparation might be difficult even using the FIB. Thus, in order to investigate the most appropriate specimen preparation, a pen-shaped diamond knife was used in this study. The details are described in Section 4.1.4, “Ceramic Sensor”.

In addition to the specimen preparation difficulty, the ceramic sensor also brings a further difficulty in the UHRLV SEM observation due to its insulating property. A conductive coating is frequently used for the insulating materials. However, in order to obtain the high-resolution images of the original structures of the sensor, a conductive coating was not used because it will mask the original structures of the surface. The cross-section of the sensor has been observed using the UHRLV SEM at acceleration voltages below 2.0 kV which is able to avoid charging without need of conductive coating.

4.2. Specimen Preparation for SFS

In this section, the appropriate SEM friendly surface (SFS) specimen preparation will be discussed for several different materials including galvanized steel, ultrasonically welded of
Al6111 and AZ31 alloys (USW joint of Al6111/AZ31 alloys), Ti6Al4V alloy honeycomb and a ceramic sensor.

The SFS specimen preparation is the most important process in the UHRLV SEM observation that is designed to reveal a clean and an unobstructed view of the original structure of a material. The SFS includes two stages, which generally are surface preparation and surface finishing using GDOES. Three common techniques were employed for a general surface preparation depending on the characteristics of the materials. For example, ultramicrotomy was used for galvanized steel, and mechanical polishing was used for a joint of Al 6111 and AZ31 alloys. Further, a pen-shaped diamond knife was employed for a ceramic sensor. Subsequently, GDOES is used for surface finishing in order to remove contamination, and to enhance the original structures of the materials without significant damages.

4.2.1. Diamond Knife Trimming Using Ultramicrotome for Galvanized Steel, Magizinc-MZ350

When a material has relatively low hardness, such as Magizinc employed in this study, ultramicrotomy may be the simplest and most appropriate process for achieving SFS.

The process of surface preparation using ultramicrotomy is shown in Figure 4.16. Initially, a piece of MZ350, including the area of interest, was cut to dimensions of 5.0 mm × 10.0 mm from the MZ350 plate (a). Further, the thickness of the MZ350 was reduced as much as possible by grinding. Subsequently, in order to make a steep edge, the triangle-shaped areas were removed from the both edges using pliers (Figure 4.16.2). The reason for creating a steep edge is that the area sliced by a diamond knife needs to be minimized to avoid cross-section surface deformation. This is because the large area may contain more debris and second phase particles that often have different hardness and crystallographic structure from a matrix. As a result, those will often cause of surface deformation.

The thin MZ350 piece with a steep edge was placed in an ultramicrotome and sliced using a diamond knife, after smoothing out the rough edges by a glass knife (Figure 4.16.3).
Unlike for TEM specimen preparation, it is not necessary to slice the specimen to an ultrathin thickness. Zinc, being the major component of coating layer of MZ350, is the main reason for that. For instance, compared with aluminium, zinc has lower hardness and higher rigidity. Further, it also has a HCP structure. According to these characteristics, to slice ultrathin can be expected to cause deformation because it applies an excessive pressure to the crystallographic structure. For the MZ350, the thickness of the slice was set between 20 nm to 60 nm depending on the material condition. For instance, relatively thick slices, within the range described above, were used in order to observe the original structures of the fragile corroded region without destroying it. Further, slicing speed may also be an important factor. As a result of a comparison of the cross-sections of MZ350, which were sliced at slow, medium and fast speeds, the medium speed was selected in this study because it appeared to be able to preserve the original structures of the surface.

After the final trimming using a diamond knife, the specimen needs to be located in the UHRLV SEM immediately. GDOES surface finishing is not often necessary after ultramicrotomy because the SFS process may be obtained after the final trimming. GDOES needs to be used when contamination and hydrocarbons are evident on the surface. Using a gentle argon ion plasma, the contamination and hydrocarbons can be removed. Further, it is also effective in removing thick hydrocarbon deposition after surface observation and EDX analysis, so that the same area can be observed repeatedly (Section 2.7.3, “GDOES Surface Finishing”). The ultromicrotomy process was applied for galvanized steel in this study. However, it may also be suitable for other low hardness metals, e.g., pure aluminium and aluminium alloys, pure magnesium; carbon steel and other mild steels (See Appendix).

4.2.2. Mechanical Polishing of the USW Joint of Al6111/AZ31 Alloys, and the Ti6AL4V Alloy Honeycomb

Mechanical polishing was used for selected materials, e.g., a USW joint of Al6111/AZ31 alloys fabricated by an ultrasonic welding process (USW), and a Ti6AL4V alloy honeycomb. These
materials are unsuitable for ultramicrotomy because both have complicated structures and the Ti6Al4V alloy, in particular, is relatively hard.

Mechanical polishing should always achieve a mirror finish with the intention of revealing the original structures of the surface without significant damages. Mirror finished condition is also necessary for homogeneous GDOES surface finishing (Section 2.7.3, “GDOES Surface Finishing”). Here, the mechanical polishing process is described specifically for the USW joint of Al6111/AZ31 alloys, and the Ti6Al4V alloy, but this process can be applied to other materials with relatively high hardness, e.g., magnesium alloys and stainless steel.

**Specimen Dimensions**

In order to achieve the mirror finish rapidly, a minimal surface area of the material is required, thus reducing the risk of plastic deformation. The dimensions of the specimen need to be at 10.0 square millimetres for GDOES surface finishing. This requirement is related to the GDOES anode diameter, which is 4.0 mm; the specimen must completely cover the anode area including the O-ring (Section 2.7.3, “GDOES Surface Finishing”).

Mechanical polishing can be carried out directly when the area of the material is larger than 10.0 square millimetres. However, the dimensions of the USW joint of Al6111/AZ31 alloys were approximately 2.5 mm × 14.0 mm, which is too small to cover the GDOES anode. Meanwhile, the dimensions of Ti6Al4V alloy honeycomb were approximately 10.0 mm × 15.0 mm, which is a sufficient size for GDOES, but it was impossible to use GDOES directly because of the complicated shape of the material. Thus, it was necessary to mount both materials in conductive resin (Figure 4.17 and Figure 4.18).

For achieving a homogeneous GDOES surface finish, the thickness of the cross-section of the USW joint of Al6111/AZ31 alloys, in particular, needed to be increased before mounting in the resin. Therefore, the material was placed between three Al6111 alloy pieces in order to reach the required width of 10.0 mm or more. This manipulation was required in order to avoid the difference in the sputtering rate of aluminium and carbon, which is a major element of the resin.
In general, carbon is sputtered faster than aluminium. Thus, when the sputtered region includes a large carbon-constituted area, carbon is sputtered quickly and may redeposit on the surface of interest.

As described, the thickness of the joint was augmented; both materials have sufficient thickness for GDOES surface finishing. Afterwards, specimens were wrapped with aluminium foil before mounting in the conductive resin in order to protect the material from the resin \( \text{(Figure 4.17 and Figure 4.18)}. \)

**Polishing Paper and Cloth, Lubricant and Suspensions**

The general process of mechanical polishing performed in this study is described in \( \text{Table 4.10}. \) Mechanical polishing was commenced using a relatively coarse silicon carbide paper of # 800. With the progress of the process, polishing papers were gradually changed to finer papers of # 1200, 2400 and 4000. Polishing was continued until a mirror finish was achieved using two polishing cloths; first, a coarse cloth, followed by a finely-woven cloth, similar to velour, were used to perfect the mirror finish.

In order to proceed with mechanical polishing efficiently, it is necessary to use an appropriate lubricant. For the joint of Al6111/AZ31 alloys, a mixed solution of ethanol and glycerin was used \( \text{[76]} \). Water should be avoided as it may produce oxides on the surface, which are difficult to remove once formed. Ethanol was used to rinse the specimen. Deionised water was suitable for the Ti6Al4V alloy honeycomb throughout polishing because of the highly passive surface of this material.

Similarly, polishing suspensions must be selected individually from those available, e.g., the variety of diamond slurry, alumina liquid and colloidal silica depending on the characteristics of the materials. For the jointed alloys, a diamond slurry of 6 μm and 0.25 μm, and alumina liquid of 0.05 μm were used in the respective order with the polishing cloths \( \text{(Table 4.10)}. \) The use of colloidal silica is considered unsuitable in this case as it may induce a large amount of oxide products on the AZ31 alloy, which are difficult to remove. Further, it may accelerate generation
of a step at the interface, which could be observed by the naked eye; oxide products are also deposited in the step. The range in height of the step was found to be 1.0 mm to 1.5 mm by a profilometer (Figure 4.19).

On the other hand, two sizes of diamond slurry, alumina liquid and colloidal silica were used with polishing cloths in the respective order for the Ti6Al4V alloy honeycomb.

**Force and Further Factors**

A further important factor for mechanical polishing is application of a uniform force to the surface in order to avoid surface deformation and to enable homogeneous argon ion plasma generation after the polishing process. Polishing time is also important, but it may change depending on the surface condition of the individual polishing stages.

The terms of reference were polishing force of stainless steel 304 (SUS304). The parameter of mirror finish for SUS 304 has been clarified in the author’s previous research (Table 4.11), which involved 100 polished pieces of SUS 304 plates per year. Compared with SUS 304, the hardness of the Al6111/AZ31 alloy joint is lower. Therefore, a relatively lower force than that required for SUS 304 was applied to the joint through the polishing process. Although the hardness of Ti6Al4V alloy is generally similar or relatively higher than that of SUS 304, a similar polishing force as for the Al6111/AZ31 alloy joint was also used for the Ti6Al4V alloy honeycomb. The following had to be considered: the Ti6Al4V alloy honeycomb contains a modified surface layer (MSL), of unclear structure, which exists within less than a 30 μm-width region near the surface. Further, the MSL layer also constitutes a junction with the CP titanium of the honeycomb core zone; the junction area may have relatively complicated structure. Thus, the polishing of Ti6Al4V alloy honeycomb needed to be relatively low force in order to protect the MSL layer.
Chapter 4  Experimental Procedure / Specimen Preparation for SFS

**GDOES Surface Finishing**

After the surface achieved the mirror finish, the specimen was carefully rinsed using an ultrasonic bath, and dried completely. Further, GDOES surface finishing of the specimen was carried out. The basic parameters of power and pressure of GDOES were 5 -10 W and 1000 Pa, respectively [77]. Operation time is approximately within 10 seconds. These parameters may slightly change depending on the material and the individual of GDOES instruments employed (Section 2.7.3, “GDOES Surface Finishing”).

**Predictable Problems: A Step during Mechanical Polishing in the USW Joint of Al6111/AZ31 Alloys**

Despite using a gentle force for the Al6111/AZ31 alloy joint, a step was generated at the interface between the two alloys. As described previously, colloidal silica may promote to accelerate generation of the step, thus, it was not used for this material. However, a slight step was evident upon achievement of mirror finish; thus, it might be occurred due to the differences in hardness of these two alloys. For instance, the hardness of the magnesium alloy is 40 Hv, which is lower than that of 105 Hv in the aluminium alloy. Further, the polishing rate of magnesium of 16 µm/min is twice as fast as that of the aluminium alloy of 8 µm/min (Table 4.12) [78]. Consequently, polishing to a step-free interface may present a considerable difficulty. Nevertheless, a step has to be minimized because it will induce inhomogeneous GDOES surface finishing process. The argon ions generally tend to concentrate on the areas of high potential, which are often the edges of cavities and steps on the surface. These high potential regions generally will be sputtered faster than other areas and, accordingly, it makes difficult to observe the original features. In order to minimize the step, polishing time for the joint of Al6111/AZ31 alloys had to be shortened, especially, after the polishing suspension had been applied.
4.2.3. **Manual Polishing for Magizinc-MZ350**

In general, mechanical polishing is not a suitable preparation for galvanized steel, because zinc has a low-hardness characteristic; hence, mechanical polishing will remove the area of interest immediately after polishing has commenced (*Figure 4.20*). Therefore, the cross-section observation is essential. However, most of the defects in this material are located on the surface; it was necessary to observe the surface for understanding the nature and origin of these defects.

In order to observe the surface using the UHRLV SEM, it is necessary to reduce to a minimum the contamination and oxide products on the surface. This is because the UHRLV SEM image is modulated by contamination and oxidation products when those are present on the surface, and contamination generally induces charging of the surface. Therefore, manual polishing was undertaken to remove the surface contamination using a cotton pad, alumina liquid of 0.05 μm and colloidal silica until surface became slightly shiny. Instead of deionised water, ethanol was used for rinsing the surface because the MZ350 coating layer containing aluminium, which would quickly produce oxide products.

After manual polishing, the specimen was immediately placed in the UHRLV SEM. GDOES surface finishing was not applied because the surface shows roughness, including scratches and cracks, which could not be removed by manual polishing and would inevitably induce non-homogeneous sputtering (Section 2.7.3, “GDOES surface finishing”). As described previously, argon ion plasma may concentrate on to the edges of the rough surface and destroy the original structures of the specimen.

4.2.4. **Fracture Method for Alumina Ceramic Sensor SFS preparation**

A specimen preparation difficulty in the alumina ceramic is apparent due to the hardness and brittleness; difficult to polish mechanically, and impossible to use ultramicrotomy. Therefore, for the materials with difficulty in specimen preparations, the focused ion beam (FIB) technique is
generally used, although, it is a lengthy and laborious process. In order to devise a simple and quick SFS process, suitable for the brittle alumina ceramic, a pen-shaped diamond knife was used in this study for making a fracture, instead of FIB.

Initially, the ceramic sensor surface was protected using a relatively thin layer of resin on the surface. Subsequently, the specimen was placed on a clean bench top after turned the surface over, then, the pen-shaped diamond knife was gently applied was slightly attached to the back face of the specimen. A fracture was generated after some pressure was added to the diamond pen-shaped knife (Figure 4.21). In the next preparation step, GDOES surface finishing was applied to the fracture using the small sample holder, which is a special GDOES device for a small specimen (Figure 4.22). The argon ions concentrate on the fractured edge of the ceramic sensor which is a high-potential area of the surface and clean it as a result of gentle sputtering. Following the GDOES surface finishing, the specimen was immediately placed in the UHRLV SEM chamber.

4.3. Acceleration Voltages for the UHRLV SEM

In order to reveal the original structures of the surface using the UHRLV SEM, an acceleration voltage was selected from 0.5 kV to 2.5 kV for the individual materials (Literature survey, Section 2.3, “Electrons” and Section 2.4 “Ultra high resolution Low voltage SEM”). Further, acceleration voltages of 5.0 kV and 10.0 kV were used for the EDX analysis; that of 15.0 kV was used for the AsB imaging.

In order to present a clear compositional contrast of the dissimilar materials, which are contained in a USW joint of Al6111/AZ31 alloys, the effect of different incident angle of primary electrons was investigated between 0˚ and 70˚; similarly, the effects of different filtering grid voltages to the ESB imaging were also examined between 250 V and 1500V.
Tables

**Table 4.1.** Chemical compositions of Al6111 alloy and Mg AZ31 alloy used in this study [55].

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Si</th>
<th>Cu</th>
<th>Mn</th>
<th>Mg</th>
<th>Al</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al 6111</td>
<td>0.85</td>
<td>0.70</td>
<td>-</td>
<td>0.75</td>
<td>Balance</td>
<td>-</td>
</tr>
<tr>
<td>AZ31</td>
<td>-</td>
<td>-</td>
<td>1.0</td>
<td>Balance</td>
<td>3.0</td>
<td>1.0</td>
</tr>
</tbody>
</table>

**Table 4.2.** Thermal and physical properties of aluminium and magnesium [53-56]. List of expected advantages and disadvantages of ultrasonic welding of dissimilar materials, referenced from [51, 55].

<table>
<thead>
<tr>
<th>Properties</th>
<th>Al</th>
<th>Mg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (ρ₂⁵)</td>
<td>2.70</td>
<td>1.74</td>
</tr>
<tr>
<td>Youngs modules (E)</td>
<td>71</td>
<td>45</td>
</tr>
<tr>
<td>Thermal expansion (α × 10⁶ K⁻¹)</td>
<td>23.1</td>
<td>24.8</td>
</tr>
<tr>
<td>Heat capacity (CP)</td>
<td>0.897</td>
<td>1.023</td>
</tr>
<tr>
<td>Thermal conductivity (λ)</td>
<td>2.37</td>
<td>1.56</td>
</tr>
<tr>
<td>Melting point (tm °C)</td>
<td>660.4</td>
<td>650.0</td>
</tr>
<tr>
<td>Boiling point (tb °C)</td>
<td>2519</td>
<td>1090</td>
</tr>
<tr>
<td>Tensile strength</td>
<td>125- 400</td>
<td>93</td>
</tr>
</tbody>
</table>
Table 4.3. List of expected advantages and disadvantages of ultrasonic welding of dissimilar materials, referenced from [51, 55].

<table>
<thead>
<tr>
<th>Advantage</th>
<th>Disadvantage</th>
</tr>
</thead>
</table>
| **Welding dissimilar materials, Aluminium to Magnesium** | • The formation of intermetallic compounds  
• Low melting point reactions (e.g. eutectics)  
• Inter diffusion  
• Surface oxide layers  
• Differences in thermal expansion and residual stresses |
| It is possible to reduce the weight of joining |  
| **Ultrasonic welding technique** | • Specimen limitation, e.g. thin sheets and wires  
• Impossible bond large area |
| • Bonds without melting with self cleaning nature  
• Short processing time  
• Low energy and low cost |  

Table 4.4. Strength and general composition of the commercially pure (unalloyed grads) titanium and the general Ti6Al4V alloy [61]. CP titanium has six grades depending on the amount of impurity elements.

<table>
<thead>
<tr>
<th>Designation</th>
<th>Tensile strength (min)</th>
<th>0.2% yield strength (min)</th>
<th>Impurity limits, wt% (max)</th>
<th>Nominal composition, wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MPa</td>
<td>ksi</td>
<td>MPa</td>
<td>ksi</td>
</tr>
<tr>
<td>Unalloyed grades</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ASTM grade 1</td>
<td>240</td>
<td>35</td>
<td>170</td>
<td>25</td>
</tr>
<tr>
<td>ASTM grade 2</td>
<td>340</td>
<td>50</td>
<td>280</td>
<td>40</td>
</tr>
<tr>
<td>ASTM grade 3</td>
<td>450</td>
<td>65</td>
<td>380</td>
<td>55</td>
</tr>
<tr>
<td>ASTM grade 4</td>
<td>550</td>
<td>80</td>
<td>480</td>
<td>70</td>
</tr>
<tr>
<td>ASTM grade 7</td>
<td>340</td>
<td>50</td>
<td>280</td>
<td>40</td>
</tr>
<tr>
<td>ASTM grade 11</td>
<td>240</td>
<td>35</td>
<td>170</td>
<td>25</td>
</tr>
<tr>
<td>α-β alloys</td>
<td>900</td>
<td>130</td>
<td>830</td>
<td>120</td>
</tr>
</tbody>
</table>

Table 4.5. Advantages of the equiaxed and the acicular structures [61].

<table>
<thead>
<tr>
<th>Microstructure</th>
<th>Advantage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Equiaxed</td>
<td>Higher ductility and formability</td>
</tr>
<tr>
<td></td>
<td>Higher threshold stress for hot-salt stress corrosion</td>
</tr>
<tr>
<td></td>
<td>Higher strength (for equivalent heat treatment)</td>
</tr>
<tr>
<td></td>
<td>Better hydrogen tolerance</td>
</tr>
<tr>
<td></td>
<td>Better low-cycle fatigue (initiation) properties</td>
</tr>
<tr>
<td>Acicular</td>
<td>Superior creep properties</td>
</tr>
<tr>
<td></td>
<td>Higher fracture toughness values</td>
</tr>
</tbody>
</table>
Table 4.6. Room-temperature yield strength, the tensile strength and microstructure of the Ti6Al4V alloy in different thermal treatments [61].

<table>
<thead>
<tr>
<th>Thermal treatment</th>
<th>Yield strength</th>
<th>Tensile strength</th>
<th>Elongation at fracture, %</th>
<th>Reduction, in area, %</th>
<th>Microstructure at 25°C (77°F), -vol% phases</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MPa ksi</td>
<td>MPa ksi</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>955 C (1751 F)</td>
<td>834 121</td>
<td>937 136</td>
<td>19</td>
<td>46</td>
<td>90% alpha; 10% beta</td>
</tr>
<tr>
<td>furnace cooled</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>955 C (1751 F)</td>
<td>951 138</td>
<td>1117 162</td>
<td>17</td>
<td>60</td>
<td>50% primary alpha; 50% alpha prime + alpha double prime + retained beta</td>
</tr>
<tr>
<td>water quenched</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>900 C (1652 F)</td>
<td>855 124</td>
<td>965 140</td>
<td>17</td>
<td>43</td>
<td>90% alpha; 10% beta</td>
</tr>
<tr>
<td>furnace cooled</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>900 C (1652 F)</td>
<td>923 134</td>
<td>1117 162</td>
<td>15</td>
<td>54</td>
<td>60% primary alpha; 40% alpha prime + alpha double prime + retained beta</td>
</tr>
<tr>
<td>water quenched</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 4.7. Aging effect to Room-temperature on the yield and tensile strength of the Ti6Al4V alloy[61].

<table>
<thead>
<tr>
<th>Thermal treatment</th>
<th>Yield strength</th>
<th>Tensile strength</th>
<th>Elongation at fracture, %</th>
<th>Reduction in area, %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MPa ksi</td>
<td>MPa ksi</td>
<td></td>
<td></td>
</tr>
<tr>
<td>955 C (1751 F)</td>
<td>951 138</td>
<td>1117 162</td>
<td>17</td>
<td>60</td>
</tr>
<tr>
<td>water quenched + age 1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>955 C (1751 F)</td>
<td>1069 155</td>
<td>1186 172</td>
<td>17</td>
<td>56</td>
</tr>
<tr>
<td>water quenched + age 2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>900 C (1652 F)</td>
<td>924 134</td>
<td>1117 162</td>
<td>15</td>
<td>54</td>
</tr>
<tr>
<td>water quenched + age 1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>900 C (1652 F)</td>
<td>1013 147</td>
<td>1117 162</td>
<td>15</td>
<td>48</td>
</tr>
<tr>
<td>water quenched + age 2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 4.8. General composition of properties of metals, ceramics and polymers [74, 75].

<table>
<thead>
<tr>
<th>Property (approximate values)</th>
<th>Metals</th>
<th>Ceramics</th>
<th>Polymers</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density, g/cm³</td>
<td>2 to 22 (average -8)</td>
<td>2 to 19 (average -4)</td>
<td>1 to 2</td>
</tr>
<tr>
<td>Melting points</td>
<td>Low (Ga=29.78°C to high (W=3410°C)</td>
<td>High (up to 4000°C)</td>
<td>Low</td>
</tr>
<tr>
<td>Hardness</td>
<td>Medium</td>
<td>High</td>
<td>Low</td>
</tr>
<tr>
<td>Machinability</td>
<td>Good</td>
<td>Poor</td>
<td>Good</td>
</tr>
<tr>
<td>Tensile strength, Mpa (Ksi)</td>
<td>Up to 2500 (360)</td>
<td>Up to 400 (58)</td>
<td>Up to 140(20)</td>
</tr>
<tr>
<td>Compressive strength, MPa (ksi)</td>
<td>Up to 2500 (360)</td>
<td>Up to 5000 (725)</td>
<td>Up to 350 (50)</td>
</tr>
<tr>
<td>Young’s modulus, GPa(10⁶ psi)</td>
<td>15 to 400 (2 to 58)</td>
<td>150 to 450 (22 to 65)</td>
<td>0.001 to 10(0.00015 to 1.45)</td>
</tr>
<tr>
<td>High-temperature creep resistance</td>
<td>Poor to medium</td>
<td>Excellent</td>
<td>...</td>
</tr>
<tr>
<td>Thermal extension</td>
<td>Medium to high</td>
<td>Low to medium</td>
<td>Very high</td>
</tr>
<tr>
<td>Thermal conductivity</td>
<td>Medium to high</td>
<td>Medium, but often decreases rapidly with temperature</td>
<td>Very low</td>
</tr>
<tr>
<td>Thermal shock resistance</td>
<td>Good</td>
<td>Generally poor</td>
<td>...</td>
</tr>
<tr>
<td>Electrical characteristics</td>
<td>Conductors</td>
<td>Insulators</td>
<td>Insulators</td>
</tr>
<tr>
<td>Chemical resistance</td>
<td>Low to medium</td>
<td>Excellent</td>
<td>Good</td>
</tr>
<tr>
<td>Oxidation resistance</td>
<td>Generally poor</td>
<td>Oxides excellent; SiC and Si₃N₄ good</td>
<td>...</td>
</tr>
</tbody>
</table>
Table 4.9. Hardness comparison between alumina ceramic (Al$_2$O$_3$), anodized aluminium and stainless steel 304, referenced from [72-74].

<table>
<thead>
<tr>
<th>Material</th>
<th>Crystal structure</th>
<th>Theoretical density, g/cm$^3$</th>
<th>Vickers hardness HV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al$_2$O$_3$</td>
<td>Hexagonal</td>
<td>3.97</td>
<td>1835 – 2345 (converted from GPa)</td>
</tr>
<tr>
<td>Anodized aluminium</td>
<td>cubic</td>
<td>n/a</td>
<td>300 – 400 (depending on the anodized time and temperature, distance from metal substrate)</td>
</tr>
<tr>
<td>SUS 304</td>
<td>cubic</td>
<td>8.0</td>
<td>157 (converted from HRB81)</td>
</tr>
</tbody>
</table>
Table 4.10. General mechanical polishing process for a USW joint of Al6111/AZ31 alloys, and Ti6Al4V alloy.

<table>
<thead>
<tr>
<th>Process</th>
<th>Paper/ cloth</th>
<th>Ti6Al4V alloy honeycomb</th>
<th>A joint metal of Al6111 and AZ31</th>
<th>Suspension</th>
</tr>
</thead>
<tbody>
<tr>
<td>1\textsuperscript{st}</td>
<td>Silicon carbide paper, # 800 $\rightarrow$ 1200 $\rightarrow$ 2400 $\rightarrow$ 4000</td>
<td>Water</td>
<td>•Ethanol + water, *75% ethanol + 25% glycerol, e.g.</td>
<td>–</td>
</tr>
<tr>
<td>2\textsuperscript{nd}</td>
<td>Polishing cloth (coarse)</td>
<td></td>
<td></td>
<td>Diamond slurry (3.0 \textmu m)</td>
</tr>
<tr>
<td>3\textsuperscript{rd}</td>
<td>Polishing cloth (coarse)</td>
<td></td>
<td></td>
<td>Diamond slurry (0.25 \textmu m) Alumina (0. 3 \textmu m)</td>
</tr>
<tr>
<td>4\textsuperscript{th}</td>
<td>Polishing cloth (fine)</td>
<td></td>
<td></td>
<td>Alumina (0.05 \textmu m)</td>
</tr>
<tr>
<td>5\textsuperscript{th}</td>
<td>Polishing cloth (fine)</td>
<td></td>
<td></td>
<td>Colloidal silica</td>
</tr>
<tr>
<td>Final</td>
<td>Polishing cloth (fine)</td>
<td></td>
<td></td>
<td>Ethanol / Water</td>
</tr>
</tbody>
</table>

- 75\% ethanol + 25\% glycerol was used for a USW joint metal of Al6111/AZ31 alloys
- Step 5 is for Ti6Al4V alloy only
Table 4.11. Conditions of the polishing machine for a USW joint of Al6111/AZ31 alloys, stainless steel and Ti6Al4V alloy.

<table>
<thead>
<tr>
<th>Material Hardness</th>
<th>Al alloy + Mg alloy</th>
<th>SUS304 (default)</th>
<th>Ti6Al4V alloy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polishing force 1st step</td>
<td>1.0 - 1.5</td>
<td>1.5 - 2.0</td>
<td>1.0</td>
</tr>
<tr>
<td>2nd</td>
<td></td>
<td>1.5</td>
<td></td>
</tr>
<tr>
<td>3rd</td>
<td></td>
<td>1.5</td>
<td></td>
</tr>
<tr>
<td>4th</td>
<td></td>
<td>1.5</td>
<td></td>
</tr>
<tr>
<td>5th</td>
<td>0.5 - 1.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>final</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

- Polishing force is parameter for the polishing machine (PRESI)
Table 4.12. Polishing rates of common metals polished with 6 μm diamond abrasive [78].

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Condition</th>
<th>Melting range, °C</th>
<th>Hardness, HV</th>
<th>Polishing rate, μm/min</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sb–Sn–Pb eutectic</td>
<td>As-cast</td>
<td>95</td>
<td>11</td>
<td>24</td>
</tr>
<tr>
<td>Tin</td>
<td>Annealed</td>
<td>231</td>
<td>9</td>
<td>9</td>
</tr>
<tr>
<td>Cadmium</td>
<td>Annealed</td>
<td>321</td>
<td>22</td>
<td>14</td>
</tr>
<tr>
<td>Lead</td>
<td>Annealed</td>
<td>327</td>
<td>5</td>
<td>7</td>
</tr>
<tr>
<td>Zinc</td>
<td>Annealed</td>
<td>421</td>
<td>50</td>
<td>12</td>
</tr>
<tr>
<td>Magnesium</td>
<td>Annealed</td>
<td>650</td>
<td>40</td>
<td>16</td>
</tr>
<tr>
<td>Aluminum alloy</td>
<td>Heat treated</td>
<td>580–650</td>
<td>105</td>
<td>13</td>
</tr>
<tr>
<td>Aluminum alloy</td>
<td>Annealed</td>
<td>580–610</td>
<td>40</td>
<td>8</td>
</tr>
<tr>
<td>Aluminum</td>
<td>Annealed</td>
<td>660</td>
<td>25</td>
<td>9</td>
</tr>
<tr>
<td>Brass (40% Zn)</td>
<td>Annealed</td>
<td>900–905</td>
<td>155</td>
<td>15</td>
</tr>
<tr>
<td>Brass (30% Zn)</td>
<td>Annealed</td>
<td>915–955</td>
<td>95</td>
<td>14</td>
</tr>
<tr>
<td>Silver</td>
<td>Annealed</td>
<td>960</td>
<td>30</td>
<td>12</td>
</tr>
<tr>
<td>Copper</td>
<td>Annealed</td>
<td>1083</td>
<td>45</td>
<td>11</td>
</tr>
<tr>
<td>Austenitic steel (18% Cr, 8% Ni)</td>
<td>Annealed</td>
<td>1400–1425</td>
<td>170</td>
<td>3</td>
</tr>
<tr>
<td>B.S. 970:En9 Steel</td>
<td>Annealed</td>
<td>1425–1450</td>
<td>250</td>
<td>1.2</td>
</tr>
<tr>
<td>B.S. 970:En9 Steel</td>
<td>Hardened</td>
<td>1425–1450</td>
<td>800</td>
<td>1.1</td>
</tr>
<tr>
<td>B.S. 970:En2A Steel</td>
<td>Annealed</td>
<td>1450–1500</td>
<td>150</td>
<td>1.2</td>
</tr>
<tr>
<td>Nickel</td>
<td>Annealed</td>
<td>1452</td>
<td>125</td>
<td>0.3</td>
</tr>
<tr>
<td>Titanium</td>
<td>Annealed</td>
<td>1725</td>
<td>275</td>
<td>0.1</td>
</tr>
</tbody>
</table>
Chapter 4

Experimental Procedure / Materials

Figures

![Diagram showing the development history of galvanized steel and chemical compositions of major Zn-Al-Mg coatings including Magizinc-MZ350.](image)

<table>
<thead>
<tr>
<th>Trade name</th>
<th>Al (wt.% )</th>
<th>Mg (wt.% )</th>
<th>Other Elements (wt.% )</th>
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</thead>
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<td>0.1</td>
<td></td>
</tr>
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<td>3.0</td>
<td>0.2 Si</td>
</tr>
<tr>
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<td></td>
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<tr>
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<td></td>
</tr>
<tr>
<td>Magizinc</td>
<td>1.6 - 1.8</td>
<td>1.6 - 1.8</td>
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**Figure 4.1.** (a) Schematic diagram showing the development history of galvanized steel [43, 44]; (b) chemical compositions of major Zn-Al-Mg coatings including Magizinc-MZ350, referenced from [43, 44, 48].
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Chapter 5. Galvanized Steel

5.1. Result

5.1.1. Visual Observation

The appearance of the coating on the front and the back faces of the MZ350 plate was relatively similar. The defects, which were pointed out in reference [48] and Figure 4.2 in Section, 4.1.1, “Galvanized Steel”, such as, for example, the shiny edge lines, the angel hair lines, the dark patterns and the colour difference, have been evident in the same location as reported in [48]. In addition to the abovementioned defects, numerous zones with colour variability, parallel to each other and perpendicular to the shiny edge lines, were evident on both faces (Figure 5.1).

5.1.2. General Surface Area of the Coating after Manual Polishing and Cross-Section Prepared by Ultramicrotome

The primary electron energies of 5.0 kV were used for the UHRLV SEM surface observation. Low acceleration voltages, such as 1.1 kV and 1.5 kV, are not suitable for surface observation because contamination and deformation may still remain on the surface after manual polishing. Since low primary electron energies are able to penetrate only the near-surface region, the image will be modulated by surface contamination and oxide layers if these are present on the surface (Section 2.2, “SEM and Low-Voltage SEM”).

Figure 5.2 shows the general surface of the Magizinc-MZ350 coating layer after manual polishing. The primary zinc phases of equiaxed structure display a bright contrast. Further, the binary and ternary eutectic phases filled the gaps between the primary zinc phases (Figure 5.2.a); however, it is difficult to distinguish between those two phases. The difficulty arises because deformation, contamination and oxides may be still present on the surface after manual polishing; accordingly, such artifacts mask the original structures.
Interestingly, two dark contrast areas, which are indicated by the yellow line circles in Figure 5.2.b, appear to be parallel to each other on the surface. Further, similar contrast regions are present on the surface; thus, these may be related to the areas of colour variability which were mentioned previously (Figure 5.1).

The cross-sectional images of the general coating area on the front face are shown in Figure 5.3. For cross-sectional observation, acceleration voltages from 1.1 kV and 1.5 kV were selected for UHRLV SEM.

The thickness of the coating layer is 30 µm on the front face (Figure 5.3 and Table 5.1). The coating layer appears to be relatively uniform; however, a little surface roughness is evident on the top of the coating layer.

In order to investigate the microstructures of the coating layer on the front face, the magnification has been increased (Figure 5.4). At the magnification employed, it is possible to distinguish the primary zinc phases, the binary eutectic phases and the ternary eutectic phases, which are indicated by areas 1, 2 and 3 respectively in Figure 5.4. In previous studies [43, 48, 79], it has been revealed that the primary zinc phases consist of zinc with aluminium-rich particles, and the binary eutectic phases consist of zinc and MgZn\(_2\); zinc, aluminium and MgZn\(_2\) are contained in the ternary eutectic phase (Figure 5.5.a and Figure 5.5.b). According to the EDX analysis in this study, the presence of the aluminium-rich particles in the primary zinc phases and, the Mg-Zn elements which are expected to be MgZn\(_2\), are evident (Figure 5.5.c and Figure 5.5.d). Further, it is also revealed that primary zinc phase consists of relatively small zinc grains which had not been revealed in previous studies [1-3].

In addition to the previous structures, area 4 in the ESB image presents significantly dark contrast compared with the adjacent areas (Figure 5.4.b). It may be assumed that area 4 is oxidized and contaminated because, theoretically, the contrast of the ESB image relies on atomic number; thus, the contrast is brighter with increasing atomic number. Thus, the area of dark contrast in area 4 suggests a region containing elements lighter than magnesium, and possibly including carbon and oxygen.
Area 5 shows the interface between the coating layer and the steel substrate (Figure 5.6). According to the EDX analysis, the Fe-Al intermetallics, which are expected to be the Fe$_2$Al$_5$ [43], are evident at the interface (Figure 5.6.c).

In order to verify the crystal structures of the MgZn$_2$ and the Fe-Al intermetallics, XRD analysis was carried out (Figure 5.7). Accordingly, peaks of the primary zinc and MgZn$_2$ intermetallic are evident in the data. However, the presence of the Fe$_2$Al$_5$ intermetallics was not clearly evident; the Fe$_7$Al$_{11}$ composition was detected rather than Fe$_2$Al$_5$. Possibly, the amount of Fe$_2$Al$_5$ intermetallic is too small to be identified readily by XRD.

Meanwhile, the general surface of coating layer on the back face of the MZ350 is presented in Figure 5.8. The coating thickness of 40 µm was slightly thicker than that of the front face. Similar to the coating layer on the front face, three phases are present on the back face; the primary zinc phases with aluminium-rich particles, the binary eutectic and the ternary eutectic phases are revealed (Figure 5.9.a to Figure 5.9.d). The Fe-Al intermetallics also are present at the interface between the coating layer and the steel substrate (Figure 5.9.e and Figure 5.9.f). As a result, the general coating areas on the front and back faces of the material are relatively similar to each other.

### 5.1.3. Shiny edge lines

For the initial surface observation of the shiny edge lines on the back face of the MZ350, two shiny edge lines, with different widths of 800 µm and 40 µm, were selected. Similar to the general coating surface observation, an acceleration voltage of 5.0 kV was used for the shiny edge surface observation (Section 5.1.2, “General Surface Area on the Coating after Manual Polishing and Cross-Section Prepared by Ultramicrotome”).

Figure 5.10 shows the shiny edge line of 800 µm width after manual polishing; several cracks across the surface are evident in the In-lens image, although it is difficult to obtain further information (Figure 5.10.a). The reason is that basically the In-lens image shows a surface potential mapping using secondary electrons without depth information (Section 2.4.1, “In-lens
detector). However, the surface coating layer is homogeneous in the specimen; thus, the surface potential is also uniform on the surface, cracks excepted. Further, it is also susceptible to contamination and surface oxide, which are possibly still present on the surface after manual polishing.

On the other hand, it is possible to observe the surface microstructure in the SE2 image. This is because the SE2 detector employs secondary electrons and backscattered electrons, which include depth information (Section 2.4.2, “SE2 detector”). Accordingly, wavy structures were evident passing perpendicular to the shiny edge line in the SE2 image (Figure 5.10.b). An area, which is indicated with the red lined circle in Figure 5.10.b, was enlarged and presented in Figure 5.11. As a result, the area of the boundary between the shiny edge line and the wavy structure were revealed. Near the boundary, the relatively small equiaxed primary zinc phases appeared to be arranged in three band-structures with the binary and the ternary eutectic phases filling the gap in the bands. It appears that the dimensions and forms of the primary zinc phases near that boundary of the line may be related to the wavy structures (Figure 5.10.b and Figure 5.11). Further, the wrinkle structures, which are thinner than the wavy structures, are also evident adjacent to the edge of the primary zinc bands. The wrinkle structures have similar orientation as the wavy structures (Figure 5.11.a).

The magnification has been increased further for observation of a primary zinc band (Figure 5.12). As a result, it is revealed that the primary zinc phases are surrounded by the binary and the ternary eutectic phases; however, unlike the cross-sectional observation of the general coating area, aluminium-rich particles and fine zinc grains are not evident (Section 5.1.2, “General Coating Area on the Surface Area after Manual Polishing, and Cross-Section by Ultramicrotome).

The binary and the ternary eutectic phases in Figure 5.12 can be distinguished with reference to the cross-sectional images of the general coating surface (Figure 5.4 and Figure 5.9). For example, the relatively large structures are the binary eutectic and the relatively small structures are the ternary eutectic phases.
The areas of dark contrast along with the primary zinc phases in the ESB image show the effect of contamination and oxidation that have been mentioned previously. Interestingly, the formation of the crack has been evident in a similar location to the oxide area (Figure 5.12.b).

At the end of the surface observation of the 800 µm-width shiny edge line, the elemental distributions of the line have been examined using EDX (Figure 5.13). Comparing the areas within the line and outside the line, elemental compositions are relatively similar; the amounts of magnesium, aluminium and zinc within the line were a little lower than outside of the lines (Figure 5.13, Spectrum 2). In contrast, phosphorus content within the line was a little higher than in the areas surrounding it (Figure 5.13, spectrum1). A passivation process was carried out on the back face; thus, the presence of phosphorus is possible, although it is unclear how phosphorus influenced the shiny edge line generation.

Subsequently, the surface of the 40 µm-width shiny edge line of was observed (Figure 5.14). Similar to the 800 µm-width line, wavy structures are evident at the top and the bottom of the line. However, unlike the previous shiny edge line, this line consisted of two rows of the acicular primary zinc; the two rows are not in close contact, and the binary and ternary eutectic phases are present between the primary zinc phases (Figure 5.14.c and Figure 5.14.d). Further, the primary zinc shows dark contrast in the ESB image (Figure 5.14.d, yellow line circle), that may be a contamination deposition or oxidation of the primary zinc, as in the previous observations. In addition to that structure, a relatively small crack across the line is also evident in Figure 5.14.a; it appears to be a crack, but it is actually a defect. It may occur due to the presence of an acicular primary zinc, which is represented in the orange line circle 1. The acicular primary zinc has grown in a different orientation from the other primary zinc (Figure 5.15); however, the 40 µm shiny edge line has passed across this defect. Further, on the border of this flaw, the primary zinc phases are slightly bent along the defect that is indicated in the area within orange line circle 2 (Figure 5.15). Considering these microstructures, the defect is possibly arises after generation of the shiny edge.

The cross-sectional image of the 800 µm-width shiny edge line is presented in Figure 5.16. As for the previous cross-sectional observation, an acceleration voltage between 1.1 kV and 1.5 kV of the UHRLV SEM was used. It is clear that the surface microstructure is not continued throughout the coating layer. By gradual increase of the magnification in the area within the
orange line circle, the valley structure is clearly displayed in a dark contrast; it appeared to consist of the ternary eutectic phases (Figure 5.16.c and d). Further, in areas 1 and 2 in Figure 5.16, the boundary between the primary zinc phase and the ternary eutectic phase shows dark contrast, which suggests the possibility of oxidation. The EDX results revealed that the areas dark contrast has been oxidized (Figure 5.17). Further, the oxidation of area 1 is likely to be associated with oxidation of the ternary eutectic phase on the surface (Figure 5.16.d). Meanwhile, considering the microstructures of the coating layer, area 2 may also related to the ternary eutectic phase on surface. As described, the difference between the shiny edge line and the general coating layer were obtained by surface observation. However, relatively fine details of the microstructures could only be revealed in cross-sectional observation.

5.1.4. C1 and C2, the Areas of Colour Difference

Colour differences were evident to the naked eye (Figure 5.1). Interestingly, area C1 in the front face presents a relatively similar colour to the general coating area on the back face; area C2 presents a similar colour to the general coating layer on the front face. According to the references [48, 79], the colour difference may be related to passivation. Therefore, as an initial step to investigate the cause of the colour difference, EDX analyses were carried out at C1, C2 and the general coating areas on the both faces of the specimen individually. For this investigation, the surface was not manually polished in order to preserve any phosphorus present on the surface. As a result, the presence of phosphorus in each area, which is a consequence of the passivation, is clearly evident in area C1 on the front face and the general coating layer on the back face. Further, the other contents of elements are relatively similar to each other. Likewise, the general coating layer on the front face and area C2 on the back face show relatively similar contents of elements; a small amount of phosphorus was present only in area C2 only (Table 5.1).

Cross-sectional observation was made in C1 on the front face and in C2 on the back face, (Figure 5.18 and Figure 5.25) using an acceleration voltage between 1.1 kV and 1.5 kV. The thicknesses of areas C1 and C2 were 45 µm and 55 µm respectively. Areas C1 and C2 are
slightly thicker than individual general coating layers, and the back face coating layer is thicker than that of the front face (Table 5.1).

In area C1, the primary zinc phases formed relatively large and elongated shapes (Figure 5.18). Three interesting features are evident: firstly, the crack, which passed through the coating layer and is located adjacent to the large primary zinc structure (Figure 5.19). Further, the interface between the crack and the steel substrate is shown in area 1 (Figure 5.20); crack propagation is also shown in areas 2 (Figure 5.21 to Figure 5.23). A 10 µm particle deposition in area 3 will be described in C2 (Figure 5.25) because similar particles were evident in C2.

Area 1 of the interface between the crack and the steel substrate is shown in Figure 5.20. The void did not emit sufficient amounts of backscattered electrons toward the ESB detector; as a result, the void of the crack displayed dark contrast similar to the oxide area in the ESB image. At the boundary between the primary phase and the ternary eutectic phase, the primary zinc phase shows a relatively smooth structure. On the other hand, the ternary eutectic phase displays a relatively rough structure (Figure 5.20.a and Figure 5.20.b). Further, the surface of the steel substrate appears non-uniform in the ESB image and a relatively narrow oxidation area is evident in the primary zinc phase near the area where the crack tip reached the steel substrate (Figure 5.20.c and Figure 5.20.d). The oxidation propagates towards the zinc because that the crack and oxidation can not propagate through the steel substrate. In addition, compared with the cracks area 1 and area 2 in Figure 5.19, it appears that growth of the crack tip 1 is greater than that of the crack tip 2. It may be also related to the presence of the ternary eutectic phases, which are evident near the crack tip 1.

Area 2 reveals a further crack propagation above a crack tip (a); a crack tip (a) is shown in Figure 5.21 and the crack tip (b) is presented in Figure 5.21 and Figure 5.22. Both cracks passed through the primary zinc phase. Interestingly, it appears that the crack tip (a) stops at the MgZn₂ phase in the binary eutectic phase (Figure 5.21). Meanwhile, the crack (b) propagated further in two directions (Figure 5.22). The crack tip (b-1) appears to stop in the middle of the large zinc grain, although it may propagate further in the primary zinc phase. Meanwhile, the crack tip (b-2) stops at the MgZn₂ phase in the binary eutectic phase (Figure 5.22.c).
In order to observe the primary zinc structure near the crack more clearly, the magnification has been further increased (Figure 5.23). The edge of the crack shows a slight edge effect and charging; therefore, the primary zinc structure is not clear in the SE2 image (Figure 5.23.a). ESB image, on the other hand, enables a clear view of the primary zinc structures (Figure 5.23.b). Considering the contrast near the edges of the crack, it is possible that those areas have been oxidized. Therefore, edge effects and charging occurred in the SE2 image; the original structures were masked by them. In addition, it should be noted that some edge effect occurred even in the ESB image. It is attributed to the surface roughness of the primary zinc phases and cracks. The primary zinc phases consist of relatively small zinc grains which are randomly present; the crack is also evident in the coating layer that is the cause of the surface roughness. Thus, the edge effect in this case helps to observe the edge of the zinc grains, even though there are no elemental differences. The aluminium-rich particles and oxidized areas, on the other hand, show relatively similar contrast. Therefore, in order to clarify the compositions, it is necessary to carry out EDX analysis. Accordingly, it is revealed that the area near the edge of the crack shows oxidation and the particle consists of aluminium-rich composition (Figure 5.23.c and Figure 5.23.d).

Although further coating layers in the area C1 were observed (Figure 5.24), the structures were relatively similar to the general coating layer; the primary zinc phase, the binary eutectic phase, the ternary eutectic phase and the Fe-Al intermetallics existed in the coating layer.

Subsequently, cross-sectional observation was undertaken for area C2 on the back face (Figure 5.25). Some of the primary zinc phases show relatively large grains of 55 μm diameter, which are similar to the coating thickness and are not present in the coating layer that was previously observed (Figure 5.25.a). Likewise, the observation of area C1 revealed the following five interesting features, namely, a particle, an oxidation area, a large void at the interface, which are represented in areas (1), (2) and (3). In addition to the previous three features, two interesting structures are also observed on the steel substrate, which are presented in areas (4) and (5) respectively. Except for these features, the coating layer is relatively similar to the general coating layer.

EDX analysis was undertaken for a particle in area (1) in C2 (Figure 5.26); the particle was found to contain aluminium-iron rich components. As mentioned above, the aluminium-iron rich
components have also been found from the particle in area 3 in C1 area (Figure 5.18 and Figure 5.19).

Area (2) in C2 shows the ternary eutectic phase and oxidation within the region (Figure 5.27). In order to investigate the process of oxidation, EDX analyses were carried out at three locations. The elemental compositions were different in each area; for example, spectrum 2 may be ascribed to MgZn$_2$ phase; spectrum 3 showed high amounts of aluminium and magnesium, and spectrum 3 appeared to be zinc oxide. Considering the compositional differences, the oxidation appears to be propagating while avoiding MgZn$_2$ (Figure 5.27.c and Figure 5.27.d).

The diameter of the void in area (3) in C2 was approximately 20 µm. It appears that the coating area near the void is detached from the steel substrate. According to the ESB image, some particles are evident that may be some remains of the primary zinc phase (Figure 5.28). The generation of the void may be related to the non-uniform surface of the steel substrate; however, it is still under investigation.

The two particles in the steel substrate of areas (4) and (5) in C2 have also been examined. In order to investigate the components of the structure, EDX line analyses were undertaken in each case. According to the results, the dark contrast of the particle in area (4) is possibly due to the presence of iron oxide. Further, it appears that the iron oxide filled the cavity in the steel substrate, because the oxygen peak increased when the iron peak slightly decreased (Figure 5.29); if the oxide products were located on the surface, the iron peak would not decrease.

In contrast, a further particle is evident in the particle of area (5) in the SE2 image; some of the areas of the particle present bright contrast and show similar microstructure to the primary zinc phase (Figure 5.30.a). Further, contrast differences are also displayed within the particle in ESB image (Figure 5.30.b); the differences appear even clearer in the colour mapping image that was converted from the ESB image (Figure 5.30.c). Accordingly, it appears that the area of bright contrast may be related to the primary zinc phase component. EDX analysis disclosed that the area of dark contrast consisted of iron-oxide and the bright contrast area consisted of zinc and aluminium (Figure 5.30.d and Figure 5.30.e). Further, likewise to particle (4), area (5) on the steel substrate may also have cavity, as suggested by the distribution of the iron peak in the EDX line analysis.
5.2. Discussion

*Shiny edge lines*

Surface and cross-sectional observations clearly indicate that the shiny edge lines are not scratches. They consist of the band structures of the primary zinc phase and are surrounded by the binary and ternary eutectic phases; these might be generated during the manufacturing process. Further, interestingly, it is also revealed that the surface structures of the lines are not continued into the coating layer.

Considering the generation of the individual phases of the coating layer, these are generally formed in order of the eutectic temperatures. For example, the primary zinc phase and the binary eutectic phase are formed at 530 °C, the ternary eutectic phase is formed at 344 °C [80]. Thus, one of the possibilities for generation of the shiny edge line may arise if the temperature changes on the surface during the processes are slightly different between the shiny edge line and the general coating layer. The dimensions and forms of primary zinc in the shiny edge lines are relatively finer and narrower compared with that in the general coating layers; the binary and the ternary eutectic phases also show finer structures than other areas. Therefore, it is possible that cooling of the shiny edge line has started before the grains of primary zinc phase within the line grew sufficiently large, like those present in the general coating layer. However, the reason why the lines appear parallel to each other and are located in relatively similar orientations is still not clear.

Further, the wavy structures across the shiny edge line are considered to be associated with the wrinkles; the wavy structures may represent an oxide film skin covering the wrinkles [48]. However, the reasons for the wrinkles being perpendicular to the line, and the effects of the wrinkles on the shiny edge line formation, are also still under investigation; it may be required to understand the whole manufacturing process of MZ350.


**Colour difference**

As mentioned previously, it has been suggested that the colour difference between C1, C2 and the general coating areas may be related to the passivation process on the back face of MZ350 plate [6]. According to the EDX analyses, relatively similar amounts of phosphorus were detected in the general coating layer on the back face and also in the area C1 on the front face. Other elemental compositions were also relatively similar; especially, high amounts of oxygen and low amounts of zinc were contained in those areas. Meanwhile, phosphorus was not detected in the general coating layer on the front face, and was present in a small amounts in C2 area on the back face. The rest of the elemental compositions were broadly similar, although a slightly different tendency was evident, for example, more magnesium, aluminium and zinc were contained in C2 area than in the general coating layer on the front face.

Considering the compositional differences, the amounts of phosphorus and zinc may account for the colour differences between the shiny area and the general coating layer on the same face. Further, the colour similarity of C1 and the general coating on the back face, and C2 and the general coating on the front face, may be due to the elemental compositional similarity. However, it is still not clear why passivation is evident in area C1, rather than in C2. The variation of the passivation process from area to area and from face to face requires further consideration and may provide insight into the reasons for the colour differences.

**Wrinkles**

As described previously in the case of the shiny edge line, the wrinkles are frequently evident on the surface. It was revealed that the wavy structure appears to be related to the wrinkles and it occurs due to the oxide film skin on the wrinkles. According to [48], several studies on wrinkles have been undertaken by Huang et al [81, 82]. However, no unequivocal conclusions have been reached. Further studies are required to fully understand the nature of wrinkles.
**Effect of Manual Polishing**

Comparison of the manually polished surface and ultramicrotomed cross-section clearly shows that the aluminium-rich particles can not be revealed by polishing, but are easily discerned in cross-sectional observation. Thus, in order to achieve full understanding of the MZ350 coating layer, both approaches, such as the surface and the cross-sectional observations after manual polishing and ultramicrotomy, are necessary. The reason is that those are able to provide a broadly aspect of the coating surface and details of the coating layer respectively.

**Aluminium-Iron Rich Particles on the Coating Layer**

The particles in the coating layer, which consisted of iron and aluminium, are expected to be Fe$_2$Al$_5$, according to [48]. This intermetallic is known as one of the typical defects, which is generated in the hot dip zinc bath as a result of skimming during the process.

**Iron Oxide and Other Particles in the Steel Substrate**

The UHRLV SEM images and the EDX analyses suggest that the original steel substrate investigated in this work might have already contained voids or cavities when the coating was applied. Iron-oxide and the primary zinc phase component might fill the voids and cavities during the hot zinc bath immersion process, and grow with time and temperature. As mentioned previously, if those particles were on the steel substrate, the peak of iron would appear continuous in the line analysis without decrease of the intensity (Figure 5.29.e and Figure 5.30.e); however, a reduction of the iron peak has been revealed in the EDX data.
Oxidation and crack propagation

After surface and cross-sectional observation, it is revealed that the oxidation appears to frequently commence from the zinc component in the ternary eutectic phases. It occurs due to the presence of aluminium and magnesium \[48\]; the presence of aluminium and magnesium generally accelerates oxidation. Thus, it is possible that the ternary eutectic phases have been significantly oxidized on the surface; again, oxidation passes through the zinc-rich area and the primary zinc phases. This may be associated with the structures of the zinc-rich areas, which consist of relatively small zinc grains. Therefore, it is considered that the oxidation process readily propagates along the grain boundary of the zinc phase. A similar tendency is also found in the propagation of cracks which progress in the primary zinc phases.

Area1 in C1 that passes through the coating layer may be a void rather than a crack. It is suggested by the non-uniformity of the steel surface that was evident at the interface between the void and the steel substrate and it possibly interfered with the uniform growth of the coating layer on the steel substrate. As a result, the void structure could be generated.

Fe-Al Intermetallics at the Interface between the Coating Layer and Steel Substrate

The Fe-Al intermetallics are present at the interface between the coating layer and the steel substrate. However, their characterization using XRD was still unclear. Further research is necessary to identify fully and characterize the Fe-Al intermetallics.

5.3. Conclusions

In this study, the characteristics of defects in Magizinc-MZ350, including the microstructures of the coating layers, and the manner of the oxidation and the crack propagation through the
primary zinc grains, have been revealed by the appropriate SFS preparation methods, i.e., manual polishing and ultramicrotomy, and the UHRLV SEM. Further, manual polishing to remove contamination enabled the charging effect to be minimized. In addition, colour differences are related to the compositional differences; the cavity on the steel substrate is an original defect of the steel. However, several questions still remain to be answered. Further work is needed to examine other defects that have not been addressed in this study, such as the angel hair lines, dark patterns, and the area across the shiny edge lines.
Tables

**Table 5.1.** (a) EDX result; (b) coating thicknesses on the front and the back faces of Magizinc-MZ350 specimen.

(a) | Front (at%) | Back (at%) |
---|---|---|
 | C1 | General | C2 | General |
---|---|---|---|---|
C | 28.93 | 36.63 | 29.83 | 22.63 |
O | 47.04 | 29.84 | 24.38 | 52.48 |
Mg | 4.16 | 4.81 | 6.37 | 3.72 |
Al | 4.09 | 6.14 | 7.38 | 4.28 |
P | 4.96 | | 0.28 | 6.36 |
Zn | 10.82 | 22.89 | 31.77 | 10.53 |

(b) | Front (µm) | Back (µm) |
---|---|---|
 | Shiny | Dark | Shiny | Dark |
---|---|---|---|---|
Coating thickness | 45 | 30 | 55 | 40 |
Figures

**Figure 5.1.** Digital micrographs showing the area of colour variability, including C1 on the front face and C2 on the back face. The purple line circles represent the location of further colour differences on the surface, which appear to be present at a constant orientation.
Figure 5.2. Scanning electron micrographs showing the surface after manual mechanical polishing in SE2 images: (a) broad area; (b) selected area of (a). The yellow circles indicate the remains of the diagonal lines, which are parallel to each other.
Figure 5.3. Scanning electron micrographs showing the cross-section of the coating layer and steel substrate on the front face, prepared with a diamond knife: (a) In-lens image; (b) SE2 image. The coating layer consists of relatively large primary zinc phase, binary and ternary eutectic phases. The area displayed in the yellow circle is presented in Figure 5.4.
Figure 5.4. Scanning electron micrographs showing the area represented by the yellow line circle in Figure 5.3: (a) SE2 image; (b) ESB image: Area (1) primary zinc phase; (2) binary eutectic phase; (3) ternary eutectic phase. Area (4) may be oxidized because of the contrast in the ESB image. The dark contrast area should have elements lighter than aluminium, magnesium and zinc. Area (5) is the interface between the coating layer and the steel substrate. The area indicated with a red lined circle is presented in Figure 5.5.
Chapter 5

Galvanized Steel

(a) Ternary eutectic

Primary Zn

Binary eutectic

MgZn$_2$

Al rich particles

(b) Primary Zn

Binary eutectic

MgZn$_2$

Al rich particles

1 µm
Figure 5.5. Scanning electron micrographs showing the selected area of Figure 5.4: (a) SE2 image; (b) ESB image. The primary zinc phases consist of small zinc grains and aluminium-rich particles. The binary eutectic phase consists of the MgZn$_2$ components and zinc, the ternary eutectic phase contains aluminium-rich particles, zinc and MgZn$_2$: (c) EDX point analysis and (d) EDX line analysis of the aluminium-rich particle and MgZn$_2$ components.
Chapter 5

Galvanized Steel

(a) Al rich particles
Primary Zn
Ternary eutectic phase
Fe-Al intermetalics

(b) Al rich particles
Primary Zn
Ternary eutectic phase
Fe-Al intermetalics

100 nm
Figure 5.6. Scanning electron micrographs showing area 5 of the interface between the coating layer and the steel substrate on the front face of MZ350: (a) SE2 image; (b) ESB image; (c) EDX analysis. Fe-Al rich components are evident at the interface.
Figure 5.7. (a) XRD data; (b) peak locations for zinc, MgZn$_2$, aluminium and Fe$_7$Al$_{12}$ signals. The presence of zinc, MgZn$_2$, aluminium was evident; however the expected Fe$_2$Al$_5$ was not detected. Further investigation is needed to determine whether the amount of Fe$_2$Al$_5$ is too small to be detected, or the composition of the intermetallic is different.
Figure 5.8. Scanning electron micrographs showing cross-sections of the general coating layer and steel substrate on the back face, prepared with a diamond knife: (a) In-lens image; (b) SE2 image. The area indicated by the yellow circles discloses a crack, produced during specimen preparation.
Chapter 5

Galvanized Steel

(a) Binary eutectic

(b) Ternary eutectic phase

Primary Zn

2 µm
Chapter 5

Galvanized Steel

Binary eutectic
Primary Zn

(c)

Binary eutectic
Primary Zn

(d)

1 µm

Ternary eutectic phase

Ternary eutectic phase
Figure 5.9. Scanning electron micrographs of increased magnification showing, SE2 images of the coating layer and steel substrate on the back face: (a),(c) and (e) SE2 image, primary zinc phase, binary and ternary eutectic phase, respectively; with incorporated individual Fe-Al intermetallics; (b),(d) and (f) ESB images of (a),(c) and (e).
Figure 5.10. Scanning electron micrographs showing an area that includes a shiny edge line of 800 µm-width: (a) In-lens image; (b) SE2 image. The area indicated with the red lined circle is presented in Figure 5.11.
Figure 5.11. Scanning electron micrographs showing the interface between the shiny edge line of 800 µm-width and the wavy structures in the increased magnification SE2 image of Figure 5.10: (a) broad area; (b) the area in the yellow circle in (a). The equiaxed primary zinc phase forms band-structures, the binary and the ternary eutectic phases fill the gap between the primary zinc phases. The wrinkles, which may be slightly affected by wavy structures area, are also evident between the primary zinc bands.
Figure 5.12. Scanning electron micrographs showing the primary zinc phases and the binary and the ternary phases on the shiny edge line of 800 µm-width: (a) SE2 image; (b) ESB image. Areas indicated by the yellow dashed line circles show cracks around the primary zinc phases.
Figure 5.13. Scanning electron micrograph showing area where EDX analysis was undertaken: spectrum 1 within a shiny edge line and spectrum 2 outside the line; (b) EDX analysis data. The composition of both areas is relatively similar; increased amount of phosphorus is present within the lined region compared with the area outside the line.
Figure 5.14. Scanning electron micrographs showing a shiny edge line of 40 µm-width in the SE2 image: (a) broad area; (b) area of the orange line circle of (a); (c) with increased magnification image of (b) in SE2 image; (d) ESB image of (c). The edge of the primary zinc phase within the yellow circles of (d) may be oxidized.
Figure 5.15. Scanning electron micrographs showing the crack in Figure 5.14.a: (a) In-lens image and (b) SE2 image. Areas of primary zinc phase, which are indicated by the orange line circles, appear to change their direction along the crack.
Figure 5.16. Scanning electron micrographs showing cross-sectional images of the 800 μm-width shiny edge line in the SE2 image: (a) broad area; (b)(c) and (d) images of the area within the yellow circle in (a) at increasing magnifications. Above the red line circle, a valley is displayed in dark contrast. Along with this, oxidation appears to be evident in the red dashed circles 1 and 2. The oxidation of areas 1 and 2 appears to occur along the ternary eutectic phases; it is possible because aluminium and magnesium which are contained in the ternary eutectic phase is generally able to accelerate oxidation. The EDX analyses results of both areas of 1 and 2 are presented in Figure 5.17.
## Chapter 5

### Galvanized Steel

(a) 

(b) 

<table>
<thead>
<tr>
<th></th>
<th>Spectrum1 (at %)</th>
<th>Spectrum2 (at %)</th>
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<tbody>
<tr>
<td>O</td>
<td>49.57</td>
<td>1.38</td>
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<tr>
<td>Mg</td>
<td>6.82</td>
<td>-</td>
</tr>
<tr>
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<td>Zn</td>
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</tr>
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</table>
Figure 5.17. (a) EDX analysis of area 1 in Figure 5.16; (b) and (c) that for area 2 in Figure 5.16. A high yield of oxygen indicates that the area of dark contrast is oxidized.
Figure 5.18. Scanning electron micrographs showing C1 on the front face: (a) In-lens image; (b) SE2 image. There are interesting features, such as the interface between the coating layer and the steel substrate, a crack tip and a particle, which are represented in areas 1, 2 and 3, respectively.
Figure 5.19. Scanning electron micrograph showing area 1 in C1 on the front face in Figure 5.18 at increased magnification: (a) In-lens image; (b) SE2 image; (1) the interface between a crack and the steel substrate, (2) a crack tip at the primary zinc phase and (3) a 10 μm particle. The features are further examined in Figure 5.20 to Figure 5.22.
Chapter 5

Galvanized Steel

Crack propagates in this direction

Ternary eutectic phase

Primary Zn

Oxidized area

(b)

2 µm
Figure 5.20. Scanning electron micrographs showing area 1, the interface between the crack and the steel substrate: (a) SE2 image; (b) ESB image; (c) with increased magnification of the red circle area of (a); (d) ESB image of (c). The steel substrate shows the surface roughness, which is indicated by the red dashed line circles. Further, when the crack reached the steel substrate, it propagated into the primary zinc phase, because the crack and oxidation cannot pass through the steel.
Figure 5.21. Scanning electron micrographs showing crack area 2: (a) SE2 image; (b) ESB images. Crack tip (a) appears to change the direction when it encounters a MgZn$_2$ in a binary eutectic phase. Crack tip (b) is presented in Figure 5.22.
Chapter 5

Galvanized Steel

(a) Crack tip (b-2)

(b) Crack tip (b-1)

Primary

Binary eutectic

2 µm
Figure 5.22. Scanning electron micrographs showing the crack tip (b) propagating in Figure 5.21. The crack propagates in two directions, tip (b-1) and (b-2): (a) SE2 image; (b) the ESB image. Crack tip (b-1) changes direction upon approaching a relatively large zinc grain; (c) SE2 image with increased magnification of the crack tip (b-2).
Figure 5.23. Scanning electron micrographs showing the crack tip b-2 in Figure 5.21 and Figure 5.22 at increased magnification: (a) SE2 image; (b) ESB image, (c) EDX line analysis area of primary zinc phases and the crack; (d) EDX point analysis data. The crack includes cavities, the oxidized areas and aluminium-rich particles.
Figure 5.24. Scanning electron micrographs showing ESB images of further area in C1: (a) the interface between the coating layer and the steel substrate and Fe-Al intermetallics; (b) three different phases, the primary zinc phase, the binary and the ternary eutectic phases with aluminium-rich particles are evident.
Figure 5.25. Scanning electron micrographs showing cross-sectional image of C2 on the back face, the coating layer and steel substrate: (a) SE2 image; (b) area indicated with yellow line circle in (a). Area (1) represents a particle in the coating layer; area (2) oxidation; area (3) a void at the interface. Area (4) represents a particle of 10 µm-diameter and area (5) shows a further particle on the substrate.
Figure 5.26. (a) EDX point analysis of the particle in area (1) in C2 on the back face; (b) EDX analysis data. The particle is Al-Fe rich. A similar composition was detected in the particle of area 3 in C1 on the front face.
Figure 5.27. Scanning electron micrographs showing the ternary eutectic phase of area (2) in C2 on the back face: (a) SE2 image; (b) ESB image; (c) EDX analyses area; (d) EDX data of three different points. Spectrum 4 shows a high yield of oxygen and low yield of zinc. According to the ESB image and EDX analysis, the oxidation proceeds by avoiding the MgZn$_2$. 

<table>
<thead>
<tr>
<th></th>
<th>Spectrum 2</th>
<th>Spectrum 3</th>
<th>Spectrum 4</th>
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<tr>
<td>C</td>
<td>7.21</td>
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<td>4.43</td>
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<tr>
<td>O</td>
<td>3.17</td>
<td>3.73</td>
<td>46.19</td>
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<tr>
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<td>7.62</td>
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</tr>
<tr>
<td>Z</td>
<td><strong>81.59</strong></td>
<td><strong>62.49</strong></td>
<td><strong>45.52</strong></td>
</tr>
</tbody>
</table>
Figure 5.28. Scanning electron micrographs showing a void in area (3) in C2 on the back face: (a) SE2 image; (b) ESB image. It appears that the coating layer is detached from the steel substrate.
Chapter 5

Galvanized Steel

EDX line analysis

(a)

(b)

2 µm
Figure 5.29. Scanning electron micrographs showing a particle-like structure in the steel substrate, area (4) in C2: (a) SE2 image; (b) ESB image; (c) EDX line analysis. The particle-like structure may be iron oxide. It appears that a cavity has been filled with the iron oxide because the peak of iron is slightly decreased, whereas the oxygen peak is increased. If the iron oxide particle was superficial, the iron peak would not have decreased.
Similar microstructure to the primary zinc phase

1 µm
Figure 5.30. Scanning electron micrographs showing a particle in area (5) in C2: (a) SE2 image; (b) ESB image; (c) colour mapping image of (b); (d) EDX line analysis area; (e) EDX data. Similar to area (4), the steel substrate is likely to contain a cavity, because the line intensity of the iron peak decreased while the zinc peak increased, which would not have happened if the particle was present on the surface. The particle consisted of iron-oxide and primary zinc component.
Chapter 6. USW Joint of Al6111/AZ31 Alloys

6.1. Result

6.1.1. Polishing Effect on the Interface and UHRLV SEM Imaging of Dissimilar Materials

Polishing Effect and GDOES Surface Finishing Effect on the Interface

As described in the Experimental Procedure 4.1.2, “USW Joint of Al6111/AZ31 Alloys”, magnesium can be polished faster than aluminium because the hardesses of the individual materials are different. Therefore, it is considered that a slight height difference may be evident at the interface after mechanical polishing. In order to verify the polishing effect on the surface, mechanical polishing was suspended before generating the height differences; however, the surface condition did not appear to achieve a mirror-finished condition to the naked eye. Using the UHRLV SEM, it is clear that there is little difference in height. Further, Al-Fe particles and Al-Mn particles are present in the Al6111 alloy and the AZ31 alloy respectively. However, several scratches are present on the surface due to insufficient mechanical polishing. Thus, it is difficult to reveal the original microstructures from this surface at the low acceleration voltages because the original structures are masked by the deformation (Figure 6.1.a).

Meanwhile, after continuing the final polishing to achieve a mirror finish with perfection, a slight height difference appeared at the interface (Figure 6.1.b). GDOES surface finishing was performed on the surface; accordingly, the grains of the Al6111 alloy are clearly presented. Such grains were not able to be observed at the surface before mirror finishing (Figure 6.1.a). Further, damage caused by GDOES was not evident on the surface. Therefore, relatively uniform GDOES surface finishing is possible to be performed in order to minimize the difference in height on the surface; thus, it is possible to generate the SFS for the UHRLV SEM (Section 2.7, “Damage less Specimen Preparation”).
A specific effect of GDOES surface finishing can be obtained in the In-lens image; an acceleration voltage of 1.5 kV was used for the image. The area to which GDOES was applied presents a relatively dark contrast; in comparison, the area without GDOES treatment shows bright contrast, which is similar to a charging effect (Figure 6.2). Charging is generally related to the presence of surface contamination and oxide; hence, it is clear that GDOES surface finishing removed contamination and oxide products from the surface, and enhanced the appearance of the surface microstructure.

6.1.2. **The Efficient Use of the In-lens and the SE2 Detectors for Dissimilar Aluminium and Magnesium**

The USW joint of the Al6111/ AZ31 alloys in this study consists of dissimilar metallic elements of aluminium and magnesium, with only a small atomic number difference, 1, between them. Further, the interface has a small difference in height. It is considered that the previous characteristics of the material may interrupt surface sensitive UHRLV SEM imaging. Thus, as the first area of attention in this research, the effect of low acceleration voltages on the two detectors, e.g., the In-lens and the SE2 detectors, was investigated. Acceleration voltages included 0.5 kV, 1.5 kV, 2.5 kV and 5.0 kV.

The In-lens and the SE2 images at the individual acceleration voltages are displayed in Figure 6.3 and Figure 6.4 respectively. The specific features of the In-lens and the SE2 images at each acceleration voltage are displayed in Table 6.1. Considering the features of each image, surface sensitive imaging may be obtained at an acceleration voltage of 1.5 kV for the following reasons. For example, in the In-lens image at an acceleration voltage of 0.5 kV, the interface between the coating layer and the Al6111 alloy is evident; however, the Al-Fe rich particles and Al-Mn rich particles (Figure 6.3, a), cavities and contamination are displayed with similar contrasts. Further, a strong shadow effect was evident in the SE2 image that is considered to be related to the location of the SE2 detector; the boundary of the aluminium coating and the Al6111 alloy is not clearly presented (Figure 6.4.a).
At an acceleration voltage of 1.5 kV, several scratches appeared in the In-lens image that are not clearly present in the image at 0.5 kV. Further, the interface between the aluminium coating and the A6111 alloy is revealed; the particles, contamination and cavities are distinguishable individually in the In-lens image (Figure 6.3.b). Meanwhile, the shadow effect was still evident on the SE2 images, but the boundary of the aluminium coating layer and the Al6111 alloy is clearly presented (Figure 6.4.b).

The interface has been observed using the increased acceleration voltages of 2.5 kV (Figure 6.3.c and Figure 6.4.c) and 5.0 kV (Figure 6.3.d and Figure 6.4.d). Compared with the In-lens images at acceleration voltages below 2.5 kV, scratches on the surface were reduced at the interface; in contrast, cavities and the grains of the aluminium coating layer, which were not disclosed below 2.5 kV, have gradually appeared (Figure 6.3.c and Figure 6.3.d). Further, comparing the In-lens images at 2.5 kV and 5.0 kV, less beam irradiation damage appears at an acceleration voltage of 5.0 kV. The reason is that hydrocarbons possibly are disrupted and removed when the primary electron energies are increased to 5.0 kV.

Meanwhile, the SE2 images also increase the depth information with increase of primary electron energies; in particular, the grain structures of the aluminium coating layer are evident at 5.0 kV (Figure 6.4.c and Figure 6.4.d). Thus, the edge effects gradually appeared at the edge of the interface structures. In addition to that, the commonly-termed shadow effect or illumination effect is also evident. It generally occurs due to the position of the SE2 detector; one side of the surface which is close to the SE2 detector has contrast that is brighter than the other side. Therefore, it is possible to consider that the SE2 detector is located on the right area of the images in Figure 6.4.

In this way, it is clear that the UHRLV SEM will show different information depending on the acceleration voltage employed. In this study, an acceleration voltage of 1.5 kV appears to be appropriate condition for the In-lens and the SE2 imaging with surface sensitivity. Based on this examination, the appropriate filtering grid voltage and an incident angle for the ESB image were investigated at an acceleration voltage of 1.5 kV (Section 6.1.3, “The Effect of the ESB Detector and the Filtering Grid Voltage Selections for the dissimilar aluminium and magnesium”).
6.1.3. **The Efficient Usage of the ESB Detector and the Filtering Grid Voltage Selections for the Dissimilar Aluminium and Magnesium**

On the basis of the fact that an acceleration voltage of 1.5 kV is one of the efficient voltages for the surface sensitive imaging of the In-lens and the SE2 detector, the appropriate filtering grid voltage for ESB detector has also been investigated at 1.5 kV. In order to select the filtering grid voltage, the Monte Carlo simulation was utilized. The Monte Carlo simulation allowed calculation of the energy distribution of backscattered electrons. It is necessary because, as described in the Section 2.4.3, “ESB Detector and The Filtering Grid”, the high resolution ESB image requires high-energy backscattered electrons, avoiding detection of the secondary electrons. Accordingly, a filtering grid voltage of approximately 750V was selected (Figure 6.5).

It appears that limited contrast differences are presented in the ESB image (Figure 6.6). For example, the areas of the aluminium coating layer appear to be displayed with slightly dark contrast compared with the adjacent areas of the Al6111 alloy and Al-Mg interface. However, the difference is not clearly presented between aluminium and magnesium. Hence, the average intensities in the ESB image were investigated for the areas represented 1 to 5 in Figure 6.7.a, using Gatan digital micrograph software; the areas include the AZ31 alloy, Al-Mg intermetallics and the aluminium coating and the Al6111 alloy. The intensities on each area are represented on the graph in Figure 6.7.b. Accordingly, the average intensity of each area shows a subtle difference (Figure 6.7.c); for example, area 4, which contained pure aluminium, indicates the lowest average intensity of 162.83, which is the area of the darkest contrast of aluminium; area 1 shows the highest intensity of 167.23, which is the magnesium-rich area. Meanwhile, areas 2 and 3 indicate almost similar numbers because those areas are of relatively similar composition of $\text{Al}_{12}\text{Mg}_{17}$. Further, the numbers are slightly higher than that of areas 4 and 5, of aluminium-rich compositions, because areas 2 and 3 consist of magnesium-rich components. Therefore, it appears that the ESB image displays relatively correct information; however, the differences were too small to distinguish individual compositions by the naked eye. In addition to that, in the colour mapping image, which is converted from the ESB image, it is also difficult to show the subtle differences.
6.1.4. The Beam Tilting Effect on ESB Imaging

According to Reimer [3], the backscattered electron coefficient increases when the primary electron beam is tilted (Section 2.3.2, “Backscattered Electrons”, Figure 2.4). Comparing the backscattered coefficients of aluminium and magnesium with incident angles of 0˚ and 70˚, which is generally used for the EBSD analysis, it is clear that the backscattered coefficient of 70˚ reaches approximately twice that of 0˚ for both elements (Table 6.2 and Table 6.3). Thus, in order to investigate the effect of the incident angle difference at the ESB imaging, the primary electron beam is tilted to 70˚ at an acceleration voltage at 1.5 kV. The filtering grid voltages of 1458 V and 1500 V were examined because the Monte Carlo simulation shows the highest energy range was very narrow, which is between 1300 V to 1500 V (Figure 6.8). As a result, firstly, the images are distorted (Figure 6.9.a). Further, the contrast of the image appears to be slightly different on the left and the right areas of the image with a filtering grid voltage of 1458V, that is clearly presented in the colour mapping image which is converted from the ESB image (Figure 6.9.b). Further, with a filtering grid voltage of 1500 V, the contrast of the ESB image is divided into the bright and dark contrasts in the middle of the image that appear not to be related to the elemental composition (Figure 6.9.c). As a result, it is revealed that the backscattered electron penetration increased when the primary electrons are tilted; however, the image may not show the contrast correctly. The reason may be associated with the location of the EBSD analysis detector, which generally faces the specimen. Thus, large yield of backscattered electrons are able to reach to the EBSD detector. On the other hand, the ESB detector is located above the specimen; thus, a sufficient amount of backscattered electron is not detected by the ESB. Therefore, it is revealed that tilting the primary electron may not increase the ESB image contrast.
6.1.5. The Weld Zones Observation Using the UHRLV SEM and Characterization Using XRD

Weld Zones Observation Using the UHRLV SEM

Several weld zones have been observed using the UHRLV SEM at an acceleration voltage of 1.5 kV which was selected as a result of the appropriate primary electron examination.

Zone 1 shows the interesting features of the welded interface (Figure 6.10). For example, a boundary is evident between the Al6111 alloy and the aluminium coating layer that appears to be deformed; the Al-Mg intermetallics, which were considered to be Al$_{12}$Mg$_{17}$ intermetallics in previous studies[51, 57], are located along the coating layer; a step is evident between the intermetallics and the aluminium coating; areas of dark contrast between the intermetallics and the AZ31 alloy are also evident (Figure 6.10.a and Figure 6.10.b). Firstly, it is clear that the thickness of the coating layer, which was uniformly 50 µm before the USW process, has gradually changed depending on the area after the USW process. Further, the step is one of the interesting features which is present at the examined interface between the aluminium coating layer and the Al$_{12}$Mg$_{17}$ intermetallics in the In-lens image (Figure 6.10.a and Figure 6.10.c); however, the step is not clearly presented in the SE2 image (Figure 6.10.b). Thus, there may not be a significant difference in height. Due to the characteristics of the SE2 detector, which enable the depth information and surface roughness to be presented, a difference in height should be revealed if present. According to EDX line analysis; there was a slightly different peak between the general Al$_{12}$Mg$_{17}$ intermetallics compounds and the step (Figure 6.10.d). Thus, it is possible to consider that the step may be related to the compositional differences.

EDX analysis was also carried out on the area of dark contrast. As a result, it is revealed that the area may be related to the oxidation on the AZ31 alloy (Figure 6.10.e). In addition, a particle is evident near the oxidized area, which is located within the red lined circle in Figure 6.10.b. In order to investigate the area including the particle more clearly, the magnification was gradually increased (Figure 6.11 and Figure 6.12). Accordingly, it appeared that significant oxidation is evident close to the Al$_{12}$Mg$_{17}$ intermetallic propagated on the AZ31 alloy; however, oxidation disappeared with increasing the distance from the intermetallics (Figure 6.11). The oxidation is
neither evident on the aluminium coating layer and the Al6111 alloy. Further, it is also revealed in the ESB image and colour converted image from the ESB, that intermetallics which appear to be relatively similar to the particle, have propagated to the grain boundaries in the AZ31 alloy (Figure 6.11.b, Figure 6.11.c and Figure 6.12). Meanwhile, the Al$_{12}$Mg$_{17}$ intermetallics and the AZ31 alloy displayed relatively similar contrast in the ESB image and also the colour converted image from the ESB image (Figure 6.11.b and Figure 6.11.c). As mentioned in the previous Section 6.1.3, “The Efficient Usage of the ESB Detector and the Filtering Grid Voltage Selections for the Dissimilar Aluminium and Magnesium”, this contrast difficulty occurs due to the elemental dissimilarity, which has only a small difference in atomic number.

In order to reveal the elemental composition of the particle and the components in the grain boundaries, EDX analyses were carried out. As a result, the particle contains Al-Mn rich elements; thus, the components which have been finely propagated in the grain boundary areas are the Al-Mn intermetallics (Figure 6.12.d and Figure 6.12.e). The Al-Mn rich particle and the intermetallics in the grain boundaries may be associated with the Al-Mn rich precipitates in the AZ31 alloy; it appeared to be originally present in the AZ31 alloy (Figure 6.12.e).

Zone 2 shows a further interesting area of the interface, which has a gap of approximately 2 µm to 6 µm between the Al$_{12}$Mg$_{17}$ intermetallics. The gap appears to be oxidized (Figure 6.13.a); dendrite structures are also evident within the gap (Figure 6.13.b). Further, similar to zone 1, the aluminium coating layer has been slightly deformed, and the Al-Fe rich particle is also evident on the Al$_{12}$Mg$_{17}$ intermetallics (Figure 6.13.a, Figure 6.13.b and Figure 6.13.e). However, it is difficult to obtain the elemental difference between the aluminium coating and the Al$_{12}$Mg$_{17}$ intermetallics in the ESB image (Figure 6.13.c and Figure 6.13.d). As shown in Figure 6.11, this is because of the dissimilarity of the aluminium and the Al$_{12}$Mg$_{17}$ intermetallics. Further, the differences in the height between the intermetallics and the gap also hinder provision of the correct information. In addition, the colour mapping image appears to display slightly different contrast in the dendrite structure compared with the Al$_{12}$Mg$_{17}$ intermetallics; thus, the dendrite structures may have different compositions from that intermetallics.

Further welded zones were observed (Figure 6.14); accordingly, it is revealed that the boundaries are relatively similar to the previous areas. For example, the aluminium coating layer is deformed (Figure 6.14.a) or has partly disappeared (Figure 6.14.b); the step, the Al$_{12}$Mg$_{17}$
intermetallics, the Al-Mn rich particles and the Al-Fe rich particles are evident in the AZ31 alloy and the Al6111 alloy respectively. Further, in the area include the Al-Mn rich particle in Figure 6.14 and Figure 6.15, the Al-Mn rich intermetallics also appeared to fill the grain boundaries in AZ31 alloy.

**X-Ray diffraction (XRD) analysis**

As described previously, there are Al-Mg intermetallics at the boundaries between the aluminium coating layer and the AZ31 alloy that are expected to be the Al\(_{12}\)Mg\(_{17}\) components from the Al-Mg system phase diagrams and previous research [50, 51, 57, 83] (Figure 4.4, Section 4.1.2, USW Joint of Al6111/AZ31 Alloy). In order to investigate the actual components of the intermetallics in this specimen, the X-ray diffraction analysis was carried out. As a result, the presence of the Al\(_{12}\)Mg\(_{17}\) components are confirmed in this USW joint of Al6111/AZ31 alloys in this study (Figure 6.16).

Further, as a result of the EDX analysis, the step shows a slightly different composition from the Al\(_{12}\)Mg\(_{17}\) components. According to the previous studies and the Al-Mg system phase diagram (Figure 4.4) [50, 51, 57, 83], there is a possibility that the component of the gap is Al\(_3\)Mg\(_2\) components. The reason is due to the characteristics of the USW joint, which is a solid state joint system below the eutectic temperature; hence, theoretically, it is possible to produce the Al\(_3\)Mg\(_2\) components in addition to Al\(_{12}\)Mg\(_{17}\) components. However, the peak of Al\(_3\)Mg\(_2\) was not evident in this XRD analysis. It may be the amount of the Al\(_3\)Mg\(_2\) components are too small to be detected by the XRD.
6.2. Discussion

*The UHRLV SEM imaging*

In order to use efficiently the UHRLV SEM, an acceleration voltage of 1.5 kV, a filtering grid voltage of 750 V and incident angle 0° appeared to be appropriate conditions in this study. The reason is that it is revealed that contamination, cavities and particles displayed relatively similar dark contrast below 1.5 kV in the In-lens image; the surface sensitivity has been slightly lost above 1.5 kV.

Considering the reason of the contrast similarity of cavities and contamination at an acceleration voltage of 0.5 kV, it may occur under the following conditions; sufficient yields of secondary electrons were not achieved in the In-lens detector from cavities, and a positive charge occurred around contamination (Section 2.5.2, “Charging”). Meanwhile, the Al-Mn particles and the Al-Fe particles show relatively similar contrast, although the contrast of the Al-Fe particles is slightly brighter than that of the Al-Fe particles. Those dark contrasts appeared to show that subtle amounts of secondary electrons have been employed by the In-lens detector. For example, in manganese at an acceleration voltage of 0.5 kV, the majority of primary electrons may reach a range of approximately 1.3 nm to 2.1 nm from the surface, which is relatively similar to the generation area of the secondary electrons. Meanwhile, the majority of backscattered electrons may be generated in the area 0.21 nm to 0.64 nm from the surface (Figure 6.17.a and Figure 6.17.b).

This small difference between the both generation areas may affect to the imaging confusions. Further, compared with the backscattering coefficients of manganese, iron, aluminium and magnesium at an acceleration voltage of 0.5 kV, those of manganese and iron are approximately twice those of magnesium and aluminium (Table 6.2 and Table 6.4). Thus, it is considered that a large amount of backscattered electrons have been generated from the particle that reduced the amount of secondary electrons generated and increased the SE3 (secondary electrons 3) generation, which are not employed for the In-lens imaging (Section 2.3.1, “Secondary electron”). Further, the ESB detector is located above the In-lens detector; thus, a large amount of backscattered electrons and SE3 are absorbed in the ESB detector after passing through the In-
lens detector; a small amount of secondary electrons may pass through the In-lens detector. As described, contamination, oxidation and particles are displayed with the similar dark contrast, the reasons are different individually.

These contrast difficulties are improved at an acceleration voltage of 1.5 kV; the reason is expected to be related to the generation depth of secondary electrons and the backscattered electrons are clearly separated (Figure 6.17.c and Figure 6.17.d). Further, the yield of backscattered electrons generated slightly decreased with increasing acceleration voltages. For example, the backscattering coefficients of iron are 0.37 and those of manganese are 0.36 at an acceleration voltage of 1.5 kV, those are 0.43 and 0.42 respectively at an acceleration voltage of 0.5 kV (Table 6.4). Accordingly, the yield of SE3, which is produced by backscattered electrons, also reduced. As a result, sufficient amounts of secondary electrons may have been achieved in the SE2 detector.

Meanwhile, after increasing the acceleration voltage further to 2.5 kV and 5.0 kV, the In-lens images shows cavities and also the grain structures, which are not evident below 2.5 kV. This suggests that the images include depth information similar to the SE2 images.

Further, for the SE2 detector, an acceleration voltage of 1.5 kV appears to be an appropriate condition. The reason is that it is not possible to obtain the surface topographic information at 0.5 kV and the images gradually present depth information, such as the grain structures and strong edge effect at more than 2.5 kV. On the basis of this, efficient ESB imaging examination was undertaken at an acceleration voltage of 1.5 kV. Accordingly, it is revealed that the image enables the appropriate information to be presented, although it is difficult to distinguish dissimilar elements due to subtle differences. It may be due to the imaging capabilities of the computer rather than it is due to the detection capabilities of the ESB detector.

**Weld Zone, Metallurgical Welding and Solid-state at Welding**

It is revealed that two welding results are evident on the interface between the Al6111 alloy and the aluminium coating and between the aluminium coating and the AZ31 alloy. The interface
between the Al6111 alloy and the aluminium coating layer is expected to be joined with a metallurgical bond without melting [49, 57] (Figure 6.18). Thus, in order to investigate welding structures, EBSD analysis is necessary; however, it could not be undertaken in this study because of the specimen dimensions. It was too large to tilt the specimen to 70°; also, it was impossible to remove the welded materials from the resin without damage. It may be a future work, but it is required to consider improving the specimen preparation for EBSD analysis.

Meanwhile, the joint between the aluminium coating layer and the AZ31 alloy must be complete without eutectic reaction, which is unable to produce the intermetallics. This is because the intermetallics generally provide lower strength at the interface. According to the surface observation, the Al$_{12}$Mg$_{17}$ intermetallics were often observed at the interface, which suggests the eutectic reaction has not occurred. However, dendrite morphologies, which generally appear after the eutectic reaction, were also often observed between the gap of the Al$_{12}$Mg$_{17}$ intermetallics; the colour mapping image suggested slightly different composition from the Al$_{12}$Mg$_{17}$ intermetallics. Further, Al-Mn rich components also filled the grain boundaries on the AZ31 alloy. Accordingly, it is possible to consider that the interface may be partly reached to the eutectic point and the materials were re-crystallized.

**Intermetallic Components**

According to the UHRLV SEM observation, the Al$_{12}$Mg$_{17}$ intermetallics and the Al-Mn intermetallics appear to grow from the aluminium coating layer toward to the AZ31 alloy, which may be related to the physical and thermal properties of the alloys (Section 4.1.2, “USW Joint of Al6111/AZ31 Alloys, Table 4.2). Firstly, the magnesium alloy has a significantly low tensile strength compared with the aluminium alloy. Thus, it is considered that the intergranular cracking by friction, rather than deforming the grain structures, may be readily generated near the joint interface of the AZ31 alloy. Following that, the eutectic reaction may partly occur; as a result, the fine Al$_{12}$Mg$_{17}$ intermetallics and the Al-Mn intermetallics filled the gap of the cracks. Further, the reason that oxidation is often evident near the Al$_{12}$Mg$_{17}$ intermetallics and especially the areas the finely propagated Al-Mn component may also be related to the intergranular
cracking and the presence of Al-Mn precipitates. This is because the crack can be readily oxidized and aluminium also accelerates the oxidation.

**Steps**

Steps are the final interesting features of the weld zone, which are evident along the edge of the aluminium coating layer. The step may be emphasized by GDOES because the sputtering rate of GDOES is theoretically different depending on the element and the crystallography of the surface. Thus, it can be considered that the steps may have slightly different composition or crystallography from the Al$_{12}$Mg$_{17}$ intermetallics. EDX analysis of the step also shows a subtle difference (Figure 6.10.d); previous studies [1-5] and the phase diagram also suggested the presence of the Al$_3$Mg$_2$ intermetallics below the eutectic temperature. Therefore, steps may due to be the Al$_2$Mg$_3$ intermetallics. However, as described in the Section 2.2.2, “X-ray Diffraction (XRD) Analysis”, a small peak of Al$_{13}$Mg$_{17}$ was presented in the peak list; Al$_3$Mg$_2$ was not evident in the peak list. It may be that the steps are too small to be detected by XRD. Thus, a different approach is required to identify the step in the future work.

### 6.3. Conclusions

In order to efficiently use the UHRLV SEM, it is revealed that appropriate specimen preparation and UHRLV SEM condition, rather than the beam tilting technique, are important factors. The difficulty in elemental contrast of dissimilar aluminium and magnesium is not fully solved in this study; however, it is revealed that the ESB detector enables the subtle differences to be recognized.

As described, the surface observations using the UHRLV SEM have revealed the original structures of the weld joint, for example, the possibility that the joint surface has partly reached the eutectic temperature. In order to gain a further understanding of the characterization of the dissimilar materials, EDX analysis and further analytical instruments are necessary.
Tables

**Table 6.1.** Characteristics of the images using different detectors at acceleration voltages of 0.5 kV, 1.5 kV, 2.5 kV and 5.0 kV.

<table>
<thead>
<tr>
<th></th>
<th>In-lens</th>
<th>SE2</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5 kV</td>
<td>• Bad contrast of particles, cavities and contamination</td>
<td>• A few Shadow effect</td>
</tr>
<tr>
<td></td>
<td>• Interface between Al coating and Al6111 are clearly shown</td>
<td>• Bad contrast of the particles, contamination and cavities are not evident</td>
</tr>
<tr>
<td>1.5 kV</td>
<td>• Bad contrast of 0.5 kV is not evident</td>
<td>• Clear contrast</td>
</tr>
<tr>
<td></td>
<td>• Interface between Al coating and Al6111 is clear</td>
<td>• Edge effect is strongly evident on the right side of the image</td>
</tr>
<tr>
<td>2.5 kV</td>
<td>• Scanning mark appeared</td>
<td>• Contrast of the interface between Al coating and Al6111</td>
</tr>
<tr>
<td></td>
<td>• Scratches which are evident at 0.5 kV and 1.5 kV slightly disappear</td>
<td>• Edge effect of right side are slightly decreased</td>
</tr>
<tr>
<td></td>
<td>• Grains on the Al6111 appeared</td>
<td></td>
</tr>
<tr>
<td>5.0 kV</td>
<td>• Scanning mark become slightly weaker than that at 2.5 kV</td>
<td>• Grains are clearly appeared</td>
</tr>
<tr>
<td></td>
<td>• Grains on the Al6111 are clearly shown</td>
<td>• Edge effect of the right side are still evident</td>
</tr>
</tbody>
</table>
Table 6.2. Backscattering coefficients of Mg and Al at acceleration voltages from 0.5 kV to 5.0 kV and an incident angle of 0°, calculated by Monte Carlo simulation. The simulated numbers of electron trajectories are 200,000.

<table>
<thead>
<tr>
<th>Acceleration voltage</th>
<th>Mg (%)</th>
<th>Al (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5 kV</td>
<td>0.227985</td>
<td>0.258005</td>
</tr>
<tr>
<td>1.0 kV</td>
<td>0.199630</td>
<td>0.227340</td>
</tr>
<tr>
<td>1.5 kV</td>
<td>0.187665</td>
<td>0.209690</td>
</tr>
<tr>
<td>2.0 kV</td>
<td>0.174955</td>
<td>0.200455</td>
</tr>
<tr>
<td>2.5 kV</td>
<td>0.170765</td>
<td>0.191770</td>
</tr>
<tr>
<td>3.0 kV</td>
<td>0.165005</td>
<td>0.185460</td>
</tr>
<tr>
<td>3.5 kV</td>
<td>0.159915</td>
<td>0.180645</td>
</tr>
<tr>
<td>4.0 kV</td>
<td>0.156390</td>
<td>0.176690</td>
</tr>
<tr>
<td>4.5 kV</td>
<td>0.153520</td>
<td>0.172425</td>
</tr>
<tr>
<td>5.0 kV</td>
<td>0.145415</td>
<td>0.170720</td>
</tr>
</tbody>
</table>
Table 6.3. Backscattering coefficients of Mg and Al at acceleration voltages from 0.5 kV to 5.0 kV and an incident angle of 70˚, calculated by Monte Carlo simulation. The simulated numbers of electron trajectories are 200,000.

<table>
<thead>
<tr>
<th>Acceleration voltage</th>
<th>Mg (%)</th>
<th>Al (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5 kV</td>
<td>0.519110</td>
<td>0.542655</td>
</tr>
<tr>
<td>1.0 kV</td>
<td>0.503815</td>
<td>0.526410</td>
</tr>
<tr>
<td>1.5 kV</td>
<td>0.495180</td>
<td>0.518830</td>
</tr>
<tr>
<td>2.0 kV</td>
<td>0.489925</td>
<td>0.510050</td>
</tr>
<tr>
<td>2.5 kV</td>
<td>0.487190</td>
<td>0.504255</td>
</tr>
<tr>
<td>3.0 kV</td>
<td>0.481920</td>
<td>0.501890</td>
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<tr>
<td>3.5 kV</td>
<td>0.480995</td>
<td>0.497655</td>
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<tr>
<td>4.0 kV</td>
<td>0.477450</td>
<td>0.495605</td>
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<tr>
<td>4.5 kV</td>
<td>0.475970</td>
<td>0.494390</td>
</tr>
<tr>
<td>5.0 kV</td>
<td>0.474820</td>
<td>0.491140</td>
</tr>
</tbody>
</table>
Table 6.4. Backscattering coefficients of Fe and Mn at acceleration voltages from 0.5 kV to 5.0 kV and an incident angle of 0°, calculated by Monte Carlo simulation. The simulated numbers of electron trajectories are 200,000.

<table>
<thead>
<tr>
<th>Acceleration voltage</th>
<th>Fe (%)</th>
<th>Mn (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5 kV</td>
<td>0.425860</td>
<td>0.416755</td>
</tr>
<tr>
<td>1.0 kV</td>
<td>0.388840</td>
<td>0.378095</td>
</tr>
<tr>
<td>1.5 kV</td>
<td>0.368780</td>
<td>0.358360</td>
</tr>
<tr>
<td>2.0 kV</td>
<td>0.354805</td>
<td>0.347165</td>
</tr>
<tr>
<td>2.5 kV</td>
<td>0.347435</td>
<td>0.337305</td>
</tr>
<tr>
<td>3.0 kV</td>
<td>0.338565</td>
<td>0.328990</td>
</tr>
<tr>
<td>3.5 kV</td>
<td>0.332030</td>
<td>0.323055</td>
</tr>
<tr>
<td>4.0 kV</td>
<td>0.328305</td>
<td>0.318165</td>
</tr>
<tr>
<td>4.5 kV</td>
<td>0.323130</td>
<td>0.315655</td>
</tr>
<tr>
<td>5.0 kV</td>
<td>0.320255</td>
<td>0.309345</td>
</tr>
</tbody>
</table>
Figure 6.1. Scanning electron micrographs showing the interface of the USW joint of Al6111/AZ31 alloys in the SE2 image at an acceleration voltage of 1.5 kV. Specimen preparation was terminated prior to generation of a mirror finish; (b) the interface, after mirror finishing and GDOES surface finishing, in the SE2 image at an acceleration voltage of 5.0 kV.
Figure 6.2. Scanning electron micrograph showing the area with GDOES surface finishing and the area without it, at an acceleration voltage of 5.0 kV. An effect similar to charging is evident in the area without GDOES surface finishing because the oxide and contamination masked the surface. After GDOES, the oxide and contamination were removed from the surface; thus, it is possible to observe the surface using the UHRLV SEM.
Chapter 6

USW Joint of Al6111/AZ31 Alloys

**Figure 6.1**

- **Figure 6.1a**: Boundary between Al6111 and aluminium coating.
- **Figure 6.1b**: Boundary between Al6111 and aluminium coating.

Key features:
- **Al12Mg17 intermetallics**
- **Al-Mn particles**
- **Cavities**
- **Oxide**
- **Al-Fe particles**
- **Contamination**

Scale bars: 10 µm and 2 µm.
Figure 6.3. Scanning electron micrographs showing the In-lens images of the weld zone at different acceleration voltages: (a) 0.5 kV; (b) 1.5 kV; (c) 2.5 kV; (d) 5.0 kV.
**Chapter 6**

**USW Joint of Al6111/AZ31 Alloys**

![Image of microstructure](image)

- **AZ31**
- **Al\textsubscript{12}Mg\textsubscript{17}** intermetallics
- **Al-Mn particles**
- **Contamination**
- **Al\textsubscript{6}Fe** particles
- **Boundary between Al6111 and aluminium coating**

![Image of microstructure](image)

- **Dark contrast**
- **Boundary between Al6111 and aluminium coating**
- **Bright contrast**
Figure 6.4. Scanning electron micrographs showing the SE2 images of the weld zone at different acceleration voltages: (a) 0.5 kV; (b) 1.5 kV; (c) 2.5 kV; (d) 5.0 kV.
Figure 6.5. Schematic diagrams showing the backscattering energy distributions in aluminium and magnesium at an acceleration voltage of 1.5 kV and an incident angle of 0°, calculated by Monte Carlo simulation. The simulated numbers of electron trajectories are 200,000. According to the simulation, backscattered electrons appear to be generated most commonly at energy ranges between 0.75 keV to 1.2 keV. In order to detect only those high energy backscattered electrons and to avoid low energy backscattered electrons below 750V, a filtering grid voltage of 750 V was selected.
Figure 6.6. (a) Scanning electron micrograph showing the ESB images of the weld zone at an acceleration voltage of 1.5 kV and an incident of 0°, with a filtering grid voltage of 750 V. The aluminium coating area using pure aluminium is presented in dark contrast, although the Al6111 alloy and the AZ31 alloy show relatively similar contrasts.
Figure 6.7. (a) Area of intensity line profiling of Figure 6.6; (b) line profile of (a), which shows the point versus intensity counts; (c) average intensities of the areas 1 to 5. The average counts show subtle differences between aluminium, intermetallics and magnesium; however, it is difficult to distinguish them with the naked eye.
Figure 6.8. Schematic diagrams showing the backscattering energy distributions in aluminium and magnesium at an acceleration voltage of 1.5 kV and an incident angle of 70°, calculated by Monte Carlo simulation. The simulated numbers of electron trajectories are 200,000. According to the simulation, backscattered electrons appear to be generated most commonly energy ranges between 1.3 keV to 1.5 keV. In order to detect only those high energy backscattered electrons, the filtering grid voltages of 1458 V and 1500 V were selected for the surface sensitive ESB imaging.
Figure 6.9. (a) Scanning electron micrographs showing the ESB image at an acceleration voltage of 1.5 kV, with a filtering grid voltage of 1458 V and an incident angle of 70°; (b) the colour mapping image converted from (a); (c) filtering grid voltage of 1500 V. As a result, it is revealed that images are distorted and image contrast is not related to the composition.
Chapter 6

USW Joint of Al6111/AZ31 Alloys

(a) Boundary between Al 6111 and aluminium coating

(b) Boundary between Al 6111 and aluminium coating

Dark contrast

\( \text{Al}_{12}\text{Mg}_{17} \) intermetallics

10 µm
Chapter 6

USW Joint of Al6111/AZ31 Alloys

(c) 222

(d)
Figure 6.10. Scanning electron micrographs showing weld zone 1 at an acceleration voltage of 1.5 kV: (a) In-lens image; (b) SE2 image; (c) EDX line analysis for the intermetallics at the interface, with different morphologies; (d) EDX analysis for the step; (e) EDX analysis for an area of dark contrast in the AZ31 alloy. According to the UHRLV SEM images of (a) and (b), the interface structures are revealed, such as the aluminium coating layer, the Al-Mg intermetallics, and a step, oxide, particles in both alloys. Further, EDX analyses suggest that the intermetallics may consist of Al-Mg components, even though they are displayed with different morphologies; the step may contain the slightly different components from the Al-Mg intermetallics; the area of dark contrast is oxide.
Chapter 6

USW Joint of Al6111/AZ31 Alloys

(a) Al-Mn rich particle

(b) Al-Mn rich particle

2 µm
Figure 6.11. Scanning electron micrographs showing the area near the particle in Figure 6.10.a and b at an acceleration voltage of 1.5 kV; (a) SE2 image; (b) ESB image; (c) colour converted image of (b). The intermetallics appear along the grain boundaries, and oxidation is evident near relatively large the Al-Mg intermetallics. Further, within the white line circle in the colour converted image, the component shows similar colour contrast to the particle. The image has been converted from the ESB image which enables the elemental composition to be from; thus, it is considered that those elements are of relatively similar compositions.
Chapter 6

USW Joint of Al6111/AZ31 Alloys

(a) Al-Mn rich particle
Al-Mn rich intermetallics
Oxide

(b) Al-Mn rich particle
Al-Mn rich intermetallics
Oxide

1 µm
Chapter 6

USW Joint of Al6111/AZ31 Alloys

(c)

(d)

<table>
<thead>
<tr>
<th>Element</th>
<th>Atomic%</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>3.11</td>
</tr>
<tr>
<td>Mg</td>
<td>0.20</td>
</tr>
<tr>
<td>Al</td>
<td>52.40</td>
</tr>
<tr>
<td>Mn</td>
<td>44.11</td>
</tr>
<tr>
<td>Zn</td>
<td>0.20</td>
</tr>
</tbody>
</table>
Figure 6.12. Scanning electron micrographs showing the images of the enlarged area in Figure 6.11 at an acceleration voltage of 1.5 kV; (a) SE2 image; (b) ESB image; (c) the colour mapping of (b); (d) EDX analysis of a particle in the AZ31 alloy; (e) EDX line analysis of a precipitate in the AZ31 alloy. It is revealed that the intermetallics near the Al-Mn particle appear to follow the grain boundaries on the AZ31 alloy; the components of the intermetallics may be Al-Mn. This is possible because Al-Mn precipitates are evident on the AZ31 alloy.
Chapter 6

USW Joint of Al6111/AZ31 Alloys

(a) Al6111

(b) AZ31

Al-Mn rich particle

\( \text{Al}_6\text{Mn} \) rich particle

Al\(_{12}\)Mg\(_{17} \) intermetallics

Al\(_{12}\)Mg\(_{17} \) intermetallics

Oxide

Al coating layer

Al coating layer

2 µm

2 µm
Chapter 6

USW Joint of Al6111/AZ31 Alloys

(c) Al-Mg intermetallics

(d) Al-Fe particle

2 µm
Figure 6.13. (a) Scanning electron micrographs showing weld zone 2 at an acceleration voltage of 1.5 kV; (b) area at an increased magnification (a); (c) ESB image of (b); (d) colour converted image from (c); (e) EDX analysis for the particle on the Al6111 alloy near the boundary between the Al coating layer and the Al6111 alloy. The gap between the relatively large Al-Mg intermetallics is oxidized. Dendrite structures are evident in the gap; these may have slightly different composition from the relatively large Al-Mg intermetallics. On the Al6111 alloy, Al-Fe particle is also frequently evident.
Figure 6.14. (a) and (b). Scanning electron micrographs showing further weld zones in the In-lens images. The structures of the weld zones are relatively similar to the areas previously observed. For example, the Al coating layer is significantly deformed; Al-Mn particles are located on the AZ31 alloy; the Al-Fe particles are located on the Al6111 alloy. A step is also evident between the Al-Mg intermetallics and the Al coating layer.
Figure 6.15. Scanning electron micrographs showing the area of Figure 6.14.b at increased magnification, at an acceleration voltage of 1.5 kV; (a) ESB image; (b) colour converted image in (a). The particles within the white line circles show slightly different contrast from the Al-Mg intermetallics. Similar to the area in Figure 6.12, they may be the Al-Mn component which appears to be originally contained in the AZ31 alloy.
Figure 6.16. (a) XRD analysis data. From the results, the $\text{Al}_{12}\text{Mg}_{17}$ intermetallic components are contained in the USW joint of Al6111/AZ31 alloys; however, peaks for the $\text{Al}_3\text{Mg}_2$. 
Figure 6.17. Schematic diagrams showing the Monte Carlo simulation in manganese: (a) maximum penetration depth of the primary electrons at an acceleration voltage of 0.5 kV; (b) maximum generation depth of backscattered electrons at 0.5 kV; (c) 1.5 kV; (d) 1.5 kV. The differences between the penetration depths of primary electrons which are relatively similar to the area secondary electrons generate, and generation depth of backscattered electrons, are relatively small at an acceleration voltage of 0.5 kV. Meanwhile, at an acceleration voltage of 1.5 kV, the depths of secondary electrons and backscattered electrons generation are clearly different.
Figure 6.18. Schematic diagrams showing a model of the metallurgical bond between the aluminium: (a) before welding; (b) after welding [49]. It is expected that similar interface may exist at the interface between the aluminium coating and the Al6111 alloy.
Chapter 7.  Ti6Al4V Honeycomb

7.1.  Result

7.1.1.  Modified Surface Layer (MSL) and Non-MSL Ti6Al4V Component Plates

The cross-sectional UHRLV SEM images of the MSL (RGV15500 EB VAR) and Non-MSL Ti6Al4V honeycomb plates are presented in Figure 7.1 and Figure 7.7 respectively; an acceleration voltage of 1.0 kV has been employed for the observations.

It is revealed that the MSL layer is present at the surface, with a width of approximately 20 - 30 μm, that consists of relatively thick and short acicular α phases, and the β phases which filled the gap between the acicular α phases. A transformed layer is present, with a width of 100 μm, below the MSL layer; the primary α grains are located below the transformed layer (Figure 7.1). Meanwhile, the Non-MSL Ti6Al4V alloy plate reveals a transformed layer of approximately 80 - 100 μm-width and the primary α grains below the transformed layer. Compared with the MSL specimen, the form of the α phases and the β phases are relatively thin and elongated on the Non-MSL specimen (Figure 7.7).

Further, the surface of the MSL layer is relatively coarse (Figure 7.1), which is possibly associated with the MSL layer. In order to investigate the reason for the coarse MSL surface, the top surface of the MSL layer has been observed using optical microscopy and the UHRLV SEM (Figure 7.2). As a result, the surface roughness of the MSL surface appears not to be due to the brittleness of the alloy; it might originally have a coarse structure.

According to Rolls-Royce [60], it is expected that the formation of the MSL layer possibly has a significant or subtle influence from the copper-nickel filler metal. Thus, in order to investigate the difference between the MSL and the Non-MSL specimen microstructures, including the effects of the copper-nickel filler metal, EDX analyses were carried out. Figure 7.3 shows EDX point analyses data at the acicular α phases and the β phases in the MSL layer; EDX was carried out at an acceleration voltage of 10.0 kV. Accordingly, it is revealed that the acicular α phase consists of aluminium in titanium-rich components; vanadium, iron, nickel and copper also
appear to be present, although the individual amounts are lower than aluminium (Figure 7.3). In contrast, the β phase in the MSL layer consists of aluminium, vanadium, iron, nickel and copper. Further, the amount of titanium contained in the β phase is less than in the α phase. Meanwhile, vanadium, nickel and copper are present in significantly larger amounts than the α phase; it is due to their functions as β stabilizers. Interestingly, aluminium, which has a function as an α stabilizer, is also contained in the β phases; the amount is relatively similar to the amount in the α phase (Figure 7.3). Further, in general, the Ti6Al4V alloy does not contain nickel and copper. Thus, it is clear that the previous elements, evident from EDX analyses, are the result of diffusion from the copper-nickel filler metal.

As described, the transformed layer is located below the MSL layer, and it consists of relatively thin and elongated acicular α phases and the β phases. The components of the α phase are aluminium and vanadium in titanium-rich components; small amounts of nickel and copper are also consistently revealed in the transformed layer (Figure 7.4). Compared with the α phases on the MSL layer, aluminium is significantly increased and vanadium, which is contained in small amounts in the α phase on the MSL layer, also clearly exists in the α phase; in contrast, titanium has decreased (Figure 7.3 and Figure 7.4). Meanwhile, EDX analyses were carried out for the β phases on the transformed layer; however, it was revealed that the β phases are too thin for such analysis. Therefore, EDX line analyses were undertaken for the β phases in the transformed layer (Figure 7.5). Accordingly, vanadium and copper peaks are only obtained in the β phase region; iron and nickel are not clearly present where the β phases are located, even though the amount of nickel is slightly more than that of copper.

In addition, unlike the further transformed layer on the MSL specimen, there is an area showing non-uniform structures within a relatively large grain, which is indicated by a red line circle in Figure 7.1. EDX line data show similarity to that of the general transformed layer, although iron was not detected (Figure 7.6).

Meanwhile, in order to investigate the difference between the MSL and Non-MSL specimens, EDX point analyses were also carried out for the transformed layer on the Non-MSL specimen (Figure 7.8); a range of acceleration voltage, between 10.0 kV to 15.0 kV, was employed.
Accordingly, it is revealed that the acicular α phases appear to consist of aluminium and titanium rich components with subtle amounts of vanadium, iron, nickel and copper. Further, the components of the β phases appear to contain aluminium, vanadium, nickel, copper and small amounts of iron. Interestingly, the elements of β stabilizers are little contained in the α phases; relatively high amounts of aluminium are present in the β phases.

Additionally, compared with the transformed layer in the MSL specimen (Figure 7.4), it appears that titanium and vanadium in the α phases on the Non-MSL specimen are lower than those of the MSL specimen. In contrast, aluminium is contained in the Non-MSL specimen more than that in the MSL specimen. In addition, relatively high amounts of aluminium, nickel and copper are contained in the β phase on the Non-MSL specimen.

As described, it is revealed that the ratio of the component elements is different depending on the layers. Here, in order to investigate the distribution of the elements further, EDX line analyses were carried out to the both MSL and Non-MSL specimen individually, for a region from the surface to the primary α grains (Figure 7.9). As a result, several interesting features are displayed in the MSL layer line analysis (Figure 7.9.a). For example, it appears that the coarse surface area shows only the peaks of titanium and vanadium. Further, titanium shows a non-uniform distribution; it appears to be significantly reduced at, not only the α phases, but also at the boundary of each layer. Further, little aluminium appears to be present on the coarse surface area in the MSL layer; it gradually increases and exceeds vanadium at the transformed layer. The copper peak, which appears to be gradually reduced with increasing distance from the surface, is clearly displayed. However, the nickel peak is not present, despite the total amount of nickel being relatively similar to that of copper.

Meanwhile, in the Non-MSL specimen, the titanium peak appears to be relatively smooth compared with the MSL specimen. Interestingly, the aluminium peak shows a slightly different distribution from the MSL specimen. For example, aluminium is slightly lower than vanadium near the surface; it slightly increases with increasing distance from the surface, but never exceeds the peak intensity of vanadium (Figure 7.9.b). Further, small peaks of copper and nickel are evident individually at the area where the peak of vanadium is slightly increased, although the other elemental peaks are relatively low.
As mentioned previously, it is revealed that the MSL specimen appears to have a relatively coarse surface. Further areas including the surface in the MSL and Non-MSL specimens have been observed; however, the coarse surface was only present on the MSL specimen (Figure 7.10).

In addition, ESB imaging has been undertaken in order to obtain the compositional image with surface sensitivity at a low acceleration voltage. However, as described in Section 2.1.3, “The Efficient Usage of the ESB Detector and the Filtering Grid Voltage Selections for the Dissimilar Aluminium and Magnesium”, due to the subtle differences between the α and β phases, it is challenging to obtain high resolution ESB imaging (Figure 7.11).

7.1.2 The Interface between the CP Titanium and the Ti6Al4V Alloy Plate, and the CP Titanium Honeycomb Core Zone

Figure 7.12 shows three conditions of the Ti6Al4V alloy honeycomb, including (a) the original structure of the Ti6Al4V alloy honeycomb; (b) the MSL Ti6Al4V alloy honeycomb, mounted in conductive resin and; (c) the Non-MSL Ti6Al4V honeycomb, mounted in conductive resin. The images (a) and (b) are observed using optical microscopy; the UHRLV SEM is used for observing the broad area of (c). Accordingly, it is revealed that the CP titanium core zone was detached from the Ti6Al4V alloy plate (Figure 7.12.b), and significantly deformed during the conductive resin mounting process (Figure 7.12.c).

An area which is indicated with the red line circle in Figure 7.12.c has been enlarged for further observations (Figure 7.13). Accordingly, several line structures are displayed in bright contrast on the CP titanium in the AsB image (Figure 7.13.a); some of the structures appear to follow the grain boundaries. Further, several areas are displayed in dark contrast, which appear to be spots. The details of an area within the red line circle in Figure 7.13.a, which includes the line structures and spots, are observed in Figure 7.13.b; slip planes, areas of dark contrast along the slip planes and, particles which appear to form the line structures, are evident. Further, some of particles appear to be located at the grain boundary. However, as mentioned above, the CP
titanium core zone has been deformed after the conductive resin mounting process. Thus, it appears to be difficult to discuss the original of the slip planes and grain boundaries.

Elemental composition of the area similar to Figure 7.13.b has been investigated by EDX point analyses (Figure 7.13.c). As a result, the particles appear to consist of a nickel-rich component with iron; the area of dark contrast contains slightly more aluminium, nickel and copper than the general CP titanium area. In general, nickel and copper are not contained in the CP titanium; thus, it is possible to consider that the presence of copper and nickel in the CP titanium core zone is due to the copper-nickel filler metal.

The final area of interest in the Ti6Al4V alloy honeycomb specimen is the interface between the Ti6Al4V alloy and the CP titanium. The individual interfaces on the MSL and the Non-MSL specimen are presented in Figure 7.14. Relatively similar structures are evident for both interfaces. For example, the form of the α and the β phases near the interface are significantly different from the general α and β phase structures of the specimens; different dimensions of the α-rich and the β-rich phases are revealed (Figure 7.14.a and Figure 7.14.b). In order to investigate the microstructures of the interfaces and elemental compositions, two areas have been selected that are represented in 1 to 2 by the red line circles in Figure 7.14.a and Figure 7.14.b.

Firstly, EDX line analyses were undertaken for areas 1 in both individual specimens. In the MSL specimen, a significant peak of copper is evident near the interface on the Cp titanium; as it approached the Ti6Al4V alloy plate, the copper appears to have decreased. In contrast, aluminium significantly increased with distance from the Cp titanium and nickel shows a relatively low peak, and iron was not detected from the line analysis on the MSL interface (Figure 7.15.a).

Meanwhile, in the Non-MSL specimen, significant peaks of nickel, copper and iron are evident, even though EDX analysis was undertaken at an acceleration voltage of 5.0 kV (Figure 7.15.b). Further, similar to the surface line analysis for the Non-MSL specimen, the amount of aluminium slightly increased with distance from the CP titanium; however, the amount did not appear to exceed that of vanadium. In order to verify the integrity of EDX data at 5.0 kV, an area of iron-copper-nickel rich in the Non-MSL specimen (Figure 7.15.b) has been enlarged and EDX was carried out at 15.0 kV (Figure 7.16). Accordingly, it is clear that EDX analysis at both
acceleration voltages provides relatively similar data, indicating that the β phases appear to consist of nickel-rich components with titanium, iron and copper. Further, the elemental compositions are relatively similar to the particle on the CP titanium (Figure 7.13).

EDX analyses were also carried out for areas 2 at the interfaces on the both specimen at an acceleration voltages of 10.0 kV and 15.0 kV. Accordingly, it is revealed that the elemental compositions are relatively similar in the MSL and the Non-MSL specimens. For example, copper-rich particles are located adjacent to the β phases which may be copper-nickel-rich components. Further, iron appears to be contained in the MSL specimen more than that of the Non-MSL specimen; however, the distribution of iron is not clearly obtained (Figure 7.17).

As described, relatively high amounts of iron, copper and nickel appear to be present near the interface; those element gradually decrease in amounts with increasing distance from the interface. Hence, it is possible that nickel and copper concentrated in the interface area and those are distributed toward to the CP titanium.

### 7.1.3 EBSD Analysis In Order To Investigate the Nature of the MSL Layer

EBSD analysis has been undertaken by Obashi and Preuss [65] in order to identify the nature of the MSL layer (Experimental Procedure 4.1.3, “Ti6Al4V alloy honeycomb”, Figure 7.18.a). displays an inverse pole figure β map, which shows the location of the β phase and their grain boundaries in the current condition. There are blank areas within the map, which suggest the presence of the primary α phases which have not transformed from β phases. Further, the MSL layer and the transformed layer are not separated; both layers are presented as the single layer in the β grains, which suggests that the MSL layer and the transformed layer are originally from the same β phases (Figure 7.18.a).

The α orientation map was calculated from the β orientation map after applying the Burger’s crystallographic relationship of \{110\}_β // \{0002\}_α and <111>β // <1120>α. It suggests that a bcc crystal is able to transform to 12 hexagonal variations which have different orientations that depend on the parent β crystal [65, 84-87]. Applying this theory, the MSL layer is displayed
separately from the transformed layer in the converted α orientation map (Figure 7.18.b); it is revealed the MSL layer has different crystallographic orientation from the transformed layer, although grain boundaries are not evident on the α map.

As described, the converted α orientation map suggests the possibility that the MSL layer and the transformed layer may be generated from a single layer of the β phases.

### 7.2 Discussion

**EDX Analyses at Low Acceleration Voltages and High Acceleration Voltages**

EDX analyses have been carried out frequently at an acceleration voltage of 10.0 kV and 15.0 kV; a low acceleration voltage of such as 5.0 kV was only employed for the point analyses at the interface on the Non-MSL specimen. However, as described in Literature survey (Section 2.2, “SEM and Low-Voltage SEM”), this study requires the surface sensitive information to be revealed using the low acceleration voltage for not only the high resolution imaging but also EDX analysis (Section 2.6.1, “Energy Dispersive X-Ray Analysis). Thus, using a high acceleration voltage, i.e., 10.0 kV, is not the most appropriate condition from the viewpoint of the surface sensitivity. The reason is that with increased acceleration voltages, the area from where characteristic X-rays are generated is also expanded; thus, if there are only subtle amounts of elements contained, the EDX detector may be unable to distinguish individual elements (Section 2.6.1, “Energy Dispersive X-Ray Analysis). However, there are reasons not to utilize a low acceleration voltage. In the current EDX detection system, at an acceleration voltage of 5.0 kV, the X-ray energy ranges, which is the criteria for distinguish individual elements, overlap for copper and nickel; oxygen, vanadium and titanium also overlap (Table 7.1). For example, the energy range of the nickel-L line 0.805 - 0.898 keV is similar to that of the copper-L line of 0.882 - 0.977 keV; thus, it is possible to incorrectly detect nickel as copper. In fact, EDX analysis for the MSL layer at an acceleration voltage of 5.0 kV is presented in Figure 7.19. Point analyses show unusual ratios of elements; 20 at% vanadium, 1 at% aluminium and 60 at% of titanium appear to be present at a point on the MSL layer. However, as mentioned above, it is suggested to be incorrect detection; the most likely cause of confusion is that titanium appears to
be detected as vanadium. Further, detection of aluminium, nickel and copper may also create a problem. Meanwhile, EDX line analysis for the interface in the Non-MSL specimen has been carried out at acceleration voltage of 5.0 kV. However, compared with EDX data at 15.0 kV, it is clear that the each peak appears to be detected correctly, unlike the MSL layer line. The reason for the observed confusion may be related to the amounts of elements for the detection present individually; sufficient amounts, which are necessary for the correct detection, might not be present in the MSL specimen.

As described, acceleration voltages of 10.0 kV and 15.0 kV have been employed to compensate for the instability in the low acceleration voltage EDX. However, it is still difficult to say they are the appropriate conditions, although the X-ray energy ranges of the element of interest are not overlapped (Table 7.1). In fact, despite the fact that nickel is contained at a greater level than copper in the MSL layer surface, the peak of nickel is not evident in the line analysis data (Figure 7.5 to Figure 7.9 and Figure 7.15). The reason is, as mentioned previously, the region from where characteristic X-rays are generated is expanded at increased an acceleration voltages; the EDX data are unable to present the subtle differences of elements.

Therefore, in order to distinguish subtle elements at low acceleration voltage, EDX analysis need to employ a detector with high detection capability such as the Silicon drift detector (SDD). Especially, in order to identify the distributions of nickel and copper, the combination of SDD and low acceleration voltage EDX analysis is urgently necessary. The reason is that SDD may have a relatively high capability to detect X-rays signals at low acceleration voltages, giving the only possible means to generate the surface sensitive EDX data.

**Microstructures and Surface Roughness in the MSL Specimen**

As mentioned above, the microstructures of the MSL layer are slightly different from the transformed layer. For example, relatively thick and short acicular α phases are randomly located in the β-rich condition, which may be related to the coarse surface structures. Meanwhile, relatively thin and elongated acicular α phases are evident in the transformed layer; the surface revealed a relatively smooth structure.
In order to investigate the reason of the differences in the microstructures in both layers, EBSD analysis was carried out. As a result, there is a possibility that the MSL layer and the transformed layer are generated from the same parent β phases. On the basis of this assumption, it is necessary to consider the relevance of the different microstructures, the surface roughness and the β transformation; the copper-nickel filler metal may also have important function to MSL layer generation.

In general, the phase transformation and growth process occur under the Burgers crystallographic relationship, depending on the cooling rate and alloy compositions (Section 4.1.3, “Ti6Al4V Alloy Honeycomb”). In general, the Ti6Al4V alloy was cooled at sufficiently low rates from the β region into the α+β region; the α phases commence nucleation preferentially at the β phase grain boundaries; they grow parallel plates as rapidly in the vertical direction along the plane and slowly increase the thickness until the alpha plates fill the individual colonies[87]. This process can be applicable to the transformed layer morphologies.

Further, considering the EBSD analysis, at revealed that the MSL layer is possibly generated from same β parents; the generation of the MSL layer occurred after the transformed layer generation which may be due to “acicular” martensite transformation at lower martensite transformation temperature during the bonding process [87] (Section 4.1.3, “Ti6Al4V Alloy Honeycomb”), because the acicular α phases in the MSL layer are located randomly. According to Lütjering [87], it is revealed that an acicular martensite is termed hexagonal α´ martensite, which consists of a mixture of the acicular α plate with different variant of Burgers relationship and generally contains a high dislocation density and twins. The hexagonal α´ martensite has been supersaturated with the β stabilizers, and decomposes to α+β by precipitating β particles at dislocations or β phases at plate boundaries when annealed above the α+β temperature region. The hexagonal structure of the martensite becomes distorted and the crystal structure loses the hexagonal symmetry with increased solute content; the structures are termed orthorhombic martensite of α´´. Further, the initial stage of decomposition of the orthorhombic martensite above the α+β temperature appears to be spinodal decomposition into solute lean α´´ and solute rich α´´, which enable discriminative microstructures to form, before the β phases are precipitated. By this theory, it can be explained that the reason for the random location of the α phases and increased the thickness in the MSL layer is due to the orthorhombic martensite after a
martensite transformation. Further, the cooling rate might be low because the form of the acicular α phase is relatively short.

The reason for the presence of the β-rich phases and the coarse surface in the MSL layer may need to consider the effect of the β stabilizers, including nickel and copper. During the bonding process, it is assumed that either the Ti6Al4V alloy honeycomb bonding processes with a transient liquid phase bonding (TLP) or an activated diffusion bonding (ADB) was used (Section 4.1.3, “Ti6A4V alloy honeycomb”). Also the temperature was maintained above and below the eutectic temperature respectively, copper and nickel have diffused into the titanium matrix. As a result, the components on the MSL surface are considered as the β-rich titanium in the Ti-Cu and Ti-Ni phase diagrams (Figure 7.20) [60, 88-90]. However, the diffusion rates of nickel and copper are relatively faster than other elements contained in the Ti6Al4V alloy. Hence, cavities, which are generated due to absence of nickel and copper, are unable to be filled by other elements. The cavities are termed Kirkendall voids, and they may be related to the surface roughness.

Further, as mentioned previously, α nucleation can occur after phase separation to the spinodal-type lean α'' and solute rich α'' components; the phase separation generally occurs when two components are quenched from high temperature and maintained in this state for a period [60, 87, 91]. Once α nucleation has commenced, it is expected that nickel and copper may temporarily increase near the surface due to the diffusion flux. Hence, the β-rich grains are present on the MSL layer [60]. Further, with progress of nucleation, the contained β stabilizers, including nickel and copper, appear to slightly decrease from the surface due to transformation to the α phase; as a result, the MSL layer consists of the thick and short α phases which are randomly located in the β-rich condition.

In addition, the reason for different distributions of aluminium in the MSL specimen and the Non-MSL specimen is still not revealed. In general, it is possible that aluminium increases with increasing distance from the surface because the microstructure gradually approaches the primary α phases. However, as described, in the MSL specimen, aluminium appears to exist on the rough surface area; the contained amounts of aluminium and vanadium are relatively similar in the MSL layer; later, aluminium exceeds vanadium in the transformed layer. Accordingly, compared with vanadium, which appears to be present relatively uniformly, aluminium appears
to be contained in the primary $\alpha$ grains at approximately twice the amounts in the MSL layer. Meanwhile, in the Non-MSL specimen, aluminium appears to be contained at lower levels than vanadium near the surface; aluminium slightly increases with increasing distance from the surface, although it never exceeds the amount of vanadium which appears to be present relatively uniform. In order to investigate the reason of the difference, a further study is necessary.

**Effect of Nickel and Copper**

As mentioned above, there may be effects from nickel and copper in the MSL layer generation; however, it is difficult to discuss the effects of copper-nickel filler metal by EDX analysis due to the low amounts of those elements, and the confusion in EDX detection. In contrast, relatively high amounts of nickel and copper are evident near the interface between the CP titanium and the Ti6Al4V alloy and on the CP titanium in both specimens. Therefore, it may be considered that copper and nickel appeared to be concentrated at the interface during the bonding process, rather than diffusing into the MSL layer (Figure 7.21). In addition, the amount of copper-nickel in the Non-MSL specimen appears to be slightly higher than that of the MSL specimen. The difference may be related to the manufacturing process between the MSL and Non-MSL plate; it is necessary to understand the both process in order to clarify the effects of copper-nickel filler metal.

**The originality of the MSL layer**

EBSD map analysis by Obashi and Preuss (Figure 7.18) revealed a possibility mechanism for the MSL layer generation, which is generated from the same parent $\beta$ phases as the transformed layer. However, as described previously, the details of manufacturing process of the MSL honeycomb plate, including a need of an additional $\alpha$ nucleation for the MSL and the reason of producing the MSL layer, has not been clearly disclosed; it still needs to consider further.
7.3. Conclusions

As described, the Ti6Al4V alloy honeycomb has complicated characteristics. A part of the nature of the MSL layer has been revealed in this study by the SFS preparation and the UHRLV SEM. For example, the coarse surface was not brittleness of the surface; it is one of the original features. However, there are still aspects of the Ti6Al4V alloy honeycomb that are not understood, including the origin of the MSL layer and the effects of the nickel and copper filler metals. It is difficult to discuss the subtle amount of nickel and copper, which are dissimilar elements in the Ti6Al4V using EDX analysis at both low and high acceleration voltages. Further research in different approach is necessary in to understand the complicated MSL system.
Tables

**Table 7.1.** X-ray energy range for EDX analysis associated with the UHRLV SEM at acceleration voltages of 5.0 kV, 10.0 kV and 15 kV.

<table>
<thead>
<tr>
<th>Energy Level</th>
<th>5.0 kV</th>
<th>10.0 kV, 15.0 kV</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Low - High</strong> (keV)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O Ka1</td>
<td>0.482 - 0.569</td>
<td>O Ka1</td>
</tr>
<tr>
<td>Fe La1_2</td>
<td>0.660 - 0.750</td>
<td>Fe Ka1_2</td>
</tr>
<tr>
<td>Al Ka1</td>
<td>1.435 - 1.539</td>
<td>Al Ka1</td>
</tr>
<tr>
<td>Cu La1_2</td>
<td>0.882 - 0.977</td>
<td>Cu La1_2</td>
</tr>
<tr>
<td>Ni La1_2</td>
<td>0.805 - 0.898</td>
<td>Ni Ka1</td>
</tr>
<tr>
<td>V La1_2</td>
<td>0.468 - 0.554</td>
<td>V Ka1</td>
</tr>
<tr>
<td>Ti La1_2</td>
<td>0.410 - 0.495</td>
<td>Ti Ka1</td>
</tr>
</tbody>
</table>

- Energy range of copper and nickel, vanadium, titanium and oxygen are overlapped at acceleration voltage of 5.0 kV. Meanwhile, those overlapped are not theoretically evident at an acceleration voltage of 10.0 kV.
Figure 7.1. (a) Scanning electron micrograph showing the MSL layer of the Ti6Al4V alloy in the In-lens image at an acceleration voltage of 1.0 kV. The MSL layer has a width of approximately 30 µm; the width of the transformed layer below the MSL is in the range from 150 µm to 200 µm. Within the MSL layer, relatively thick and short acicular α phase is evident and the surface is relatively coarse. The β-rich transformed layer, which is indicated with the red line circle1, has been analyzed using EDX (Figure 7.6).
Figure 7.2. (a) and (b) Digital micrographs showing the MSL surface with CP titanium core zone; (c) enlarged image of (b) after polished away the CP titanium core zone in the SE2 image. The MSL surface does not appear to be flat.
**Figure 7.3.** EDX point analyses for the primary α phase and the β phase in the MSL layer at an acceleration voltage of 10.0 kV. Accordingly, the β phase contained vanadium, iron, nickel and copper; the amount of nickel is slightly more than that of copper.
Figure 7.4. EDX point analysis for the α phases in the transformed layer on the MSL specimen at an acceleration voltage of 10.0 kV. Compared with the MSL layer, the amounts of aluminium and titanium increased, but vanadium significantly decreased. Further, the amounts of nickel and copper are relatively similar, but both elements are often obtained in the α phases. Iron is also detected, however, this is not a frequent detection.
Figure 7.5. EDX line analysis for the transformed layer in the MSL specimen at an acceleration voltage of 10.0 kV. The peaks of iron and nickel are difficult to distinguish, even though the amounts of nickel are relatively similar to copper. Thus, it is considered that nickel and copper may have diffused into both the α and β phases.
Figure 7.6. EDX line analysis for the area which includes the relatively thick beta within the transformed grain at an acceleration voltage of 10.0 kV. As a result, it is revealed that the beta has copper and vanadium rich components. Nickel also appears to be included in the β phase. Iron is not detected.
Figure 7.7. Scanning electron micrograph showing the Non-MSL specimen in the In-lens image at an acceleration voltage of 1.0 kV. The thickness of the transformed layer is approximately 100 μm. Compared with the MSL layer, the transformed layer in the Non-MSL layer is slightly thinner than that of the MSL layer, but the surface is smoother than that of the MSL specimen.
Figure 7.8. EDX point analyses for α phase and the β phase in the transformed layer on the Non-MSL specimen at an acceleration voltage of 15.0 kV: Spectra 1 and 2 represent of the β phases, and 3 represents the α phases. Unlike the MSL specimen, vanadium and nickel are relatively high yield in the β phases; aluminium is high in the α phase.
Table: Composition of Ti6Al4V Honeycomb (at%)

<table>
<thead>
<tr>
<th></th>
<th>Al</th>
<th>Ti</th>
<th>V</th>
<th>Fe</th>
<th>Ni</th>
<th>Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sum</td>
<td>8.27</td>
<td>86.29</td>
<td>3.53</td>
<td>0.48</td>
<td>0.79</td>
<td>0.65</td>
</tr>
</tbody>
</table>

Diagram: Microstructure of Ti6Al4V Honeycomb

- MSL: Martensitic Separation Line
- Primary α: Primary Alpha
- Transforme: Transformation

Area: Rough
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Ti6Al4V Honeycomb

Figure 7.9. EDX line analyses; (a) MSL specimen; (b) Non-MSL specimen at an acceleration voltage of 10.0 kV. It is revealed that vanadium appears to be constantly present from the surface through the transformed layer in both MSL and Non-MSL specimen; however, aluminium increased with distance from the surface, becoming higher in amount than vanadium in the MSL specimen. In contrast, copper slightly decreased with distance from the surface. Meanwhile, in the Non-MSL specimen, aluminium slightly increased but it appears of relatively similar amount to vanadium in the transformed layer; copper and nickel appear have reduced the amounts, although it is difficult to discuss their distribution from line analysis above. Further, the distribution of iron is also difficult to observe due to low contained amounts, and it may have diffused into both the α and β phases.
Figure 7.10. (a) and (b) Scanning electron micrographs showing the surface of the MSL specimen in the In-lens image; (c) the Non-MSL specimen in the In-lens image and (d) the SE2 image, at an acceleration voltage of 1.0 kV. The surface of the MSL layer is relatively coarse compared with that of the Non-MSL layer.
Figure 7.11. Scanning electron micrographs showing the ESB image at an acceleration voltage of 1.0 kV: (a) MSL layer; (b) Non-MSL layer. The α phase and the β phase have only subtle differences in elements. Thus, it is difficult to distinguish the differences of the alpha and beta phases in the ESB image.
Figure 7.12. Digital micrographs showing the MSL Ti6Al4V honeycomb plate: (a) original structure before conductive resin mounting; (b) after conductive resin mounting of (a). It is revealed that the CP titanium core zone was detached from the Ti6Al4V alloy plate. (c); scanning electron micrograph showing the SE2 image of the interface between the Non-MSL Ti6Al4V alloy plate and the CP titanium core zone, at an acceleration voltage of 5.0 kV. Similar to (b), it is revealed that the core zone was deformed due to the conductive resin mounting process which used heat and pressure. The interface, which is the area indicated with a red line circle, is presented in Figure 7.13.
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Ti6Al4V Honeycomb

Line structures

Dark contrast (spot s) area

Fe-Ni rich particles

(a)

(b)

20 µm

2 µm
Figure 7.13. Scanning electron micrographs showing the CP titanium core zone: (a) AsB image at an acceleration voltage of 15.0 kV; (b) SE2 image at an acceleration voltage of 1.0 kV for the area indicated with the red line circle in (a); (c) EDX point analyses for the particles and the adjacent areas, at an acceleration voltage of 15.0 kV. The Fe-Ni particles are evident near the slip planes in the CP titanium in spectrum 1. It may be possible to consider that the particles are generated during the bonding process between the Cp titanium and the Ti6Al4V alloy because the Ni-Cu metal was used as the filler metal. Meanwhile, the presence of slip planes may be related to the deformation during conductive resin mounting. Further, copper appears to be of significantly amount low compared with the nickel. Spectra 2 and 3 are selected from the areas displayed in different contrast. As a result, the area spectrum 3 may be of relatively similar composition to the general Cp titanium; nickel and copper are not evident. In contrast, the area including spectrum 2 shows slightly different compositions compared with spectrum 3; spectrum 2 contains subtle amounts of nickel and copper, and aluminium which is slightly less than that of spectrum 3.
Figure 7.14. Scanning electron micrographs showing the interface between the CP titanium and Ti6Al4V alloy plate in the SE2 images; (a) MSL specimen at 1.5 kV; (b) Non-MSL specimen at 15.0 kV. EDX analyses for areas 1 and 2, indicated with red line circles, were carried out individually (Figure 7.15 to Figure 7.17).
Chapter 7

Ti6Al4V Honeycomb

(a)

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<thead>
<tr>
<th>Sum(at%)</th>
<th>(Al)</th>
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<td></td>
<td>2.11</td>
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<tr>
<td>(Cu)</td>
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</table>

Al, V, Ti, Ni, Cu

CP Ti ← Ti6Al
Figure 7.15. EDX line analysis for area (1) in each specimen: (a) MSL specimen at an acceleration voltage of 10 kV; (b) Non-MSL specimen at an acceleration voltage of 5.0 kV. Cu and Ni are clearly evident in the Non-MSL specimen; however, nickel does not appear to be contained in the MSL specimen.
Figure 7.16. EDX point analyses for the iron-rich area in Figure 7.15.b at an acceleration voltage of 15.0 kV. As a result, it is revealed that the major components of the β phases are nickel rich, and Cu-Fe is also present.
Chapter 7

Ti6Al4V Honeycomb

(a)

20 μm

<table>
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<th></th>
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<td>Ti</td>
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<td>1.51</td>
</tr>
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<td>1.25</td>
</tr>
<tr>
<td>Ni</td>
<td>2.24</td>
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<tr>
<td>Cu</td>
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Figure 7.17. EDX line analysis for area (2) in each specimen: (a) MSL specimen at 10 kV; (b) Non-MSL specimen at an acceleration voltage of 15.0 kV. Both areas are relatively similar to each other. Further, copper-rich particles are evident adjacent to the nickel-rich β phases in the MSL and Non-MSL specimens. Although iron is not clearly presented, the absence of iron is possible because the area analyzed is the interface on the Ti6Al4V alloy, not the CP titanium.
Figure 7.18. EBSD analyses for the MSL Ti6Al4V alloy plate; (a) the inverse pole figure coloured β map with high angle grain boundaries; (b) the inverse pole figure coloured α map which is converted from (a) [65]; the map conversion was based on the Burgers relationship. Accordingly, the MSL layer appears to be generated from within the transformed layer.
Figure 7.19. EDX point analysis result at an acceleration voltage of 5.0 kV. The content of aluminium, titanium and vanadium shows unusual ratio. It occurs because some of titanium appeared to be detected as vanadium due to a similarity of the energy ranges of X-rays.
Figure 7.20. (a) Ti-Cu binary system phase diagram; (b) Ti-Ni binary system phase diagram. It is expected that the nickel and copper contents are significantly small. Further, it is considered that the temperature was maintained above and below the eutectic temperatures if the TLP or ADB bonding process was applied. In the both case, after heat treatment, the component immediately become the β-rich titanium components, which are indicated by the red line squares in the both diagrams.
Figure 7.21. Schematic diagrams showing an ideal nickel and copper distributions model (a) before bonding; (b) after bonding. According to EDX analysis, nickel and copper may concentrate near the interface, rather than the surface. Further, nickel might diffuse into the CP titanium quickly; nickel-rich components are frequently found in the CP titanium.
Chapter 8. Ceramic sensor

8.1. Result

8.1.1. Fracture Method with Surface Protection / Specimen Preparation
Comparison, between SFS Fracture Methods and Further Preparation Processes

Figure 8.1 shows the cross-sectional image of the alumina ceramic sensor with surface protection of 50 μm using epoxy resin. It appears that the cross-section is relatively clean; contamination and further debris of the alumina ceramics are not evident. Further, due to the characteristics of the ceramics, the cross-section surface is not flat. However, it appears that it is the most appropriate and simple SFS preparation for the alumina ceramic sensor. Thus, the fracture method with surface protection was employed in this study. In order to clarify the validity of the fracture method with surface coating, the specimen preparation results from four different processes are presented in following sections.

8.1.2. Fracture Method without Surface Protection

Figure 8.2 shows the cross-sectional image of the sensor without surface protection. Similar to the surface protected specimen in Figure 8.1, the cross-section was not flat. Further, the surface with a gold coating is displayed with bright contrast in the SE2 image, which is relatively similar to a charging effect; several gold particles and contamination are evident on the cross-sectional surface of alumina ceramic (Figure 8.2.b). Such effects may contribute to beam instability; thus, it is not a suitable cross-section for this specimen.
8.1.3. Mechanical Polishing

As mentioned in Section 4.1.4, “Ceramic Sensor”, it is considered that mechanical polishing was not a suitable process for the ceramic sensor because mechanical polishing may damage the sensor zone. Here, the cross-sectional condition of the ceramic sensor after mechanical polishing is displayed in order to clarify the polishing effect. A schematic illustration shows the model of the ceramic sensor in non-conductive resin for mechanical polishing (Figure 8.3). Two ceramic sensors have been located between alumina ceramic plates in order to protect the ceramic sensor. Subsequently, the specimen was wrapped with aluminium foil and mounted in non-conductive resin. A heat treatment during the conductive resin mounting process may change the ceramic sensor structures; thus, epoxy resin was used, with no need to use heat and pressure. As a result of mechanical polishing, the cross-sectional images are displayed; the impracticability of mechanical polishing for this material is clearly evident in Figure 8.4.

An issue caused by the difference in hardness between the epoxy resin and ceramics occurred during the mechanical polishing. Clearly, epoxy resin has been polished relatively rapidly; it was difficult to maintain the cross-sectional plane parallel to the polishing machine. After mechanical polishing, it appears that the alumina ceramic was well polished; however, the sensor zone was not clearly presented. In contrast, the silver component, which was generally used on the back face of the ceramic sensor, in order to provide conductivity, was evident between the ceramic plates (Figure 8.4.a and Figure 8.5). Further, a slight contrast difference is evident between the alumina ceramic and silver components in the ESB image (Figure 8.4.b). It may be aluminium-rich components because the contrast is slightly brighter than alumina ceramic area; EDX analysis shows a small peak of aluminium adjacent to the alumina ceramics (Figure 8.5). However, it is impossible to observe the details of the sensor zone; it appeared that the sensor zone has been masked with silver components and contamination. As mentioned above and in Section, 4.1.4, “Ceramic Sensor”, it may occur because that hardness of the ceramics are too high compared with the sensor zone of aluminium and aluminium oxide. Hence, the sensor zone was damaged when the ceramics have reached the mirror finished surface. Accordingly, mechanical polishing is not an appropriate procedure for ceramic sensor preparation in this study.
8.1.4. **Focused Ion Beam (FIB)**

A focused ion beam is often utilized for materials which have relatively high hardness. Considering a cross-sectional image after FIB treatment in the previous study [70] (Section 4.1.4, “Ceramic sensor”; Figure 4.15), FIB also appears not to be an appropriate process to observe the microstructures of the sensor; the porous structure appeared to be damaged or masked by the FIB process. Further, the FIB process generally required a long time to complete that contrasted with the SFS preparation which should be a simple process in this study. Therefore, it was not examined.

8.1.5. **Ultramicrotome**

A challenge has been undertaken to apply ultramicrotomy with a 45˚ diamond knife; however, it was impossible to slice only the sensor zone avoiding the alumina ceramics. Consequently, the diamond knife was damaged. Thus, similar to the further methods of fracture with no surface protection, mechanical polishing, as well as the FIB process, ultramicrotomy is not an appropriate process.

8.1.6. **Cross-Sectional Observation for Alumina Ceramic Sensor**

As described in Section 4.1.4, “Ceramic Sensor”, in order to minimize the charging effect, an acceleration voltage has been selected in the range from 1.0 kV to 2.0 kV. Accordingly, interfering of high-resolution imaging by the charging effect of alumina ceramic and epoxy surface protection, has not occurred during the following cross-sectional observation in the absence of a conductive coating. For example, slight charging effects on the epoxy surface protection are evident in the In-lens and the SE2 image; however, the sensor zone does not appear to be affected by charging (Figure 8.6). The roughness of the cross-section of the alumina ceramic sensor has been revealed in the images in Figure 8.1; further, Figure 8.6 also
presents an area of the sensor zone which appears to be detached from the alumina ceramic substrate. It is probably due to the cleavage and fragility of the alumina ceramic; it was broken or dropped off from the matrix when the fracture was produced.

In order to investigate the sensor zone further, the area which is indicated with the red line in Figure 8.6 has been enlarged in Figure 8.7. As a result, it is revealed that the sensor zone consists of four structures which are labelled in 1 to 4 in the image (Figure 8.7.a). For example, area 1 shows a honeycomb structures; area 2 has the U-shape structure; area 3 is a relatively plane structure and area 4 appears to propose mesh structures below the gold coating (Figure 8.7.a and Figure 8.7.b). The edge effect is evident in the ESB image due to the relatively rough cross-section generated by the fracture method. Except for the edge effect, there is a slight difference in contrast between the honeycomb structures and the area above them (Figure 8.7.c) that suggests two different elements are contained in the sensor zone. In order to observe the microstructure of this area further, areas 1 and 2, which are indicated with the red line circles, have been enlarged individually.

Area 1 is presented in Figure 8.8, which is the boundary area between the honeycomb structures and the U-shape structures; the areas are attached each other. Further, similar to Figure 8.7.c, a subtle contrast difference is also evident; the honeycomb structures displayed a slightly brighter contrast than the U-shape structures in the ESB image (Figure 8.8.c). Meanwhile, Figure 8.9 shows area 2 which includes the U-shape, the plane and, the mesh structures below the gold coating. The mesh structures are generally obtained after the hydration process; the sensor has been immersed in boiling water to undertake hydrothermal sealing on the top. Further, the contrast differences are not evident except for the gold coating in the ESB image (Figure 8.9.c); the U shape, the plane and the mesh structures may have relatively similar elemental compositions. In order to identify the elemental composition, EDX analyses were carried out (Figure 8.10). According to the results, it is revealed that the honeycomb structures are aluminium-rich components; the U-shape structure and the plane structure are aluminium oxide; the mesh structure is also aluminium oxide. Such elemental difference on the individual structures is clearly displayed in different contrast in the ESB images. In addition, relatively high amount of carbon is detected from the mesh structures; however, it is considered to be an effect from the epoxy resin.
Figure 8.11 shows the surface of the sensor zone of the gold coating. It appears that the top surface consists of several grains, which have relatively random dimensions. Hence, considering from the UHRLV SEM images (Figure 8.1.a and Figure 8.11), and the idea of the structure on the previous studies [71] (Section 4.1.4, “Ceramic Sensor”, Figure 4.13), it is expected that the sensor zone may consist of the unit of relatively non-uniform cells. The idea of this unit structure is presented in Figure 8.12; a cell is comprised of the honeycomb (porous) aluminium on the inside and, the U-shape and the plane aluminium oxide which are located above the honeycomb. Those are covered with the aluminium oxide layer; the top surface of aluminium oxide has been hydrated, and coated by gold particles, although, the dimensions of the cell were not uniform.

The non-uniformity of the cells can be obtained from the further cross-sectional observation in multiple locations (Figure 8.13.a to Figure 8.13.e). According to the images, it appears that the dimensions of a cell may be related to the dimensions of the grains of the alumina ceramic, which are located beneath the cell; growth of porous aluminium also appears to be affected from the dimensions of the alumina ceramic grains. Further, the U-shape aluminium oxide structures show variations in the structure length; for example, relatively long U-shape structures are evident in Figure 8.13.d, in contrast, relatively short U-shape structures are evident on the Figure 8.13.c. Meanwhile, the mesh structures, which must be present only on the surface between the plane aluminium oxide structure and the gold coating, are often evident on the alumina ceramic (Figure 8.14); thus, moistures during the hydration treatment possibly have infiltrated in the alumina ceramic substrate.

As a result, unlike the expected structures in the previous studies, it is revealed that the structures of the alumina ceramic sensor is relatively inhomogeneous; further, the growth of the cells may be related to the grain structures of the alumina ceramic beneath the sensor zone.

8.2. Discussion

It is revealed that the fracture method is one of the appropriate and simple specimen preparations for the UHRLV SEM, which enables to observe the original microstructures of the sensor zone.
Further, in combination with low acceleration voltage also enables to observe the insulating material with no conductive coating.

According to the UHRLV SEM observation, the microstructures of the sensor zone have been revealed, for example, the sensor zone consists of unit of cells which have non-uniform dimensions; and the hydrated aluminium oxide has permeated into the alumina ceramic. In addition, considering the result of previous studies [70, 71] and the current study, the drift issue may also be related to the non-uniform cells of the sensor zone. The reason is that, humidity cannot permeate inside of the each pore uniformly because the dimensions of the cells are not uniform. Further, the presence of the hydrated aluminium oxide has been confirmed on the alumina ceramic; a gap between the cells is predicted. Hence, moisture may be reached the alumina ceramic substrate without passing through the pore of the sensor zone. It may induce sensor drift.

Furthermore, as mentioned above, the dimensions of the cells appear to be related to that of alumina ceramic grains. Therefore, it may be necessary to control the grains dimensions of the alumina ceramic which enable to generate relatively uniformly. Further, in order to verify this idea, it is also required to compare the sensor on the uniform alumina ceramic and non-uniform alumina ceramic.

8.3. Conclusions
The fracture method with surface protection for SFS and following cross-sectional observation at low acceleration voltage revealed the microstructure of the ceramic sensor in this study, although, it was not similar to the structure what had been predicted by previous studies. Further, the study suggests that the structures of the sensor zone may vary depending on the alumina ceramic beneath the sensor; the drift issue may be also generated due to the non-uniformly of alumina ceramics. In future work, it may be necessary to verify whether this consideration is correct by observing further alumina ceramic sensors which had a similar drift issue.
Figure 8.1. (a) Scanning electron micrographs showing the cross-sectional images of the ceramic sensor in the In-lens image at an acceleration voltage of 1.0 kV; (b) ESB image of (a). The sensor zone exists between the resin surface protection and the alumina ceramic substrate. The grains of the alumina substrate and the top surface of the sensor zone appear to be non-uniform. The cross-section appears relatively clean because contamination and gold particles are not evident on the cross-section.
Figure 8.2. (a) Scanning electron micrographs showing the cross-sectional image of the ceramic sensor without surface protection at an acceleration voltage of 1.0 kV: (a) SE2 image; (b) ESB image of an enlarged area (a). It appears the images are similar to the images with surface protection; however, small particles, which may be gold particles, are evident on the cross-section. Thus, the surface protection may be necessary.
Figure 8.3. Schematic representation of the ceramic sensor in non-conductive resin for polishing. In order to protect the sensor, two sensors were located between two alumina ceramic plates. Subsequently, the specimen was mounted in non-conductive resin after wrapping with aluminium foil. Conductive resin was not used because heat treatment with pressure may cause damage.
Figure 8.4. Scanning electron micrographs showing the polished alumina ceramic sensor at an acceleration voltage of 2.0 kV: (a) SE2 image; (b) ESB image. It appears that the alumina ceramic was well polished; however, the sensor zone was not clearly presented. Silver paint was present in the gap between the surfaces of the two ceramic sensors.
Figure 8.5. EDX line analysis for the ceramic sensor including the silver components in the gap of Figure 8.4. According to the result, it appears that silver rich components masked the sensor zone because a relatively low peak of copper is evident above the silver peak.
Figure 8.6. Scanning electron micrographs showing a sensor zone and alumina ceramic substrate at an acceleration voltage of 1.0 kV; (a) In-lens image; (b) SE2 image. The area indicated with red line circles is presented in Figure 8.7.
Chapter 8

Ceramic Sensor

(a) Alumina

(b) Alumina
Figure 8.7. Scanning electron micrographs showing enlarged images of the sensor zone in Figure 8.6 at an acceleration voltage of 2.0 kV: (a) In-lens image; (b) SE2 image; (c) ESB image. According to the images, it appeared that a sensor zone consists of the four components, which are represented in 1 to 4 in (a), and the gold coating. A slight difference in contrast is evident in the ESB image which is indicated by white lines in (c). It suggests that the elemental composition of the area displayed in dark contrast may contain an element slightly lighter than that from the area of bright contrast. The areas which are indicated by the red line circles 1 and 2 are presented in Figure 8.8 and Figure 8.9.
Figure 8.8. Scanning electron micrographs showing area 1 in Figure 8.7.a at an acceleration voltage of 1.5 kV: (a) In-lens image; (b) SE2 image; (c) ESB image. It is revealed that area 1 consists of honeycomb structures, a U-shape structure above the honeycomb structures and a plane area. The U-shape and the plane structures are displayed in relatively dark contrast; the honeycomb structures are displayed in slightly bright contrast.
Figure 8.9. Scanning electron micrographs showing area 2 of Figure 8.7b at an acceleration voltage of 1.5 kV: (a) In-lens image; (b) SE2 image; (c) ESB image. The images present the U-shape structure, plane area, mesh structures above the plane area and gold coating. The ESB image does not display contrast differences within the sensor zone except for the gold coating layer. Thus, there may not be elemental differences within the area of dark contrast.
Chapter 8

Ceramic Sensor

(a)

(b)
Figure 8.10. EDX line analyses area and results: (a) and (b) vertical analyses, (c) horizontal analysis of (a); According to the results, it is revealed that the area above the honeycomb structures are aluminium oxide and the honeycomb structures are aluminium rich. Thus, it is revealed that the contrast differences in the ESB image are due to elemental differences.
**Figure 8.11.** Scanning electron micrograph showing a top view of the sensor surface of gold coating area in the In-lens image, at an acceleration voltage of 1.0 kV. It appears that several cells which have variations in dimensions are randomly located.
Figure 8.12. Schematic representation of the sensor zone. The sensor zone appears to consist of unit of cells. For example, porous aluminium is covered with aluminium oxide; aluminium oxide surface has been hydrated and gold coating was present on the hydrated aluminium oxide. Further, the dimensions of the individual cell are not uniform.
Chapter 8

Ceramic Sensor

2 µm

Surface

Gold

Aluminium oxide

Hydrated aluminium

Aluminium

(a)

Alumina

2 µm

Gold

Hydrated aluminium

Aluminium oxide

Aluminium

(b)

1 µm

Alumina ceramic
Chapter 8
Ceramic Sensor

(c) Hydrated aluminium
Gold

(d) Aluminium oxide
Aluminium

Surface protection

Alumina ceramic

1 µm

2 µm
Figure 8.13. Scanning electron micrographs showing several cells in the different areas of the sensor zone in the In-lens image: (a) acceleration voltage of 1.5kV; (b) to (e) 1.0 kV. According to the images, the dimensions of the cell appear to be related to those of alumina ceramic grains.
Figure 8.14. Scanning electron micrographs showing the areas of the hydrated aluminium which appear to be permeated into the alumina ceramics in the In-lens image at an acceleration voltage of 1.0 kV: (a) a broad area; (b) an enlarged image of the hydrated aluminium on ceramic.
Chapter 9. 3D Tomography, Application of the SFS and Additional Possible Approaches

9.1. Result

9.1.1. Applications of SFS for 3D X-Ray Tomography

Concerning a further possible application of SFS, its extension to 3D tomography has been investigated. A WE43 magnesium alloy, having been immersed in 3.5 % NaCl solution for 1 week, was employed. The specimen, of dimensions of 8 mm × 13 mm × 20 mm, was prepared by mechanical polishing and GDOES surface finishing. Subsequently, the specimen was placed in the 3D X-ray tomography instruments (Metris XTH scanner, Nikon Metrology NV); the challenge was to display the corrosion path by 3D tomography. However, the resolution of X-Ray tomography is not equal to that of the UHRLV SEM in general; thus, the cracks, which have propagated in the UHRLV SEM images, were not evident in the 3D X-Ray tomography images because X-rays pass through the cracks which can not be imaged (Figure 9.1 and Figure 9.2). However, it is still possible to undertake high resolution X-ray 3D tomography by using the cutting-edge, 3D X-Ray instruments. For example, a resolution of 150 nm can be provided by use of the nanoXCT (Xradia) system. However, for that resolution to be achieved the specimen dimensions need to be 100 μm or less. Consequently, the SFS need to be minimized and, hence, the advantage of the SFS cannot be used.

Meanwhile, it is expected that SFS can be applicable to focused ion beam (FIB) approaches. However, due to the characteristics of the FIB, a high acceleration voltage is necessary for imaging. Thus, it is difficult to obtain 3D tomography using the advantages of the SFS, which include observation of the original microstructures of the surface.
9.1.2. **New Approach for the in-situ 3D Tomography Using Ultramicrotomy in the SEM**

The automated 3D tomography system using ultramicrotomy is one of the state-of-the-art technologies (3view, Gatan), which was developed for biological materials. In this system, ultramicrotomy is operated inside the SEM; the SEM image can be obtained in-situ after the surface is sliced by the diamond knife of the in-SEM ultramicrotome (Figure 9.3). As represented in Figure 9.3, in the 3D system, a diamond knife is kept in the high vacuum condition and driven by the motor to slice the specimen. In contrast, the general operation of the conventional ultramicrotome is in air, with the specimen driven by a motor or manually; the diamond knife is fastened to the ultramicrotome. This is one of the significant differences in the 3D system and the conventional ultramicrotome. A further difference is the dimensions of the specimen that are not limited if it can fit the specimen holder in the conventional ultramicrotome. However, the specimen is required to have a diameter of less than 2 mm in the 3D system; again, the advantage of SFS can not be used.

Using this instrument, 3D tomography reconstruction has been examined for galvanized steel, which was provided by Tata steel. The outcome of the 3D tomography is presented in Figure 9.4 and Figure 9.5. The image of Figure 9.4 shows the cross-section after final slicing. As a result, Mg-Zn components appear to reveal their forms clearly; the primary zinc grains show different morphologies compared with the UHRLV SEM images; the primary zinc phases appear to consist of colonies of small zinc grains. Further, a line is evident on the steel substrate. However, as described in Section 5.1, “Galvanized steel”, the primary zinc grains consist of relatively small zinc grains which are randomly located within the primary zinc phase; they did not create any colonies within the primary zinc phase. Hence, it is considered that the image may present a smearing effect on the coating layer. Further, a bright contrast line is evident on the steel substrate. It appears to reveal a crack on the steel substrate, although it may be necessary to consider the originally of the crack, which is a defect of the steel substrate, or a smearing damage by ultramicrotomy.

Meanwhile, the Mg-Zn structures appear to be clearly presented in both images (Figure 9.4 and Figure 9.5). The reason that the MgZn₂ phases appear to maintain their form without any
smearing effect, unlike the primary zinc phases, is considered to be related to the difference in structures and hardness between the MgZn$_2$ phases and zinc grains. As described, the primary zinc grains consist of relatively small zinc grains of random dimensions; thus, the primary zinc grains may be readily deformed and detached compared with the MgZn$_2$. The reason is that the MgZn$_2$ phases contain magnesium which has been added in order to increase the hardness and corrosion resistance of the coating layer. Hence, 3D tomography can provide the structures of the MgZn$_2$ phases, although it may be difficult to consider the primary zinc phases further.

The quality of the 3D tomography may be improved if different conditions for ultramicrotomy are selected. As described in Section 4.2.1, “Diamond Knife Trimming Using Ultramicrotome for Galvanized Steel, Magizinc-MZ350”, the individual materials have appropriate conditions for case of ultramicrotomy, such as cutting speed and thickness of the slice. Especially, in the ultramicrotome in the 3D system, the diamond knife is driven, instead of the specimen. Therefore, it may be necessary to investigate the appropriate conditions more carefully for galvanized steel.

In addition, the use of the diamond knives of different angles, such as 25° and 35°, may also be possible to improve the quality of the 3D tomography images. The reason is that the diamond knife was damaged after the experiment; the damaged diamond knife also induces a smearing effect and further damages on the specimen. However, for using a diamond knife of decreased angle, the contact face on the specimen may be reduced; thus, damage by the diamond knife may be reduced. Further, minimizing the area for slicing also reduces the stress on the specimen; accordingly, the imaging quality can be improved.

As described, the creation of 3D tomography images is a challenging study. Due to the requirement of significantly small specimen dimensions, SFS in this study can not be applied for the instruments used. Further, the resolution capability of 3D tomography may need to be improved further; the approach to improvement may be the use of a finer knife, to change the ultramicrotome conditions and to minimize the slicing area, thereby reducing damages to the specimen.
Figure 9.1. X-Ray 3D tomography images of WE43 after 1 week immersion in 3.5\% NaCl solution, using Metris XTH scanner (Nikon Metrology NV). Specimen dimensions are $8 \times 12 \times 20$ mm. During the process, the specimen was rotated 360° and the image was taken after each approximately 0.1°, 3143 times: (a) 1st image; (2) 357th image; (c) 644th image; (d) 1576\textsuperscript{th} image. The UHLRV SEM image of the area within the red line circles is presented in Figure 9.2.
Figure 9.2. Scanning electron micrograph showing the WE43 alloy specimen after 1 week immersion in 3.5% NaCl solution in the SE2 image at an acceleration voltage of 0.95 kV. The specimen was The edge of the specimen is relatively coarse; several cracks and cavities are evident on the surface.
Figure 9.3. Schematic illustrations showing the 3view system (Gatan)[92]; (a) scanning the surface; (b) moving the specimen up to the height of the diamond knife; (c) slicing the specimen surface using diamond knife driven by the motor. Thereafter, the process returns to (a) and repeat same processes.
Figure 9.4. Scanning electron micrograph showing the cross-sectional image of the galvanized steel after the final slice using 3view. Accordingly, the distributions of the MgZn$_2$ phases are relatively similar to the UHRLV SEM. However, the primary zinc phases show different morphologies, which may be slightly deformed due to the low hardness of zinc compared with the MgZn$_2$ phases and the steel substrate. Meanwhile, a bright line is evident on the steel substrate. It is necessary to consider the origin of the line, whether may be a smearing effect, or a defect of the steel substrate that gap is filled with zinc.
Figure 9.5. 3D tomography reconstruction image using the 3view (Gatan): (a) image from beginning of the slice; (b) image from the final slice. From the final slice image, there appears to be presence a relatively large crack in the steel substrate. It may be necessary to consider the original of the crack, i.e., possibly a defect in the steel substrate or damage by ultramicrotomy.
Chapter 10. General Conclusions

In this study, it is revealed that the combination of the SFS preparation and the UHRLV SEM has enabled the original microstructures of materials to be revealed, regardless of the conductivity. As described, in order to obtain the SFS, two processes including a surface preparation and a GDOES surface finishing process are required. It is expected that the surface preparation is the most important process for obtaining the SFS; a clean and flat surface need to be prepared. The reason is that damage and contamination on the surface may mask the original structures on the surface. Further, those roughness and contamination may induce inhomogeneous surface finishing by GDOES. In general, GDOES enables the SFS to provide by enhancing the microstructures of the surface and removing contamination when the surface is sufficiently flat and clean condition. However, when the surface is not sufficiently flat and clean condition, GDOES may be damaged and contamination also redeposit on the surface. Therefore, a surface preparation which is suitable for the characteristics of the selected materials is essential. Concerning the materials examined in this study e.g., galvanized steel, a USW joint Al6111/AZ31 alloys, the Ti6Al4V alloy honeycomb and ceramic sensor, they have different characteristics. Hence, surface preparations processes including mechanical and manual polishing, ultramicrotomy and fracture methods have been selected depending on the characteristics of the materials; the individual processes led to the success in the ultra high resolution, surface sensitive observation.

The most important factor to make use of the advantages of UHRLV SEM is to understand the characteristics and functions of the UHRLV SEM. Unlike the conventional SEM, the UHRLV SEM enables ultimate surface sensitive information to be provided. However, this study revealed that it is possible to provide incorrect contrast occasionally, when an appropriate low acceleration voltage for an individual material is not selected. Thus, in order to avoid misunderstanding, the obtained UHRLV SEM images should be analysed carefully. In addition, again, it must be remembered that with only SFS can the advantages of the UHRLV SEM be utilised.
A challenging study of applying SFS to 3D tomography has been attempted; however, effort is still required to obtain the surface sensitive 3D tomography. Thanks to this meaningful challenging experiment, the excellent capability of the UHRLV SEM has been revealed clearly; it enables to provision of the surface sensitive information and assists further understanding of 3D tomography, which is revealed clearly.
Chapter 11. Suggestions of Future Work

In a field of the SFS preparation, the alumina ceramic was one of the interesting materials. The interest is now toward the polymer and plastic materials, which may have SFS preparation difficulties similar to the ceramic. Thus, to investigate the appropriate SFS preparation methods for those insulating materials are one of the interesting subjects.

In addition, several interesting materials have been developed recently in familiar fields, such as automobile and aircraft. For example, in order to achieve a global goal of CO$_2$ reduction, the development of new materials including aluminium alloy and magnesium alloys for weight reduction has been remarkable in both industries. Further, study for applications of conventional and new developed materials for humankind are also active in order to improve the quality of life. As a major example, titanium alloys are often used in the human body due to their hypo-allergic and long-life characteristics. However, those new materials may have defects and corrosion which have not been elucidated previously; the SFS process is considered to be the efficient approach to reveal those interesting features. Therefore, to investigate the appropriate SFS method for new materials is important study.

In this study, several interesting microstructures have been revealed; however, the following questions still await answers, for example, the nature of the shiny edge lines of galvanized steel; the nature of a step in the USW joint of Al6111/AZ31 alloys; the functions of the MSL layer in the Ti6Al4V alloy honeycomb; relation between the growth of the sensor zone and the alumina ceramic in the ceramic sensor. In order to provide the appropriate answers, it is essential to understand the materials further, including the individual manufacturing processes. Especially, due to the complexity of the Ti6Al4V alloy honeycomb, it is considered that the only one face of the materials is revealed in this study; further work is required to achieve full understanding.

Additionally, the investigation of new approaches to improve the ESB image contrast further between dissimilar elements is continued. This is because when ESB imaging contrast can clearly visualise a subtle difference between the dissimilar elements, the ESB image can be used as the surface sensitive elemental map instead of EDX analysis; it may be to enable the automatic colour SEM imaging.
Chapter 12. Appendix

In order to confirm that the combination of SFS and Low-Voltage SEM is also valid for materials generally, UHRLV SEM images for the following selected materials are presented in this Appendix; stainless steel, galvanized steel, aluminium alloys, magnesium alloys, a commercial product of a central processing unit of computer, and an insulating material of sea pearl. The individual images are presented with information of the SEM friendly surface (SFS) preparation, the conditions of the UHRLV SEM and relevant information in order to understand the images. All the surface observations were undertaken at a low acceleration voltage, without use of conductive coatings on the surface of the specimens.

12.1. Commercial Stainless Steel 304

- Preparation: Mechanical Polishing + GDOES Surface Finishing
- Acceleration Voltage = 0.95 kV

The images show the commercial SUS 304 surfaces using the In-lens and the SE2 detectors (Figure 12.1). The original microstructures of the surface have been revealed without damage and contamination after GDOES surface finishing; the grain structures are emphasized due to the sputtering rate of GDOES which varies depending on the elements and the crystallographic orientations on the surface (Figure 12.2). Small particles, which may be chromium oxide or chromium nitride, are evident as dark spots in the ESB image. However, one of the particles, which is indicated by the red line circle in the ESB image, has not been clearly revealed in the In-lens and the SE2 images. Therefore, in order to avoid misunderstanding, it is necessary to analyze the each image carefully.
12.2. Stress Corrosion Cracking Stainless steel 304

- Preparation: Mechanical Polishing + GDOES Surface Finishing
- Acceleration Voltages = 2.0 kV and 15.0 kV

The UHRLV SEM images display a crack tip associated with stress corrosion cracking in SUS 304, before and after GDOES surface finishing (Figure 12.3). Associated with the individual images, grains are clearly displayed in the SE2 image after GDOES surface finishing. It appeared that GDOES surface finishing was too strong for this specimen because the crack has slightly increased in width. It is possible, due to the characteristics of the plasma GDOES sputtering, that argon ions can concentrate at high potential areas on the surface, such as the edge. However, with increasing magnification, it is revealed that the area near the crack tip was not damaged by GDOES; sputtering appeared to proceed along the crystallographic structures near the crack edges. Further, the slip planes, which possibly related to the crack tip propagation, were clearly evident near the edges that were unable to be revealed before the GDOES surface finishing process (Figure 12.4). The reason is that the surface has become clean and its original microstructures were emphasized without significant damage present after the GDOES process.

The relatively similar areas in Figure 12.4 were also observed at an acceleration voltage of 15.0 kV (Figure 12.5); however, the slip planes disappeared and the thickness of the crack appeared to be more extensive than the images at 2.0 kV. This is because the high primary electrons energies, for example 15.0 keV electrons penetrate to a depth of approximately 720 nm below the surface; it is 36 times more extensive than the 20 nm penetration of 2.0 keV electrons energy (Figure 12.6). The generation depth of the secondary electrons is almost equal to the penetration depth of primary electrons; as a result, information near the surface is masked by information from beneath the surface when a high primary electron energy is applied. Thus, the surface sensitive information is unable to be revealed (Section, 2.2, “SEM and Low-Voltage SEM”). Therefore, it is clear that the Low-Voltage SEM is necessary in order to obtain surface sensitive information.
12.3. **Proton Irradiated Stainless Steel**
- Preparation: Mechanical Polishing + GDOES Surface Finishing
- Acceleration Voltage = 1.0 kV

The specimen was relatively small; the dimensions of the specimen were 2.0 mm × 4.0 mm square. It is expected that the influence of the proton irradiation was present to a depth of approximately 30 - 40 µm distance from the surface (Figure 12.7a). According to the UHRLV SEM observation, it appeared that the slip planes, due to the influence of the proton irradiation, are clearly evident on each grain within the expected region. The orientations of the slip planes depend on the individual grains (Figure 12.7.b, Figure 12.7.c and Figure 12.7.d). In addition, there are several scratch-like structures on the surface in Figure 12.7.b, Figure 12.7.c and Figure 12.7.d. However, it is revealed that those structures also may show the slip planes. The reason is that, for example in Figure 12.7.d, the scratch-like structures are evident within the circles; the lines do not appear to be present randomly and appear to be aligned parallel in certain directions.

12.4. **Al10%Zn Cold Splay Carbon Steel and Al50%Zn Mild steel**
- Preparation: Ultramicrotome
- Acceleration Voltages = 0.9 kV and 3.5 kV

The SFS preparation has been examined for the Al10%Zn cold spray carbon steel (Figure 12.8.a) and the Al50%Zn mild steel (Figure 12.9.a). The details of elemental compositions of each material are not identified. The specimen was prepared by ultramicrotomy, without mechanical polishing because that may bring damage to the coating layer (Section 5.1.1, “Galvanized Steel”); also in fact, the mild steel and carbon steel enable to slice using the ultramicrotome.
According to the cross-sectional observation, it is revealed that the coating layers and the steel substrates are non-uniform in both alloys, for example, the interfaces between the steel substrate and the coating have several detached areas (Figure 12.8.a and Figure 12.9.a).

The coating layer of the Al10%Zn cold spray on the carbon steel consists of relatively large zinc grains which exist among colonies of relatively small aluminium grains (Figure 12.8.b and Figure 12.8.c). Further, the presence of the oxidation within the zinc grain is also evident in the ESB image, the colour converted image from the ESB and EDX analysis (Figure 12.8.c, Figure 12.8.d and Figure 12.8.e).

Meanwhile, the coating layer of the Al50%Zn mild steel consists of the zinc grains and the aluminium grains, similar to the Al110%Zn specimen; however, the presence of zinc grains in the coating layer has increased with increase of zinc to 50 % (Figure 12.9.a). Further, it is revealed that a zinc grain consists of small zinc grains; aluminium-rich intermetallics between the mild steel substrate and the coating layer are also present. On the mild steel substrate, silicon oxide appears to exist (Figure 12.9.b and Figure 12.9.c); however, due to the similarity of the atomic number of aluminium and silicon, it is difficult to distinguish them in the ESB image and the colour converted image from the ESB (Figure 12.9.c and Figure 12.9.d) (Section 6.1, “USW Joint of Al6111/AZ31 alloys”). Therefore, it is necessary to compare UHLRV SEM images and EDX analyses results.

### 12.5. Aluminium alloys (Al4%Cu, Al1901, Al2024, Al2025 and Al7075)

- Preparation: ultramicrotome
- Acceleration voltages = 0.95 kV, 1.0 kV and 2.5 kV

Here, four aluminium alloys of Al4%Cu alloy, Al1901, Al2024, Al2025 and Al7075 alloys are presented in order from Figure 12.10 to Figure 12.14. Specimens were simply prepared by ultramicrotomy. The dimensions of grains and the second phase particles and their distributions are different individually. For example, except for the Al1901 (Figure 12.11) and Al2025 alloys (Figure 12.13), the grains and second phase particles are clearly presented in the cross-sectional
images (Figure 12.10, Figure 12.12 and Figure 12.14). Depending on the grains, different morphologies are evident, which are considered to relate to the crystallographic orientation. Interestingly, in the Al1901 alloy, relatively small grains consist of the microstructures of the alloy; second phase particles appear to have made a colony and, located near to the grains boundaries (Figure 12.11). Meanwhile, in the Al2025 alloy, it is possible to show the second phase particles which appear to be located in the grain boundaries; however, it is less clear compared with the cross-sectional images of the other aluminium alloys (Figure 12.13.a). The cross-sectional images of the Al2025 alloy may be able to be improved by selecting different conditions for ultramicrotomy, for example, cutting speed and slice thickness. The reason is that the appropriate condition of the ultramicrotome may be considered to be slightly different for individual materials, because the hardness of alloy matrix, the second phase particles and debris are different due to the variation of the alloying elements and the alloying process (Section 4.2.1, “Diamond Knife Trimming Using Ultramicrotome for Galvanized Steel, Magizinc-MZ350).

The final aluminium alloy specimen is the Al7075 alloy (Figure 12.14). Similar to the Al2024 alloy (Figure 12.12), grains and second phase particles are evident. Further, nano-scale particles are evident in the whole area of the cross-section; some particles are located at the grain boundaries (Figure 12.14.a). It is considered that the hardness of the second phase particles and the nano-scale particles are slightly higher than the aluminium matrix because the second phase particles are often chipped off or have completely dropped off from the alloy; relatively large cavities of approximately 1 μm or more are frequently obtained. Further, nano-scale particles also often dropped off from the matrix; the cavities due to the absence of those particles, are displayed in bright contrast in the In-lens image, dark contrast in the SE2 image (Figure 12.14.b). In addition, it is difficult to distinguish the particles and cavities in the In-lens image (Figure 12.14.a) according to the characteristics of the In-lens detector; although it does not reflect the depth information, it is susceptible to the influence of the edge effect. Meanwhile, the SE2 image includes the depth information; it is able to distinguish the differences. Therefore, it is important to compare individual images.
12.6. **Magnesium WE43 Alloy and Corrosion Tested WE43 in 3.5 % NaCl Solution for 1 hour**

- Preparation: Mechanical polishing + GDOES Surface Finishing
- An acceleration voltages = 0.8 kV and 0.95 kV

The surface of the WE43 alloy before and after the 3.5 % NaCl solution corrosion test are presented in Figure 12.15, Figure 12.16 and Figure 12.17. Specimens were prepared by mechanical polishing and GDOES surface finishing; polishing commenced with 800 # silicon carbide paper for the specimen before corrosion test, and 1200 # for the specimen after corrosion test.

In general, the microstructures of the WE43 alloy consist of the magnesium matrix, the Mg$_{14}$Nd$_2$Y, the Mg$_{12}$Nd, the Nd-rich precipitates and the Y-rich particles. The Nd-rich precipitates appear to be present across the magnesium matrix, except the precipitates free zone near the grain boundaries (Figure 12.15.a to Figure 12.15.c). Further, the orientation of the precipitates is different depending on the crystallographic orientations of the grains (Figure 12.15.d and Figure 12.15.e).

Meanwhile, Figure 12.16 shows the WE43 specimen surface after 3.5 % NaCl solution corrosion test for 1 hour. The surface was mechanically polished in order to remove corrosion products; polishing commenced from 1200 # silicon carbide paper. The corroded areas displayed dark contrast in the In-lens image, because the areas are positively charged due to the presence of the corrosion products. The SE2 detector is generally little affected by charging; thus, similar areas are clearly presented in the SE2 image. As a result, it is revealed that the cracks appear to propagate along the grain boundaries (Figure 12.16). With increasing magnification, it is revealed that corrosion has been propagated along the grain boundaries, avoiding the Mg$_{12}$Nd (Figure 12.17.a and Figure 12.17.b).

The area indicated with red line circles in Figure 12.17.a has been enlarged further in Figure 12.17.c. It appears the plate type Mg$_{14}$Nd$_2$Y precipitates of 200 nm to 400 nm existed between the colonies of the Nd-rich precipitates. It is difficult to distinguish them due to their subtle
differences in elemental composition; however, the colour converted image from the ESB image shows the individual elements which have subtle differences (Figure 12.17.d).

12.7. CPU / Central Processing Unit

- Preparation: Fracture Method
- Acceleration voltage = 1.5 kV

THE Central Processing Unit (CPU) is one of the component parts of a computer. The specimen in this experiment was removed from non-functional computer and prepared by the fracture method and GDOES surface finishing (Section, 4.2.4, “Fracture Method for Alumina Ceramics Sensor”). Although, the structure of CPU is not fully identified, it is revealed that the silicon plate is generally used as the substrate. This is a further excellent opportunity in order to reveal the efficiency of the SFS preparation and use of the UHRLV SEM for the commercial products, that background is not identified. Using the UHRLV SEM, the original microstructures of the CPU revealed. For example, Figure 12.18.b shows several cracks on the silicon substrate. However, it is considered that those cracks are the originally present in the material, rather than being generated by the fracture method. The reason is that, for example, the area within the yellow line circle in Figure 12.18.b shows slightly different contrast compared with the matrix silicon substrate in the ESB image and colour mapping image (Figure 12.18.c); crack appears to be present along the contrast difference area. Further, the pin-shaped structures are partly disappeared; the height difference of the silicon substrate beneath the pin-shaped structure is also revealed in the red dashed line circle in Figure 12.18.b. The region including the pin-shaped structures, which is indicated with the red line circle in Figure 12.18.b, was enlarged further (Figure 12.18.d and Figure 12.18.e). As a result, it appears that the region may contain leastwise four different elements because the area is displayed with four different contrasts.

In addition, Figure 12.18.g shows the image of structure similar to the CPU after mechanical polishing and ion etching by Gatan [93]. Compared with the image of the SFS, it is revealed that the SFS specimen preparation method, which is to simply make a fracture and clean the cross-
section using GDOES in short time, is the simplest and more efficient specimen preparation processes.

12.8. Damaged Sea Cultured Pearl

- Preparation: Fracture Making + GDOES Surface Finishing
- Acceleration Voltage = 1.5 kV

The final material is a sea cultured pearl, which is a biological material. In general, the pearl consists of the calcium carbonate layers with aragonite structures that are joined by a type of protein termed conchiolin. The colour and brightness of the pearl vary depending on the interference effect of light in the layer. The pearl in this experiment was provided by Fukumoto pearl (Uwajima, Japan); it was selected from among pearls which have a low market value in jewelry due to their poor colour and low brightness. In order to reveal that microstructures of that damaged pearl, the UHRLV SEM was utilized.

As mentioned previously, no conductive coating was applied for the UHRV SEM observation. Likewise to the CPU, the SFS has been prepared using the fracture method. Using the advantage of the Low-Voltage SEM, that enables charging effects to be minimized, the surface and the cross-sectional observations were undertaken. As a result, it is revealed that the grains of the pearl are relatively large, however, those are actually not uniform (Figure 12.19.a and Figure 12.19.b); it may be related to the bad colour and the low brightness of the pearl.

Meanwhile, from the cross-sectional images, it is revealed that the structure of the pearl is of layered calcium carbonate; relatively small particles exist on the calcium surface (Figure 12.20.a and Figure 12.20.b). Further, with increasing magnification, a hexagonal-like calcium carbonate also appears to consist of the layer calcium carbonate (Figure 12.20.c and Figure 12.20.d). In the ESB image, the surface of the layered calcium carbonate is presented in dark contrast. It is considered to be conchiolin which connects the calcium layers.

As described, the combination of the appropriate specimen preparation and the Low-Voltage SEM enable to observe the biological material without conductive coating.
Figure 12.1. Scanning electron micrographs showing the surface of stainless steel 304 at an acceleration voltage of 0.95 kV: (a) In-lens image; (b) SE2 image. Specimen was prepared by mechanical polishing and GDOES surface finishing. The original microstructures of the SUS304 are revealed without contamination. The surface can be useful for EBSD analysis; no extra calculation software may be necessary.
Figure 12.2. Scanning electron micrographs showing an area of Figure 12.1 at an acceleration voltage of 0.95 kV: (a) In-lens; (b) SE2 image; (c) ESB image. Depending on the grain, different morphologies are displayed, which is emphasized by GDOES surface finishing. Further, a small particle within a red lined circle of (c), which is expected to be chromium nitride or chromium oxide, is clearly presented in the ESB image. However, it is difficult to image the particle in the In-lens and SE2 images.
Figure 12.3. Scanning electron micrographs showing the crack tip of the stress corrosion cracked SUS 304 in the SE2 image at an acceleration voltage of 2.0 kV: (a) before GDOES surface cleaning; (b) after GDOES surface cleaning. Various contamination is evident on the surface, and no grains appeared before surface finishing in (a). Meanwhile, grains are relatively clear and contamination is not evident after GDOES surface cleaning. However, the crack tip appears to be expanded its width by GDOES finishing. The area indicated by the red line circle is presented Figure 12.4.
Figure 12.4. (a) Scanning electron micrographs showing the area near the crack tip of Figure 12.3 in the SE2 image at an acceleration voltage of 2.0 kV; (b) increased magnification image of the red line circle of (a). It is expected that GDOES surface finishing damages the crack tip in Figure 12.3. However, it is clear that GDOES has not damaged the edge of the crack tip in Figure 12.4. The slip planes near the crack tip appear to be enhanced by GDOES surface finishing.
Figure 12.5. Scanning electron micrograph showing the area near the crack tip in Figure 12.4. (a) in the SE2 image at an acceleration voltage of 15.0 kV. The crack tip, which is indicated with the red line circle, appears to increase the thickness of the crack; it is difficult to recognize slip plane from the image. Thus, it is difficult to recognize the slip planes near the crack from the image at 15 kV.
Figure 12.6. Schematic diagrams showing primary electrons (blue) and backscattered electrons (red) trajectories in iron, simulated by the Monte Carlo simulation at incident angle of 0°: (a) acceleration voltage of 2.0 kV; (b) 15 kV. Primary electrons reach approximately 20.0 nm from the surface and backscattered electrons are generated from 10.0 nm from the surface at 2.0 kV. Meanwhile, primary electrons reach approximately 720 μm from the surface and backscattered electrons are generated 300 nm from the surface at 15.0 kV.
Proton irradiation area
40 µm from the surface

(a) 10 µm

Scratches?

(b) 2 µm
Figure 12.7. Scanning electron micrographs showing proton irradiated stainless steel, at an acceleration voltage of 1.0 kV: (a) cross-sectional image including the proton irradiated area, which is approximately 40 μm-width from the surface; (b), (c) and (d) several areas of proton irradiation. Within each grain, several slip planes are evident that pass along different directions. There are also several lines evident, which appear to be scratches; these are indicated by the red line circles and arrows in (e). These lines also considered to be generated by proton irradiation. The reason is that some of slip planes are present parallel to each other similar to the other slip planes.
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Back ground

Cold spray
Carbon steel

Diamond knife trimming area

(a) 20 µm

Aluminium

Zinc oxide

Zinc

(b) 1 µm
Figure 12.8. Scanning electron micrographs showing cross-sectional images of the Al10%Zn cold spray carbon steel at an acceleration voltage of 0.9 kV: (a) SE2 image; (b) SE2 image of coating layer; (c) ESB image of (b); (d) colour converted image of (c); (d) EDX mapping results. From the initial image of (a), it is clear that the coating layer and steel substrate are not uniform. Further, it is revealed that the coating layer consists of fine aluminium grains, which is generally unable to be obtained by mechanical polishing. Meanwhile, the zinc grains are not often present. The ESB image suggests elemental differences within the zinc phase in (c). According to the EDX analysis, it is clear the difference is zinc oxide (e). Colour converted image, which is based on the ESB image, and the EDX mapping are relatively similar. Thus, the ESB image and colour converted image may be useful as a substitute for EDX mapping.
Diamond knife trimming area

Coating layer

Mild steel

(a) 10 µm

(b) 1 µm

Cavitie

Si rich oxide

Al rich Intermetallics

Zn

Mild steel
Figure 12.9. Scanning electron micrographs showing cross-sectional images of the Al50%Zn galvanized mild steel at an acceleration voltage of 0.9 kV. (a) SE2 image; (b) In-lens image; (c) ESB image; (d) colour converted image of (c). The images of (b), (c) and (d) show the interface between the coating layer and steel substrate. Accordingly, it is clear that the coating layer and steel surface are non-uniform. Further, the zinc phase consists of relatively small zinc grains. In the ESB image, silicon-oxide and aluminium area are presented a relatively similar contrast. It occurs because aluminium and silicon are dissimilar elements, but it is difficult to distinguish between in the ESB image. Thus, it is necessary to compare the images and EDX analysis results in order to avoid misunderstanding.
Figure 12.10. Scanning electron micrographs showing the cross-sectional images of Al4%Cu alloy in the SE2 images at an acceleration voltage of 0.95 kV. Relatively large, approximately 2 µm, irregularly shaped second phase particles, which are indicated with red line circles, appear to be often located at the grain boundaries. Meanwhile, approximately round shaped second phase particles are located within a grain. Further, different morphologies are evident within grains that may be due to the crystallographic orientation of the grains.
Figure 12.11. Scanning electron micrographs showing the cross-sectional images of the Al1901 alloy in the SE2 image at an acceleration voltage of 2.5 kV: (a) broad area; (b) enlarged image of the area which is indicated by the red line circle in (a). The Al1901 alloy appears to have colonies of the Al-Fe second phase particles within the red line circle. Unlike the Al 5%Cu alloy, large grains are not clearly evident in the broad area. However, contrast differences are evident on the image (a); individual crystallographic orientations of the Al1901 grains are displayed in different contrast.
Figure 12.12. (a) and (b) Scanning electron micrographs showing the cross-sectional images of the Al2024 alloy in the SE2 image at an acceleration voltage of 0.95 kV. Each cross-sectional image displays grains and second phase particles. Some diamond knife marks also revealed. Further, several relatively small cavities are evident across the images. It may occur because particles were removed during diamond knife trimming.
Figure 12.13. Scanning electron micrographs showing the Al2025 alloy cross-sectional image in the SE2 images at acceleration voltage of 1.0 kV: (a) broad area; (b) the area at increased magnification of the red lined circle of (a). Unlike further aluminium alloys, grains are not clearly evident in the image. Second phase particles of approximately 1 μm are evident across the whole cross-section of the Al2025 (a). The large second phase particle, which is indicated with the red line circle, is infrequently present.
Figure 12.14. Scanning electron micrograph showing cross-section of the Al7075 alloy at an acceleration voltage of 0.95 kV: (a) In-lens image; (b) SE2 image. The grains are clearly presented in each image. Further, second phase particles of approximately 1 μm dimensions are often present, but some of them are chipped off (a), or totally removed to produce a cavity in (b). Small particles of approximately 100 nm are also evident in the cross-section; however, again, some of them are removed during ultramicrotomy trimming. These small cavities present bright contrast similar to the nano-scale particle in the In-lens image because of the edge effect. The particles and cavities are able to be distinguished in the SE2 image. In order to avoid misunderstanding, it is necessary to compare the individual images.
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(a) 

100 µm

(b) 

1 µm

Mg$_{14}$Nd$_2$Y

Mg$_{12}$Nd

Nd-rich

Y-rich
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[Image of micrographs showing Nd-rich and Mg\textsubscript{12-Nd} phases with annotations]

(c)

Nd-rich

Mg\textsubscript{12-Nd}

Nd-rich

(d)

Mg\textsubscript{12-Nd}

1 µm
Figure 12.15. Scanning electron micrographs showing the Mg WE43 alloy surface at acceleration voltage of 0.8 kV: (a) In-lens image of the broad area; (b) In-lens image of the area within the red line circle of (a); (c) SE2 image of (b); (d) ESB image of (c); (e) colour converted image of (d). Precipitates are evident within each grain and their orientation appears to be related to the crystallographic orientation of individual grains. Further, precipitate free zones are also evident near the grain boundary. According to the ESB image and colour converted images, these precipitates appear to be also Nd-rich components.
Figure 12.16. Scanning electron micrographs showing the WE 43 alloy surface after the corrosion test in 3.5% NaCl solution for 1h; at an acceleration voltage was 0.95 kV: (a) In-lens image; (b) SE2 image. The corroded area is difficult to observe in detail in the In-lens image due to the positive charge; however, it is possible to observe them in the SE2 image. This is because the corroded area generally includes insulating corrosion products which induce the surface charging. Meanwhile, the SE2 image is not affected by charging; thus, the details of corroded area are able to be observed.
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(a) Mg$_{12}$-Nd

(b) Mg$_{12}$-Nd

2 µm
Figure 12.17. Scanning electron micrographs showing a corroded area at an acceleration voltage of 0.95 kV: (a) In-lens image; (b) SE2 image; (c) ESB image of a further corroded area which is indicated with a red line circle in (a); (d) colour converted image of (c). It is revealed that corrosion has propagated without damaging the Mg$_{12}$Nd. A further corroded area shows the interesting formation of precipitates that are probably Mg$_{14}$Nd$_7$Y; the precipitates displayed slightly different contrast in the ESB image and the colour converted image.
Figure 12.18. Scanning electron micrographs showing the cross-sectional images of (CPU) after the fracture method of preparation and GDOES at an acceleration voltage of 1.5 kV: (a) broad area in SE2 image; (b) area of the red line square of (a) in ESB image; (c) area of the red line circle of (b) in SE2 image; (d) ESB image of (c); (e) colour converted imaged of (d); (f) specimen after polishing and etching by PECS (precision etching coating system). The image (g) is referenced from Gatan [93]. Comparing with the image of after polishing and etching (g), it is revealed that the fracture method is the simple and efficient specimen preparation for the UHR LV SEM.
Figure 12.19. Scanning electron micrographs showing the surface of a sea pearl in the SE2 image at an acceleration voltage of 1.5 kV: (a) broad area; (b) area enlarged from (a). A conductive coating was not employed; however, it is possible to observe the surface without charging. It is revealed that the surface of the pearl, which is consists of layer of the calcium grains.
Figure 12.20. Scanning electron micrograph showing the cross-sectional images of the sea pearl after GDOES surface cleaning at an acceleration voltage of 1.5 kV: (a) broad area in SE2 image; (b) area enlarged from (a) in SE2 image; (c) calcium layers in SE2 image; (d) ESB image of (c). The forms of the calcium grains are not uniform. Further, relatively small particles are present on the calcium surface; a grain appears to consist of four calcium layers. As described, the UHRLV technique and the appropriate SFS preparation made the insulating material possible to be visualized without using a conductive coating.
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