Precipitate characterization and stability in V-based alloys for nuclear fusion reactors

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

2016

Andrea Impagnatiello

School of Materials
# LIST OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Abstract</td>
<td>5</td>
</tr>
<tr>
<td>Declaration</td>
<td>6</td>
</tr>
<tr>
<td>Copyright statement</td>
<td>7</td>
</tr>
<tr>
<td>Acknowledgements</td>
<td>8</td>
</tr>
<tr>
<td>List of acronyms</td>
<td>9</td>
</tr>
<tr>
<td><strong>1. Introduction</strong></td>
<td>10</td>
</tr>
<tr>
<td>1.1 Introduction to fusion energy</td>
<td>10</td>
</tr>
<tr>
<td>1.2 Brief description of nuclear fusion reactors and expected operating conditions</td>
<td>12</td>
</tr>
<tr>
<td>1.3 Expected material degradation phenomena during operation</td>
<td>23</td>
</tr>
<tr>
<td>1.4 Advantages of using vanadium</td>
<td>27</td>
</tr>
<tr>
<td>1.5 References</td>
<td>28</td>
</tr>
<tr>
<td><strong>2. Description of vanadium as first wall reactor material</strong></td>
<td>31</td>
</tr>
<tr>
<td>2.1 Brief history about vanadium alloys for fusion energy</td>
<td>31</td>
</tr>
<tr>
<td>2.2 Basic properties of V-4Cr-4Ti</td>
<td>32</td>
</tr>
<tr>
<td>2.2.1 Crystallography</td>
<td>32</td>
</tr>
<tr>
<td>2.2.2 Phase diagram</td>
<td>34</td>
</tr>
<tr>
<td>2.2.2 Diffusion</td>
<td>41</td>
</tr>
<tr>
<td>2.2.4 Physical properties</td>
<td>48</td>
</tr>
<tr>
<td>2.3 Microstructure</td>
<td>49</td>
</tr>
<tr>
<td>2.3.1 Recovery, recrystallization, grain growth</td>
<td>49</td>
</tr>
<tr>
<td>2.3.2 Nanoscale precipitation</td>
<td>52</td>
</tr>
<tr>
<td>2.4 Mechanical properties</td>
<td>56</td>
</tr>
<tr>
<td>2.4.1 Toughness</td>
<td>56</td>
</tr>
<tr>
<td>2.4.2 Strength</td>
<td>58</td>
</tr>
<tr>
<td>2.4.3 Thermal creep</td>
<td>62</td>
</tr>
<tr>
<td>2.5 Irradiation effects</td>
<td>68</td>
</tr>
<tr>
<td>2.5.1 Material activation</td>
<td>68</td>
</tr>
</tbody>
</table>
ABSTRACT

Andrea Impagnatiello submitted this thesis entitled “Precipitate characterization and stability in V-based alloys for nuclear fusion reactors” for the degree of Doctor of Philosophy at the University of Manchester, 2016. The aim of this work was to investigate the precipitation and stability of nm-sized Ti oxides in vanadium-based alloys, a prime candidate material for future nuclear fusion reactors based on the magnetic confinement of the plasma. Fusion energy reproduces the nuclear reactions occurring in stars. It can potentially produce more energy than current nuclear fission power plants, and it is meant to be a solution to the clash of today’s increasing energy demand with the continuous decrease of fossil-based energy sources, whose use is harmful for the environment. The operating conditions in a fusion reactor will be unprecedented in terms of ultra-high temperatures, stresses, radiation fields and very corrosive media. Only a limited number of materials may be able to withstand such combination of harsh environmental conditions, and vanadium-based alloys are among them. Recent research efforts have identified V-4Cr-4Ti as the most promising vanadium-based alloy for application in the first wall of future fusion nuclear reactors such as DEMO and beyond. The presence of TiO-type precipitates, containing relatively small amounts of C and N, strongly influences the final mechanical properties and radiation resistance of the alloy. Therefore, a thorough understanding of the precipitate structure and evolution at both relatively high temperatures and radiation dose levels is primordial to predict and optimise the final performance of the structural component in the fusion reactor.

This thesis is written in alternative format and collects one article already published in Scripta Materialia, and two additional articles to be submitted to peer-review scientific journals. Atomic resolution imaging of the precipitates, coupled with chemical analysis, constitutes the main body of the first article: a novel intergrowth of the fcc Ti oxide in the bcc V matrix is revealed at the precipitate/matrix interface. The evolution of the vacancies present in the TiO precipitates above 400°C, together with the recovery of dislocations in the matrix and the formation of extra precipitates, is studied in the second article by positron annihilation spectroscopy and micro-hardness measurements. The formation of additional precipitates below 400°C induced by radiation is assessed in the third article using proton irradiation as a surrogate of neutron damage. The structure of those additional precipitates and of the dislocation loops induced by the proton bombardment is characterized by advanced analytical electron microscopy.
DECLARATION

I, Andrea Impagnatiello, declare that no portion of the work referred to in the thesis has been submitted in support of an application for another degree or qualification of this or any other university or other institute of learning.
COPYRIGHT STATEMENT

I. The author of this thesis (including any appendices and/or schedules to this thesis) owns certain copyright or related rights in it (the “Copyright”) and s/he has given The University of Manchester certain rights to use such Copyright, including for administrative purposes.

II. Copies of this thesis, either in full or in extracts and whether in hard or electronic copy, may be made only in accordance with the Copyright, Designs and Patents Act 1988 (as amended) and regulations issued under it or, where appropriate, in accordance with licensing agreements which the University has from time to time. This page must form part of any such copies made.

III. The ownership of certain Copyright, patents, designs, trade marks and other intellectual property (the “Intellectual Property”) and any reproductions of copyright works in the thesis, for example graphs and tables (“Reproductions”), which may be described in this thesis, may not be owned by the author and may be owned by third parties. Such Intellectual Property and Reproductions cannot and must not be made available for use without the prior written permission of the owner(s) of the relevant Intellectual Property and/or Reproductions.

IV. Further information on the conditions under which disclosure, publication and commercialisation of this thesis, the Copyright and any Intellectual Property University IP Policy (see http://documents.manchester.ac.uk/display.aspx?DocID=24420), in any relevant Thesis restriction declarations deposited in the University Library, The University Library’s regulations (see http://www.library.manchester.ac.uk/about/regulations/) and in The University’s policy on Presentation of Theses
ACKNOWLEDGEMENTS

I acknowledge my supervisor Enrique Jimenez-Melero for having taught me about one of the most beautiful jobs. Our differences in character were filling the gaps of my formation as a scientist capable to work with others.

I acknowledge the rest of my team and every person that during my PhD was so kind to share part of his time that has been used to construct my development. My mother Theodora Karavioti and the rest of my family were always present to support me.

I acknowledge the Engineering and Physical Sciences Research Council (EPRSC) for having funded this project, I also thanks for additional funding and trust Paul Mummery, Martin O'Brien and Simon Pimblott. I thank finally the Dalton Cumbrian Facility, where I was based, for having hosted me in all these years.
LIST OF ACRONYMS

bcc – body-centered cubic
CBED – convergent beam electron diffraction
CCD – charge coupled device
CW – cold work
DBTT - ductile-to-brittle transition temperature
DEMO – DEMOnstration Power Plant
DSC – differential scanning calorimetry
EBSD – electron backscatter diffraction
EDS – energy dispersive spectroscopy
EELS – electron energy loss spectroscopy
fcc – face-centered cubic
FFT – fast Fourier transformation
FW – first wall
GB – grain boundary
GBS – grain boundary sliding
HAADF – high angle annular dark field detector
IFC – inertial fusion confinement
ISDC – ITER structural design criteria
ITER – International Thermonuclear Experimental Reactor
JET – Joint European Torus
MFC – magnetic fusion confinement
NIFS – National Institute for Fusion Science (Japan)
ODS – oxide dispersion strengthened
PAS – positron annihilation spectroscopy
PKA – primary knock-on atom
PLB – power-law-breakdown
RAFM – reduced activation ferritic-martensitic
RT – room temperature
SA – solution annealing
SAA – solution annealing & aging
SAACW – solution annealing, aging & cold working
SACWA – solution annealing, cold working & aging
SADP – selected area diffraction pattern
SE – secondary electrons
SEM – scanning electron microscopy
SIA – self-interstitial atoms
STD – standard thermal treatment
TBR – Tritium breeding ratio
TEM – transmission electron microscopy
UTS – ultimate tensile strength
1. INTRODUCTION

"Man will learn one day to free this energy and use it to his own ends"

Arthur Eddington (1882-1944)

In section 1.1 an introduction to what fusion energy is and its similarities with fission energy will be given. Afterwards in section 1.2 we will describe how fusion energy can be implemented in the future, together with the operating conditions expected in the fusion reactor. Some of the main remaining material challenges, such as the changes in the structure of the material under irradiation and the effects on the structural integrity of the reactor component, are addressed in section 1.3. Finally, the advantages of using vanadium alloys as structural materials in the construction of a fusion power plant are described in section 1.4.

1.1 Introduction to fusion energy

Fusion energy, as well fission energy, is produced by nuclear reactions where a comparatively large amount of energy is released according to Einstein’s energy-mass equivalence formula:

\[ E = \Delta m \cdot c^2 \] (1)

This released energy E comes from the difference in mass between reactants and products (\(\Delta m\)). \(c\) denotes the light velocity. The released energy is manifested as an increase in temperature of the system where the reaction takes place.

Figure 1.1 Sun coronal mass ejection (CME), credit: NASA/SDO (see http://www.nasa.gov).
In fusion energy generation, light nuclides fuse together to form a heavier nuclide. This process occurs naturally in the sun (Fig. 1.1). In contrast, when producing fission energy there are no nuclei merging, but a fragmentation of the relatively heavy unstable nuclide into smaller nuclides with a higher stability. Figure 1.2 shows the binding energy per nucleon as a function of mass number, together with the yields of fission and fusion energy production. Note that fission takes place at relatively large values of the mass number, where fusion of nuclides would require external energy to occur.

![Figure 1.2](http://www.ncssm.edu/) Binding energy per nucleon as a function of the mass number. The yield obtained by fission and fusion energy generation is indicated in the graph. (taken from https://www.ncssm.edu/).

To trigger these nuclear fusion reactions, nuclei need to be closer than the limit posed by the electrostatic potential. To overcome this Coulomb potential, the kinetic energy of the reactants must be increased. For fusion energy generation, one way to achieve this is to heat the nuclides to $150 \times 10^6$ °C, 10 times higher than the temperature at the core of the sun [1]. Nuclei and electrons now separated at those high temperatures constitute an “ionised gas”, called plasma, which is considered to be the fourth state of the matter. The most promising nuclear reaction for fusion power applications involves two hydrogen isotopes [2], deuterium ($^2H$) and tritium ($^3H$), that react to form an $\alpha$-particle ($^4He$) plus a neutron ($^1n$):

$$^2H + ^3H \rightarrow ^4He + ^1n + 17.6 \text{ MeV}$$

(2)
In this process, due to the energy and momentum conservation, neutrons with an energy content of 14.1 MeV are released. The remaining energy is carried away by the $\alpha$-particles.

Tritium is not found abundantly in nature: it is an unstable isotope with a half-life of 12.3 years. However, tritium can be produced by the following nuclear reaction:

$$\text{n} + ^{6}\text{Li} \rightarrow ^{3}\text{H} + ^{4}\text{He} + 4.8 \text{ MeV}$$

where the necessary neutrons are generated by the main reaction in the reactor plasma (2).

When dividing the released energy $E$ by the total mass (in energy) of the reactants we obtain a fractional yield of 0.00375 for fusion, while for fission energy this is of 0.00098 if we take for the products an average mass-energy equivalent of 215 MeV. This means that, for equal masses of reactants, fusion produces about 4 times more energy than fission. However, the construction of a fusion power plant that can withstand this increased energy load released by the fusion reaction is very challenging from the materials point of view and is nowadays subject of intense international research. Moreover, the plasma is very harmful if it gets in contact with the reactor materials, and its confinement is compulsory. There are currently two approaches to confine the plasma: to use strong magnetic fields (MFC: magnetic fusion confinement), or to initiate chain reactions inside a chamber by heating and compressing a fuel target using lasers (IFC: inertial fusion confinement). The potential way to implement both approaches in a future nuclear reactor is described in the next section.

### 1.2 Brief description of nuclear fusion reactors and expected operating conditions

The initial challenges to overcome in order to build a fusion reactor are: (1) the start of the nuclear fusion reaction and (2) the confinement of the plasma in such a way that it is not in contact with the structural components of the reactor. Moreover, a tritium breeding system is required to produce tritium at a rate higher than that of its consumption in the plasma, in order to make the whole process self-sufficient. It is also important that the reactor is equipped with appropriate diagnostic systems to control: (1) the progression of the reactions and (2) other important parameters for the safe and efficient reactor operation, such as the flux of neutrons and the temperature in the reaction chamber. The structural materials will need to maintain their properties during the scheduled reactor life time which, together with the materials costs, manufacturing and reactor power efficiency, determine the economical
feasibility of this ‘new form’ of nuclear energy generation. As anticipated earlier, there are two approaches: IFC and MFC. The latter will be described in more detail in this report, since it constitutes the potential application of the vanadium-based alloys studied in this project.

In inertial fusion confinement (ICF) the starting point is a spherical liquefied mixture of deuterium and tritium of few millimetres of diameter called target, see Fig.1.3. The target is located in the centre of a chamber of several meters of radius, and heated by an impressive laser system with a power of several hundreds of TW. The heated outer layer of the target explodes outwards, producing a reaction force against the remainder of the target, which is accelerated inwards and compressed. The density rises until the ignition conditions for the fusion reaction are reached. The products of this thermonuclear burn will be removed from the chamber and a new pellet of fuel will be put in place [3, 4].

In magnetic fusion confinement (MFC), see Fig.1.4, deuterium and tritium fill the vacuum of a toroidal chamber in the gas state, and they are subsequently heated by electromagnetic waves. Once the ignition conditions are reached, the plasma is formed in the chamber [1]. In order to confine the plasma and avoid any harmful contact with the chamber wall, a toroidal system of coils, together with a poloidal system and a central solenoid, is used. These coils generate a magnetic field which shapes the plasma into a torus, where charged particles will start to circulate along its circumference, ideally without hitting the chamber. Nowadays, efforts focus on maximising the plasma stability and its confinement, in order to avoid particle dispersions that would be harmful for the chamber.
Magnetic confinement was the first tested fusion energy approach [5]: first experiments were conducted secretly after the end of the Second World War by several countries. Only after the International Conference on the Peaceful Uses of Atomic Energy in Geneva in 1958 was the importance of fusion energy recognized worldwide and international scientific collaboration to develop fusion reactors initiated. In 1968 Russia announced the Tokamak: the first device whose concept involved toroidal magnetic fields to confine the plasma. The results were promising and the concept was scaled up to accommodate higher plasma currents and larger sizes with the development of JET (Joint European Torus) and TORE SUPRA (from the French words for torus and superconductor) during the 70’s and the 80’s, respectively [5].

After examining their cost, lifetime and energy efficiency, it was concluded that these devices with a major radius of the vacuum chamber of about 3m were not profitable for energy production on a large scale. To improve their economical potential, it was necessary to enlarge the plasma volume significantly, and a device expected to have a power production of 2GW is currently under development. Its name is DEMO (DEMonstration Power Plant) [6, 7, 8], and it is intended be the first fusion power plant on a large scale with a plasma major radius of about 7.7 m. Scaling up brings new technological challenges about plasma confinement and materials integrity [9].

The development of DEMO requires an intermediate device whose operating conditions are closer to DEMO than those of the Tokamak devices built in the 70’s and the 80’s. The results from the study of the behaviour of such device will be used in the final DEMO design. This
intermediate device is called ITER (International Thermonuclear Experimental Reactor) with a plasma major radius of 6.2 m [10, 11]. Its goal is to produce 500MW of fusion power. Its construction, sponsored by several countries, has already started in France and the first plasma is scheduled in December 2025 [1]. Its current design is shown in Fig. 1.5.

The magnetic coils, made of superconductors, will produce fields of around 10 T. These coils are quite expensive and represent nearly a third of the total cost of ITER [12]. A cryostat system is present to keep the coils below their superconducting temperature. The vacuum vessel constitutes the reaction chamber containing the plasma [13]. This vessel is kept at a vacuum level of \(\sim 10^6\) Pa and is protected from the harmful effects of the plasma by the blanket and the divertor [14]. The latter is the only component in direct contact with the plasma. Figure 1.5 shows the cross section of the vacuum vessel covered by the blanket and the divertor, together with the shape of plasma in the proximity of both components.

**Figure 1.5** Sketch of the ITER structural design. Its main components are also indicated in the figure [1].
The divertor is the main heat extraction component (Fig. 1.6). It also removes the $\alpha$-particles produced in the fusion reaction and other impurities present in plasma that may compromise its stability. The divertor deals with the major heat and neutron load. It needs to be made of materials capable of operating up to 3000°C: the current ITER project will use either carbon composites or tungsten alloys as the plasma facing materials in the divertor [15, 16, 17].

The blanket (Fig. 1.7) gives protection to the vacuum vessel in other areas apart from the divertor [18]. It will be composed by modules of $1.0 \times 1.45$ m mounted on the internal wall of the vessel. The side of the modules facing the plasma is called the first wall (FW) and, as
the divertor, will deal with a huge flux of heat and particles. In ITER, the FW will be made of beryllium, while for the remaining blanket structure high-strength copper alloys and stainless steels are going to be used. For both the divertor and the blanket, an appropriate cooling system will be implemented in order to remove the heat from these devices and convert that heat into electrical energy.

Figure 1.7 ITER blanket design where the main components are shown from different points of view: (a) front, (b) lateral and (c) rear [1].

Several windows are present on the equatorial line of the vacuum vessel: they will host additional devices such as the heating system which “triggers the plasma”, diagnostics components and the tritium breeding module. In the DEMO project, every blanket module is intended to produce tritium in order to guarantee an adequate tritium production [19]. In ITER, six different types of breeding modules are going to be tested, and the results will influence the future design choice for DEMO [20]. The design of a breeding module, which implies how lithium is exposed to neutrons and how tritium is extracted for its insertion into the plasma, changes with the structural material selected for the breeding module [20]. In the
case of modules made of vanadium alloys, liquid lithium constitutes the coolant, and tritium is produced by the interaction of the coolant with the neutrons produced in the plasma.

Definitive designs for DEMO are not established due to the early stage of the project. Proposed concepts change continuously with the income of newer ideas that increase the quality and feasibility of the reactor. Fig. 1.8a shows the DEMO configuration in the 2014 with a shield meant to protect the magnets from the plasma neutron irradiation. The realization of such shield inside the toroidal chamber would be quite demanding and impractical [21]. The vacuum vessel, built outside the toroidal chamber, is thought to protect the magnets in the DEMO configuration of the 2015 (Fig. 1.8b), at the condition to afford properly the incoming radiation [22].

![Figure 1.8 DEMO configuration showing components as the vacuum vessel (VV), the blanket with manifold, the divertor and the coils to generate the magnetic fields. (a) concept of the 2014 with shield (b) concept of the 2015 without shield [21, 22].](image)

In both cases the blanket is decomposable in modules in order to improve maintenance and building feasibility. The nowadays general design of the DEMO blanket involves the use of EUROFER steel and a 2 mm thick FW made of tungsten. Inside the blanket module (Fig. 1.9)
there will be the coolant and the breeding system meant respectively to lower the blanker temperature and produce the tritium needed to run the fusion nuclear reactions [23].

**Figure 1.9** Blanket modules in DEMO, the production of tritium occurs in the breeder zone and the first wall provides protection from the plasma [23].

As mentioned previously, fusion reactors are intended to operate at more extreme conditions than fission reactors. Fig. 1.10 gives an overview of the operating temperature and the expected radiation damage levels over 60 years of reactor operation showing also in years the experience with that particular type of reactor [24]. DEMO is scheduled to operate at least 30 years [25].

Table 1.3 summarizes the expected operation conditions of the structural materials in the plasma environment of ITER and DEMO [26, 27]. Fusion power corresponds to the expected energy that the power plant can produce and put into the grid. The heat flux and the neutron load are the energy and the neutrons flux emitted by the plasma, respectively. The expected damage (dpa) generated during the whole device lifetime (∼ 30 y) is also indicated, together with the rate of potential transmutation products. While a damage level of less than 3 dpa is expected in materials used for ITER, after 30 years the DEMO materials will need to withstand a level of 50-80 dpa.
1. Introduction

Figure 1.10 Overview of the operating temperatures and radiation damage level expected after 60 years for different fission and fusion nuclear reactors. DEMO reactor is named among Fusion, the abbreviations for the fission reactors are: GEN II, Generation II; GFR, gas-cooled fast reactor; LFR, lead-cooled fast reactor; LWR, light-water-cooled fission reactor; MSR, molten salt–cooled reactor; SCWR, supercritical water reactor; SFR, sodium-cooled fast reactor; VHTR, very high temperature reactor. [24].
Table 1.3 Principal operating conditions of structural materials in ITER and DEMO [26, 27].

<table>
<thead>
<tr>
<th></th>
<th>ITER</th>
<th>DEMO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fusion power</td>
<td>0.5 GW</td>
<td>2.5 - 5 GW</td>
</tr>
<tr>
<td>Heat flux</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(first wall)</td>
<td>0.1-0.3 MW/m²</td>
<td>0.5 MW/m²</td>
</tr>
<tr>
<td></td>
<td>~ 10 MW/m²</td>
<td>~ 15-20 MW/m²</td>
</tr>
<tr>
<td>(divertor)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Neutron Load (FW)</td>
<td>0.78 MW/m²</td>
<td>&lt; 2 MW/m²</td>
</tr>
<tr>
<td>Integrated Neutron Load (FW)</td>
<td>0.07 MW-years/m² (3 years operation)</td>
<td>5 - 8 MW-years/m²</td>
</tr>
<tr>
<td>Displacements per atom (dpa)</td>
<td>&lt; 3 dpa</td>
<td>50 - 80 dpa</td>
</tr>
<tr>
<td>Trasmutation product rates at FW</td>
<td>~ 10 appm He / dpa</td>
<td>~ 45 appm H / dpa</td>
</tr>
</tbody>
</table>

With a stationary heat load of 1 MWm⁻² over the FW of a DEMO blanket, the temperatures of W and EUROFER steel are calculated in Fig. 1.11. The temperature drop can be around 100 °C in the areas close to the coolant system. Disruptive instabilities of the plasma increase the heat load with deleterious effects for the materials, Fig. 1.12 shows the temperature rise in the DEMO blanket during stationary heat load of 1 MWm⁻² with additional periodic loads of 20 MW m⁻². These loads increase the temperature of the EUROFER steel above its allowed range, also the W temperature rises above the limits and the W coating gets locally melted [28].
1. Introduction

**Figure 1.11** The temperatures profile in a DEMO blanket plotted versus the depth from the FW surface. The solid line is for the hot spot position (the farthest to the coolant tube) and the dashed one is for the cool spot position (the nearest to the coolant tube) [28].

**Figure 1.12** The temperatures profile in a DEMO blanket of the cooling tube, EUROFER steel and W first wall plotted versus time. The heat load has a stationary component of 1 MW m\(^{-2}\) with additional loads of 20 MW m\(^{-2}\) at a frequency of 0.8 Hz and deposition time of 0.6 ms. The coloured bars represent the allowed temperature ranges[28].
1.3 Expected material degradation phenomena during operation

In general, when an energetic particle hits an atom in the lattice of the target material, three different processes may occur [29]:

- Inelastic collisions (d): where bombarding particles transfer energy to the lattice atoms, which can move from their initial position in the lattice. This would generate atomic displacements.
- Nuclear reactions (n): where fast particles take part in nuclear reactions with the target nuclei. This may produce considerable amounts of foreign elements within the material.
- Electronic excitations/ionizations (e): are of only very limited importance for metals and the irradiation damage process.

The stopping power \( \frac{dE}{dx} \) denotes the change in energy \( E \) of the bombarding particle as a function of the penetration depth \( x \) in the material. It contains the three terms mentioned above:

\[
\frac{dE}{dx} = \left( \frac{dE}{dx} \right)_d + \left( \frac{dE}{dx} \right)_n + \left( \frac{dE}{dx} \right)_e \tag{4}
\]

Nuclear reactions are important for safety reasons because the nuclear transmutation processes may involve radioactive decays with emission of neutrons, protons and/or \( \alpha \)-particles. The decay may be immediate or extend over several years. Inelastic collisions are mainly responsible for the changes in the mechanical properties of the structural material. When the transferred energy exceeds the threshold energy for atomic displacement, the atom is moved away from its equilibrium position in the lattice and a vacancy-interstitial pair (Frenkel defect) is created. If the transferred energy is significantly higher than the threshold energy, the atom firstly hit by the bombarding particle becomes a “primary knock-on atom” PKA (Fig. 1.12). This PKA is able to transfer energy by moving further in the crystal creating additional point defects, a process called displacement cascade. An important quantity to evaluate the radiation damage is the number of \textit{displacements per atom} (dpa) in the radiated volume, i.e. the number of times that an atom has been displaced from its equilibrium position in the lattice.
The radiation-induced point defects consist of self-interstitial atoms (SIA) or vacancies (VAC). At longer timescales (after a few ps), those defects may annihilate by recombination between them. Otherwise SIAs and VACs can combine with defects of the same type to form new lattice defects of higher dimensionality, such as dislocation loops and voids, or be trapped by other pre-existing defects (Table 1.4).

Table 1.4 Some examples of defect reactions occurring in the radiated material [29].

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>Recombination of SIA and VAC</td>
<td>Vanishing point defects</td>
</tr>
<tr>
<td>Clustering of SIAs</td>
<td>Di-interstitial</td>
</tr>
<tr>
<td></td>
<td>Tri-interstitial</td>
</tr>
<tr>
<td>Clustering of VACs</td>
<td>Dislocation loops</td>
</tr>
<tr>
<td></td>
<td>Di-vacancies</td>
</tr>
<tr>
<td></td>
<td>Tri-vacancies</td>
</tr>
<tr>
<td>Trapping of SIAs and VACs:</td>
<td>Dislocation loops, stacking fault tetrahedra, voids</td>
</tr>
<tr>
<td>At impurities</td>
<td>Mixed arrangement</td>
</tr>
<tr>
<td>At dislocations</td>
<td>Dislocation climb</td>
</tr>
<tr>
<td>At voids</td>
<td>Void growth</td>
</tr>
<tr>
<td>At grain boundaries</td>
<td>Microstructural damage</td>
</tr>
<tr>
<td>At precipitates etc</td>
<td></td>
</tr>
<tr>
<td>Clustering of helium atoms</td>
<td>Helium bubbles</td>
</tr>
</tbody>
</table>

As a consequence of the evolution of SIAs and VACs and their clustering, dense zones are formed where the dislocation density is higher, and where phase transformations and
precipitation reactions may occur, i.e. radiation-induced transformations. In addition to this, the formation of a diluted zone, may lead to void growth and material swelling. The consequences of these and other effects of SIAs and VACs reactions for the material degradation are summarized in Table 1.5.

Table 1.5 Different types of radiation damage and the resulting consequences for the degradation of a nuclear component [29].

<table>
<thead>
<tr>
<th>Effect</th>
<th>Consequence in material</th>
<th>Kind of degradation in component</th>
</tr>
</thead>
<tbody>
<tr>
<td>Displacement damage</td>
<td>Formation of point defect clusters and dislocation loops</td>
<td>Hardening, embrittlement</td>
</tr>
<tr>
<td>Irradiation-induced segregation</td>
<td>Diffusion of detrimental elements to grain boundaries</td>
<td>Embrittlement, grain boundary cracking</td>
</tr>
<tr>
<td>Irradiation-induced phase transitions</td>
<td>Formation of phases not expected according to phase diagram, phase dissolution</td>
<td>Embrittlement, softening</td>
</tr>
<tr>
<td>Swelling</td>
<td>Volume increase due to defect clusters and voids</td>
<td>Local deformation, eventually residual stresses</td>
</tr>
<tr>
<td>Irradiation creep</td>
<td>Irreversible deformation</td>
<td>Deformation, reduction of creep life</td>
</tr>
<tr>
<td>Helium formation and diffusion</td>
<td>Void formation (inter- and intra-crystalline)</td>
<td>Embrittlement, loss of stress rupture life and creep ductility</td>
</tr>
</tbody>
</table>

The mobility of the defects at a given temperature strongly influences the resultant irradiated microstructure. At low temperatures the diffusion of defects induced by irradiation predominates over thermal diffusion. As a consequence, the density of radiation-induced defects becomes higher than that corresponding to thermal equilibrium. By contrast, at high temperatures the diffusion and the density of thermally induced defects dominate over the effects of irradiation. Figure 1.13 shows the influence of the irradiation temperature on the formation of different types of lattice defects.
Figure 1.13 Influence of irradiation temperature on the formation of different lattice defects, taking austenitic steel as an example [30].

The lattice type seems to have a correlation with the resultant irradiated microstructure: fundamental differences in the behaviour of face centred cubic (fcc) and body centred cubic (bcc) metals have been observed. Although the defect production was similar, the average size of voids in bcc metals was much smaller, indicating a greater swelling resistance [31]. Solute additions to pure metals generally increase the nucleation rate of dislocation loops [32]. On the other hand, alloying additions can also create second phases that may improve the strength of the material. A fine dispersion of highly stable nanoscale precipitates, as well a high grain boundary density due to the fine grain structure of the matrix, can be very effective in providing resistance to radiation damage by acting as effective sinks for radiation-induced defects [33].
1.4 Advantages of using vanadium alloys as blanket materials

Vanadium alloys are considered as promising candidates for the fusion blanket due to the following properties [34, 35]:

- **Low activation:** vanadium nuclei do not activate easily under irradiation of 14 MeV neutrons. As a consequence, the material does not become radioactive and the blanket modules will not constitute a high-level radioactive waste after the shutdown of the power plant [36, 37].

- **High temperature strength:** vanadium has melting point about 1800°C. This allows to maintain good strength at the high temperatures expected in fusion reactors where other potential alloys, such as ferritic/martensitic steels, would start to weaken and therefore compromise the structural integrity of the blanket [38, 39].

- **Swelling resistance:** vanadium as a bcc metal has a relatively high swelling resistance as compared to fcc metals, allowing to extend the lifetime of the blanket [40, 41].

- **Compatibility with liquid lithium as a coolant,** combined with a low neutron absorption cross section: the required production of tritium can be achieved without neutron-multiplying materials such as beryllium, which poses additional challenges in terms of safe handling of materials and natural resource limitations. The design of the blanket is also simplified, as periodic replacements of ‘burned beryllium’ are not anymore needed [42].

- **Non-magnetic vanadium components** will not be affected by the relatively intense magnetic fields required to confine the plasma [43, 44].
1.5 References

1. Introduction


2. DESCRIPTION OF VANADIUM AS FIRST WALL REACTOR MATERIAL

A brief history about basic research on vanadium for fusion applications and the motivation behind the selection of the alloy V-4Cr-4Ti as the main vanadium-based material candidate for the reactor blanket are presented in section 2.1. The physical properties of this alloy, together with its phase diagram, diffusivity and crystallography, are addressed in section 2.2. In section 2.3 and 2.4 the microstructure and the mechanical properties are discussed in relation to the thermo-mechanical treatments and the chemical composition. Section 2.5 contains information about the irradiation effects on the structure and properties of this material and finally, section 2.6 describes the upfront research to improve the performance of V-based alloys in radiation environments.

2.1 Brief history about vanadium alloys for fusion energy

Vanadium (V) was initially discovered in 1801 by the Spanish scientist Andres Manuel del Rio in New Spain (Mexico) and he called it erythronium. However, in 1805 the French chemist Hippolyte-Victor Collet-Desotils examined erythronium and concluded that it was actually impure chromium. In 1831 Nils Gabriel Sefström in Stockholm found a new metal in a Swedish iron ore. He called this new element vanadium after “Vanadis” the Scandinavian goddess of beauty, due to the beautiful multicolored compounds formed by the new metal. In the same year, the German chemist Friedrich Wöhler reinvestigated the Mexican ore and discovered that the erythronium mineral indeed contained vanadium [1].

One noticeable property of vanadium is its high melting point (1910°C), more than 350°C higher than pure iron. This fact manifests in the high-temperature strength of vanadium and its alloys, as was already reported during the 60’s [2, 3]. The first experiments for a potential application of vanadium alloys in fusion reactors were conducted in the 70’s [4-6]. The results were encouraging as vanadium also had favourable neutronics properties: low absorption cross section for neutrons, what reduces the material’s activation and allows to have a high production rate of tritium by the reaction between neutrons and lithium nuclei.
One of the first reviews of vanadium alloys for fusion reactor applications was published by Gold et al. in 1981 [7]. The most studied vanadium alloys during the 80’s were the V-15Cr-5Ti, V-20Ti and the VANSTAR (V-9Cr-3.3Fe-1.2Zr-0.054C) [8, 9]. Chromium (Cr) has been identified to be an effective solid-solution strengthener that increases the creep and oxidation resistance of the alloy. Titanium (Ti) instead acts as a scavenger for interstitial impurities forming precipitates. Ti is also a solid-solution strengthener like Cr, and improves fabricability and resistance to radiation swelling [10]. On the other hand, relatively high amounts of Cr and Ti (i.e. Cr+Ti > 10wt.%) cause some negative effects for the alloy, such as excessive irradiation hardening and a decrease in creep resistance [10]. Researchers started to decrease the concentrations of Cr and Ti in vanadium alloys, and at the end of the 90’s the alloy V-4Cr-4Ti was widely considered as the reference vanadium alloy for structural application in fusion reactors [11].

In 2000 India and Russia developed two blanket concepts for DEMO based on this vanadium alloy as structural material [12, 13]. Since then, several experiments have been conducted to extend the mechanistic understanding about its thermal [14, 15] and irradiation creep resistance [16, 17], the irradiation effects on the microstructure and on the mechanical properties [18, 19], and about the role of the precipitates and interstitial atoms on the alloy performance [20, 21]. However, basic questions about the evolution of the microstructure under irradiation at the expected operating temperatures, and its influence on the integrity of the reactor component, still remain unsolved [17].

2.2 Basic properties about V-4Cr-4Ti

2.2.1 Crystallography

Vanadium crystallizes in a body-centered cubic (bcc) structure that is stable from room temperature (RT) up to its melting point of 1910°C. The lattice parameter takes a value of 3.026 Å at RT [22].
2. Description of vanadium as first wall reactor material

Table 2.1 shows the lattice parameter of V-Cr-Ti alloys for different compositions. Cr and Ti exert an opposite effect on the lattice parameter. The difference can be mainly attributed to the relative atomic sizes: Cr is undersized respect to V and crystalizes in a bcc structure with a smaller lattice parameter of 2.880 Å, whereas Ti is oversized with respect to V and its low-temperature bcc structure presents a lattice parameter of 3.268 Å [23]. The effect of variable amounts of Ti on the V lattice parameter is shown in Fig. 2.2.

Table 2.1 Lattice parameter of V-Cr-Ti alloys for different compositions [24].

<table>
<thead>
<tr>
<th>Composition (at%)</th>
<th>phase</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>BCC</td>
</tr>
<tr>
<td>V</td>
<td>Ti</td>
</tr>
<tr>
<td>70</td>
<td>10</td>
</tr>
<tr>
<td>70</td>
<td>15</td>
</tr>
<tr>
<td>70</td>
<td>5</td>
</tr>
<tr>
<td>80</td>
<td>10</td>
</tr>
<tr>
<td>60</td>
<td>10</td>
</tr>
<tr>
<td>80</td>
<td>0</td>
</tr>
<tr>
<td>60</td>
<td>20</td>
</tr>
<tr>
<td>80</td>
<td>5</td>
</tr>
<tr>
<td>60</td>
<td>15</td>
</tr>
</tbody>
</table>

Figure 2.1 Model of a bcc unit cell (space group Im-3m).
2. Description of vanadium as first wall reactor material

2.2.2 Phase diagram

The binary V-Ti and V-Cr phase diagrams are shown in Fig. 2.3 [25]. Cr is totally soluble in V forming a uniform bcc phase. For Ti the situation is different, it precipitates in the bcc V matrix as hcp even at concentration of V above 50 at.%. Figure 2.4 shows the binary Ti-Cr phase diagram [25], there are present three different allotropes (α, β and γ) of the intermetallic compound TiCr₂, which precipitates as a Laves phase. The α-TiCr₂ has cubic MgCu₂-type crystal structure (space group Fd 3m), the other two (β and γ) both belong to the space group is P 6₃/mmc with hexagonal crystal structure.

The phase diagram of the V-4Cr-4Ti system is shown in Fig. 2.5 at selected temperatures [26]. The V-4Cr-4Ti alloy retains the bcc structure up to the melting point of 1890°C. The increase in Ti content leads to a decrease in melting point (Fig. 2.6) [25]. Moreover, at Cr concentrations above ~10-15 wt% the intermetallic α-TiCr₂ phase is formed within the bcc matrix, above 900 °C it appears also the β -TiCr₂ phase. Increasing the temperature reduces the stability of the TiCr₂ Laves phases in the bcc matrix.

Figure 2.2 Experimental values of the room-temperature lattice parameter of bcc V as function of Ti content [23].
2. Description of vanadium as first wall reactor material

Figure 2.3 Calculated phase diagrams of the (a) Ti–V and (b) V-Cr system. β and α are respectively bcc and hcp phases [25].

Figure 2.4 Calculated phase diagram of Ti–Cr system showing the 3 (α-β-γ) TiCr₂ Laves phases, β and α are respectively bcc and hcp phases [25].
2. Description of vanadium as first wall reactor material

Figure 2.5 Calculated phase diagram of the ternary V–Cr–Ti system at selected temperatures. β and α-TiCr$_2$ are bcc phases, while α and β-TiCr$_2$ are hcp phase [26].
2. Description of vanadium as first wall reactor material

Figure 2.6 (a) Calculated solidus, $\beta/(\beta+\text{liquid})$, contour (in °C) in the ternary Ti–Cr–V system, and (b) experimental solidus contour [25].

The presence of O can lead to the formation of other phases as oxides, Fig. 2.7 and Fig. 2.8-9 show the V-O and Ti-O phase diagrams respectively [27, 28]. Both diagrams are characterized by a large number of different oxides phases, it is remarkable to note that the VO and the $\gamma$TiO have both NaCl type crystal structure with lattice constant very similar: 0.408 nm and 0.418 nm respectively [27, 28]. The phase diagram of the ternary V-Ti-O system is presented in Fig. 2.10 together with the ternary V-Ti-C and V-Ti-N systems (Fig. 2.11 and Fig. 2.12) [29, 30, 31]. It is possible the simultaneous presence of TiO, TiC and TiN at temperatures above 1000°C where the concentration of Ti is locally high, like areas with Ti precipitates. These compounds have the same type of crystal structure of NaCl type, and similar lattice parameter: 0.418 TiO [32], TiC 0.4328 nm [33], TiN 0.4259 nm [33].
2. Description of vanadium as first wall reactor material

Figure 2.7 Calculated phase diagram of V-O system, courtesy of ASM International [27].

Figure 2.8 Calculated phase diagram of Ti-O system [28].
2. Description of vanadium as first wall reactor material

Figure 2.9 Calculated phase diagram of Ti-O system, from 58 to 68 at.\% O [28].

Figure 2.10 Calculated phase diagram of V-Ti-O system at 1200°C, courtesy of ASM International [29].
2. Description of vanadium as first wall reactor material

Figure 2.11 Calculated phase diagram of V-Ti-C system at 1000°C, courtesy of ASM International [30].

Figure 2.12 Calculated phase diagram of V-Ti-N system at 1200°C, courtesy of ASM International [31].
2.2.3 Diffusion

The atomic diffusion in vanadium alloys relates to the migration of substitutional (Ti, Cr) and interstitial (C,O,N) atoms in the host crystalline lattice. In general, an atom migrates by jumping from its atomic position in the lattice to an adjacent position. This process is thermally activated. The migrating atom requires that the thermal energy is high enough to break all the bonds with the other neighbouring atoms and distort locally the lattice as required during the jump.Interstitial diffusion is faster since the local bonds are weaker and the presence of an adjacent vacancy is not required. The diffusion can be described by the two Fick laws (1-2), for the steady and non-steady state respectively [34]:

\[
J = -D \frac{dc(x)}{dx} \tag{1}
\]

\[
\frac{\partial c(x,t)}{\partial t} = - \frac{\partial J}{\partial x} = D \frac{\partial^2 c}{\partial x^2} \tag{2}
\]

where \(J\) is the flux of diffusing particles; \(c\) is the concentration of the diffusing particles as function of position \(x\) and time \(t\). \(D\) is finally the diffusion coefficient, whose temperature dependence can be expressed by an Arrhenius-type equation:

\[
D = D_0 e^{-Q/RT} \tag{3}
\]

where \(Q\) is the activation energy for diffusion and as deductible: the highest \(Q\), the lowest diffusion. The gas constant is \(R\) and \(D_0\) is called the pre-exponential factor, or diffusion constant, and it takes into account parameters such as the vibrational frequency of the atom in the lattice and its coordination number. Values of \(D\) can be obtained experimentally using radioactive tracer isotopes. The term ‘self-diffusion’ denotes the case when the diffusing atom is of the same species of that of the host lattice. \(2.4\sqrt{D \cdot t}\) corresponds to the diffusion range assuming a ‘random walk’, that is to say, the direction of one atomic jump is not correlated with the previous jump of the same atom [35].
Diffusion of interstitial species

From first-principles calculations it is evidenced that O, N and C atoms in a V matrix prefer to occupy an octahedral interstitial site rather than a tetragonal one which is occupied only during the jump from one octahedral site to the other in the so called hopping mechanism shown in Figure 2.13 [36]. It would be expected that the tetragonal site is occupied since it provides the highest volume for the interstitial atom but 4 host atoms have to be displaced. In the octahedral position instead, the interstitial is surrounded by 6 host atoms but only the two closer atoms will be displaced significantly due to the irregularity of a bcc octahedral position. In the case of C in Fe, it happens that the remaining 4 host atoms will move towards the C atoms after the Poisson compression [37].

The difference in energy between an octahedral and tetragonal site is the activation energy Q. Table 2.2 provides the estimated Q and $D_0$ for O, N and C compared with experimental values. O, N and C exhibit repulsive interactions with the neighbour vanadium atoms leading an outward expansion by about 25%. The formation energy of O, N and C in the octahedral interstitial site are respectively $-5.12$ eV, $-2.97$ eV and $-2.1$ eV, C and O have so the lowest and highest solubility in V [36].

![Figure 2.13](image-url) (a) Diffusion energy curves of O atom (red balls) moving from an octahedral site (*) to another through a tetragonal one (+^) in V (green balls) [36].
Figure 2.14 shows for O, C and N the deductible plot of the natural logarithm of D with the inverse of T (Arrhenius plot) [36]. C diffuses faster, follows O and N. This order is the same met for Q: the lowest activation energy equals to the highest diffusivity.

Table 2.2 Pre-exponential factor and activation energy (diffusion barrier) of the diffusion of C, O, N in pure V calculated by first-principles calculations [36] and compared with experimental values [38].

<table>
<thead>
<tr>
<th>Impurity</th>
<th>Diffusion barrier (eV)</th>
<th>Diffusion constant (cm² s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>This work</td>
<td>Expt.</td>
</tr>
<tr>
<td>O</td>
<td>1.23</td>
<td>1.275</td>
</tr>
<tr>
<td>N</td>
<td>1.48</td>
<td>1.539</td>
</tr>
<tr>
<td>C</td>
<td>1.14</td>
<td>1.206</td>
</tr>
</tbody>
</table>

Figure 2.14 Temperature dependence of the diffusion coefficient of O, C and N in pure V [36].

Regarding the effect of alloying elements in the interstitial diffusion, experimental data is shown for O in Table 2.3 [39]. Cr increases diffusion of O as it extends the lattice parameter (Par. 2.1.1) that would lead to a decrease of the activation energy as the repulsive interactions are lowered and the bonds are weakened. Such effect of the lattice parameter has been confirmed by other first-principle calculations [40]. The addition of Ti has a total opposite effect and it appears to act as a trap for O. One explanation that has been suggested [39] relates the O diffusivity with the Gibbs free energy of formation of the oxide formed with the host metal, as listed in Tab. 2.4. The table does not list all the different Ti and V oxides that
may form according to the phase diagrams (Par. 2.2.2) and differences on type among the 
oxides impede a direct comparison, but it is worth mentioning that the free energy of the Ti 
oxide has the highest magnitude, suggesting the presence of a strong affinity between Ti and O. Another explanation is possible comparing O diffusivity in pure V and Ti, both bcc. The Q 
in Ti is 288.3 kJ/mol [41] and is more that the double of the Q in bcc V (121 kJ/mol). The 
addition of Ti in V will lead to the appearance of bcc Ti (Par. 2.2.2) and it will impede O 
diffusion since O diffuses much slower in Ti rather than in V.

Table 2.3 Pre-exponential factor \( D_0 \) and activation energy \( Q \) of the diffusion O for in pure and alloyed V [39].

<table>
<thead>
<tr>
<th>Matrix</th>
<th>( D_0 ) (m(^2) s(^{-1}))</th>
<th>( Q ) (kJ mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>V</td>
<td>((1.3^{+0.3}_{-0.2}) \times 10^{-6})</td>
<td>121.6 ± 2.5</td>
</tr>
<tr>
<td>V-1Si</td>
<td>((1.1^{+0.2}_{-0.2}) \times 10^{-5})</td>
<td>131.5 ± 4.9</td>
</tr>
<tr>
<td>V-5Fe</td>
<td>((3.0^{+0.3}_{-0.3}) \times 10^{-6})</td>
<td>128.9 ± 4.9</td>
</tr>
<tr>
<td>V-5Mo</td>
<td>((2.9^{+0.6}_{-0.6}) \times 10^{-7})</td>
<td>115.2 ± 1.1</td>
</tr>
<tr>
<td>V-5Nb</td>
<td>((2.9^{+0.3}_{-0.3}) \times 10^{-6})</td>
<td>128.3 ± 5.0</td>
</tr>
<tr>
<td>V-5Cr</td>
<td>((1.0^{+0.4}_{-0.4}) \times 10^{-7})</td>
<td>110.6 ± 2.5</td>
</tr>
<tr>
<td>V-0.1Al</td>
<td>((1.3^{+0.6}_{-0.6}) \times 10^{-5})</td>
<td>132.8 ± 2.1</td>
</tr>
<tr>
<td>V-0.1B</td>
<td>((3.6^{+1.0}_{-1.0}) \times 10^{-6})</td>
<td>127.9 ± 1.6</td>
</tr>
<tr>
<td>V-3Ti-2Si</td>
<td>((0.9^{+0.3}_{-0.3}) \times 10^{-4})</td>
<td>163.6 ± 9.7</td>
</tr>
<tr>
<td>V-5Ti</td>
<td>((3.1^{+1.7}_{-1.7}) \times 10^{-4})</td>
<td>171.8 ± 4.7</td>
</tr>
</tbody>
</table>

Table 2.4 Gibbs free energy of formation of different oxides at 600K [39].

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Gibbs energy (kJ mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Fe} + \frac{3}{2}\text{O}_2 = \frac{3}{2}\text{Fe}_2\text{O}_3 )</td>
<td>-304</td>
</tr>
<tr>
<td>( \text{Fe} + \frac{1}{2}\text{O}_2 = \text{FeO} )</td>
<td>-226</td>
</tr>
<tr>
<td>( \text{Cr} + \frac{3}{2}\text{O}_2 = \frac{3}{2}\text{Cr}_2\text{O}_3 )</td>
<td>-513</td>
</tr>
<tr>
<td>( \text{Mo} + \text{O}_2 = \text{MoO}_2 )</td>
<td>-477</td>
</tr>
<tr>
<td>( \text{Nb} + \frac{1}{2}\text{O}_2 = \text{NbO} )</td>
<td>-359</td>
</tr>
<tr>
<td>( \text{Nb} + \text{O}_2 = \text{NbO}_2 )</td>
<td>-343</td>
</tr>
<tr>
<td>( \text{B} + \frac{3}{2}\text{O}_2 = \frac{3}{2}\text{B}_2\text{O}_3 )</td>
<td>-548</td>
</tr>
<tr>
<td>( \text{Al} + \frac{3}{2}\text{O}_2 = \frac{3}{2}\text{Al}_2\text{O}_3 )</td>
<td>-742</td>
</tr>
<tr>
<td>( \text{Si} + \text{O}_2 = \text{SiO}_2 )</td>
<td>-797</td>
</tr>
<tr>
<td>( \text{Ti} + \text{O}_2 = \text{TiO}_2 )</td>
<td>-808</td>
</tr>
<tr>
<td>( \text{V} + \frac{3}{2}\text{O}_2 = \frac{3}{2}\text{V}_2\text{O}_3 )</td>
<td>-543</td>
</tr>
</tbody>
</table>
2. Description of vanadium as first wall reactor material

**Diffusion of substitutional species and V self-diffusion**

Figure 2.15 shows the Arrhenius plot of the self-diffusion coefficient of V modelled with the CALPHAD method (CALculations of PHase Diagrams) and compared with experimental results from literature [42].

How the self-diffusion of V is affected by Ti is shown in Figure 2.16a while Figure 2.16b shows diffusion of Ti in V. At the limit of Ti weight fraction towards 1, the self-diffusion coefficient of V becomes the impurity diffusion coefficient of V in Ti and the diffusion coefficient of Ti in V becomes the self-diffusion coefficient of Ti [42].

![Arrhenius plot of the self diffusion coefficient of V with values from experiments (dots) and modelling analysis by CALPHAD method (line) [42].](image)

**Figure 2.15** Arrhenius plot of the self diffusion coefficient of V with values from experiments (dots) and modelling analysis by CALPHAD method (line) [42].

![CALPHAD calculated (lines) and experimental (dots) diffusivities of V (a) and Ti (b) is V-Ti alloy for different Ti concentrations [42, 43].](image)

**Figure 2.16** CALPHAD calculated (lines) and experimental (dots) diffusivities of V (a) and Ti (b) is V-Ti alloy for different Ti concentrations [42, 43].
Regarding the effect of Cr on the diffusivities of Ti and V, the V-Ti-Cr has been modelled [26] and the diffusion coefficients of V, Cr and Ti are evaluated with the Einstein relation, having strongly assumed that the correlation effects are negligible. The results of the model are in good agreement with available literature data. Fig. 2.17 and 2.18 are calculations based on that model showing how Ti and V diffusivities rise with the amount of Ti, as reported before [42, 43]. The addiction of Cr decreases the diffusivities of all elements (Fig. 2.19). Fig. 2.20 shows the average of the diffusional range of V, Ti and Cr after 2 h at 1200 °C, Ti is the most mobile element followed by V and Cr.

Figure 2.17 Calculations from [26] of the diffusion coefficients of V in a V-Cr-Ti alloy for different temperatures
2. Description of vanadium as first wall reactor material

Figure 2.18 Calculations from [26] of the diffusion coefficients of Ti in a V-Cr-Ti alloy for different temperatures.

Figure 2.19 Calculations from [26] of the diffusion coefficients of Cr in a V-Cr-Ti alloy for different temperatures.
2. Description of vanadium as first wall reactor material

2.2.4 Physical properties

Some physical properties of V-4Cr-4Ti are collected in Table 2.5 [44]. The melting point is well above the expected reactor operating conditions of about 800°C (Par. 1.2). The thermal expansion and conductivity are key parameters to consider during the design of the blanket reactor in order to avoid excessive changes in dimensions of the blanket with temperature, and also to maximise the heat transfer to the coolant. The thermal conductivity of the V alloy is meant to be good as higher than that of EUROFER, main candidate material for DEMO, which is about 30 W/mK between 400-800°C [45]. Also the linear thermal expansion is better than in EUROFER since it is shorter, values for this latter alloy are 11.9 and 12.5 \(10^{-6}\) K at 400 and 600°C respectively [46].
One other important property of V is its magnetic susceptibility $\chi$ of $34.1 \cdot 10^{-6}$ [47] at standard conditions which relates the magnetization of a metal ($M$) with the applied magnetic field ($H$) according to the equation: $M = \chi H$. The sign of $\chi$ is positive as the unpaired electrons align the spin accordingly to $H$. The magnetization of V is limited defining it as a paramagnetic metal that will not be affected relevantly by the magnetic fields applied to confine the plasma in the fusion nuclear reactor.

### 2.3 Microstructure

#### 2.3.1 Recovery, recrystallization, grain growth

The evolution of the deformed microstructure of V-4Cr-4Ti during annealing in the temperature range from RT to 1100°C is shown in Figure 2.21. The V-4Cr-4Ti microstructure is recovered below 800°C, and full recrystallization occurs in 1h at around 1000°C. At 1100°C significant grain growth can be observed [48]. As revealed by the results of the differential scanning calorimetry (DSC) (Fig. 2.22), recrystallization starts at around 900°C, and before that recovery of the deformed microstructure takes place. Significant grain growth has been reported at 1100°C, although Heo et al. showed that this phenomenon is dependent on the level of interstitials in the structure (Fig. 2.23). Results for pure V are
similar to those of the alloy, but shifted down in temperature by approximately 200°C (Fig. 2.24) [49, 50]. The presence of a fine dispersion of precipitates (Par. 2.3.2) in alloyed V would retard recrystallization and grain growth by Zener pinning mechanism.

![Microstructure evolution during annealing after cold rolling. The annealing was carried out for an hour at the selected temperature [51].](image1)

**Figure 2.21** Microstructure evolution during annealing after cold rolling. The annealing was carried out for an hour at the selected temperature [51].

![DSC thermogram for V-4Cr-4Ti obtained at a heating rate of 20 °C/min [49].](image2)

**Figure 2.22** DSC thermogram for V-4Cr-4Ti obtained at a heating rate of 20 °C/min [49].
2. Description of vanadium as first wall reactor material

It is worth noticing that Nagasaka et al. did not find any relevant effect of O and N on the grain growth of pure V [49]. Similarly to the previous review of Harrod and Gold [50], Nagasaka et al. found that the recrystallization starts around 700°C (Fig. 2.24).

Figure 2.23 Changes of grain size from 900 to 1100°C in three V-4Cr-4Ti alloys varying in oxygen content [51].

Figure 2.24 Recovery, recrystallization, and grain-growth behaviour in pure vanadium [50].
2.3.2 Nanoscale precipitation

The microstructure of the V-4Cr-4Ti alloy is characterized by precipitates of Ti with interstitials (O, N, C) in the bcc matrix, see Fig. 2.25 and 2.26. In the production of the V-4Cr-4Ti alloy (NIFS-Heat-1), three types of precipitates were found [51-54]:

(a) Blocky Ti-rich precipitates containing N, O and C, which are formed from the early stage of fabrication (hot forging at 1150°C and hot rolling at 1100°C). These precipitates are stable up to 1100°C (blocky precipitates).

(b) Thin Ti(O,C,N) precipitates which form during annealing above 700°C and dissolve at 1000-1100°C (thin precipitates).

(c) V–C precipitates which form at grain boundaries at 1100°C (GB precipitates) as a consequence of the release of C from the dissolution of the thin Ti(O,C,N) precipitates.

Figure 2.25 Precipitate formation and distribution during the fabrication process of the V-4Cr-4Ti alloy (NIFS-Heat-1) [53].
The presence of Ti precipitates should not be surprising if we consider the relatively high free Gibbs energy formation of Ti oxide (Tab. 2.4). Moreover V and Ti have a substantial difference in the crystal structure that would make the mixing harder, indeed theoretical investigation showed that Ti-V alloys exhibit a clear tendency towards phase separation [55]. The precipitate distribution can be tailored by solution annealing (SA) at 1100°C followed by a second annealing at lower temperatures for re-precipitation, see Fig. 2.18 [21]. A high density of precipitates was present at 700°C. The density of precipitates decreased with increasing temperature. The majority of the precipitates were again dissolved at 1000°C and they do not appear in the microstructure at higher temperatures. A significant hardening effect occurred already at 600°C. This effect was related to the presence of submicroscopic precipitates [21, 56]. The hardening at 600°C continued to increase with the annealing time (Fig. 2.28a). According to Muroga et al. [57], re-heating at 600°C for 20 h after precipitate dissolution is the best thermal treatment to improve the mechanical properties of this alloy, because the density of fine precipitate is the highest. Analogous hardening has not been found with prolonged annealing at 750°C. At this temperature a coarsening of the initial precipitates was observed (Fig. 2.29) simultaneously with a reduction in hardening (Fig. 2.28b) [57]. A heat treatment which maximizes the Ti-rich precipitates is considered to be effective in order to obtain good impact properties, because the interstitial atoms (C, O, N) in the matrix are bound by titanium atoms to form nano-precipitates.

**Figure 2.26** TEM images of the V-4Cr-4Ti alloy (NIFS-Heat-1) annealed at 1000 and 1100°C. Two kinds of precipitates were observed at 1000°C. Only larger precipitates were observed at 1100°C [51].
Figure 2.27 Microstructure evolution of V-4Cr-4Ti (NIFS-HEAT-2) as a function of the annealing temperature, after an initial solubilisation treatment at 1100°C for 1 h [21].
2. Description of vanadium as first wall reactor material

Figure 2.28 Vickers hardness as a function of annealing time at (a) 600°C and (b) 750°C, after precipitate dissolution at 1100°C for 1 h [57].

Figure 2.29 TEM images of the microstructure after solubilisation and subsequent annealing at 750°C for different periods of time [57].

In the temperature range of 700-900°C, Ti-enriched plate-like precipitates form with {100} habit planes lying along the V {001} habit planes (Fig. 2.20) [58]. The Ti(C,N,O) precipitates adopt a NaCl-type crystal structure with a lattice constant at RT of 0.418nm [59, 60]. The precipitate formation seems to be controlled mainly by the oxygen concentration in the matrix. However, at long annealing times precipitation could not arise only from the oxygen atoms already present in the alloy before annealing. There may be an additional contribution
coming from those oxygen atoms coming from atmosphere even if we are operating at reduced pressures or inert atmospheres [61, 62]. The possibility of external oxygen contamination has been previously studied, and results show that additional oxygen atoms are absorbed in the specimen surface (500 nm). This increased the oxygen concentration to about 100 wppm in 2 h, and enhanced the precipitation [62].

2.4 Mechanical properties

2.4.1 Toughness

Fracture toughness is very important property, since in a future fusion reactor the ductile-to-brittle transition temperature (DBTT) is required to remain below the operational temperatures of the reactor. Fig. 2.30 shows the Charpy test results of V-4Cr-4Ti after different annealing treatments which led to the different degrees of precipitation discussed in section 2.3.2. The DBTT rises with the annealing temperature above 1000°C, due to the dissolution of Ti(C,N,O) precipitates [56]. The changes in the DBTT with the amount of O, C, N and H present in the matrix are shown in Fig. 2.22. The release of interstitial atoms to the matrix at those high temperatures exerts a pinning effect on the gliding of dislocations. If the movement of dislocations is impeded, less plastic deformation (and so less absorbed energy) will occur before the induced crack propagates all through the sample fracturing it.

![Charpy test results of V-4Cr-4Ti (NIFS-HEAT-2) annealed at different temperatures for 1 h](image)

**Figure 2.30** Charpy test results of V-4Cr-4Ti (NIFS-HEAT-2) annealed at different temperatures for 1 h [56].
K. Sakai et al. found that DBTT of V–4Cr–4Ti and V–7Cr–4Ti alloys was around -190°C [63] (see Fig. 2.32), while for the alloys containing 10 wt% Cr the DBTT raised to -30°C. Further increase in chromium content shifts the DBTT above room temperature. It is possible to increase Cr concentrations as high as 7wt% in V–xCr–4Ti alloys without degrading the impact properties, but this would cause excessive irradiation hardening [63].
2.4.2 Strength

*Pure vanadium*

The stress-strain curves of ‘pure vanadium’ as a function of temperature are shown in Fig. 2.33, while the yield strength (σ_y) and ultimate tensile strength (UTS) are displayed in Fig. 2.34. The stress-strain behaviour of vanadium is similar to that of other bcc metals. The behaviour is characterized by a strong temperature dependence of the yield and tensile strength with maxima at around 400°C [50].

![Stress-strain curves of pure vanadium as function of temperature](image1)

**Figure 2.33** Stress-strain curves of pure vanadium as function of temperature [50].

![Yield strength and ultimate tensile strength of various grades of commercial pure vanadium](image2)

**Figure 2.34** (a) Yield strength and (b) ultimate tensile strength of various grades of commercial pure vanadium as a function of temperature [50].
Effect of substitutional atoms

Fig. 2.35 shows the variation of the UTS with temperature for different chromium contents. Cr clearly increases the high-temperature strength of the material. Additionally, Cr is also added to increase the creep resistance of the alloy [10]. Ti in turn increases significantly the swelling resistance of the alloy (Par. 2.5.1), and also improves creep strength up to about 3wt.%. However, further Ti additions reduce the creep strength of this alloy [10]. Further details are presented in paragraph 2.4.3 regard the effect of substitutional atoms on the creep properties.

![Figure 2.35](image)

**Figure 2.35** Temperature dependence of ultimate tensile strength for V-xCr-(4-5)Ti alloys with increasing chromium contents [64].

Effect of interstitials atoms

The mechanical properties of V-4Cr-4Ti depend on the concentration of interstitial atoms such as O, N, and C. These elements provide additional solution hardening to the matrix (section 2.3.2). The effect of those elements on the mechanical properties can be observed in Fig. 2.36. This figure shows the results of the tensile tests of the NIFS-Heat1 V-4Cr-4Ti alloy (56 C, 181 O, 103 N wppm), together with previous data on similar samples, at different temperatures [65]. The authors noticed a slight deviation of the NIFS-Heat1 results from the group average: the UTS was lower and the UE higher. This is probably due to a significant reduction of the concentration of interstitials in the matrix.
2. Description of vanadium as first wall reactor material

Figure 2.36 Temperature dependence of ultimate tensile strength and uniform elongation for the NIFS-Heat1 alloys annealed at 950 and 1000 °C, together with previous data on similar alloys [65].

Figure 2.37 shows the recovery curves for pure V for different amounts of N and O in the matrix [49]. An increase in N and O content causes a clear shift of the hardness vs annealing temperature curve to higher values, but the behaviour observed as a function of temperature remains unaltered.

![Graph showing hardness vs. annealing temperature for vanadium alloys with different concentrations of N and O.](image)

<table>
<thead>
<tr>
<th>Code</th>
<th>N</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td>V-EB-1</td>
<td>12</td>
<td>290</td>
</tr>
<tr>
<td>V-LI</td>
<td>91</td>
<td>43</td>
</tr>
<tr>
<td>V-N-3</td>
<td>540</td>
<td>56</td>
</tr>
<tr>
<td>V-O-3</td>
<td>140</td>
<td>920</td>
</tr>
</tbody>
</table>

Figure 2.37 Variation in hardness of vanadium with temperature at different concentrations of N and O in wppm [49].
Wrapping vanadium and its alloys in Zr foils for annealing treatments has proved to be an efficient technique to remove interstitials from the vanadium surface and prevent O pick-up from the furnace atmosphere [66]. Fig. 2.38a shows the changes in grain size, resistivity ratio and hardness for different annealing temperatures in the case of samples with and without Zr wrapping. The evolution of the concentration of C, N and O is shown in Fig. 2.38b. The samples wrapped in Zr foils present lower concentration of O, N, and C and an enhanced grain growth at temperatures higher than 1000°C.

**Figure 2.38** (a) Effect of wrapping vanadium samples in Zr foil on the resultant of vanadium at different temperatures, (b) Effect of annealing temperature on the concentration of carbon, nitrogen and oxygen. The annealing time was 1 h [66].
2.4.3 Thermal creep

Thermal creep is defined as the time-dependent plasticity that occurs in materials under a constant stress at elevated temperatures [67]. Figure 2.39 gives an example of the general variation of the material’s elongation with time during a creep test. Three different stages can be observed:

I. **Primary creep.** The creep-rate is relatively high, but decreases with increasing time due to work hardening effects in the material.

II. **Secondary creep.** The creep-rate has reached a constant value that is maintained over a relatively long time. This zone is also called steady-state region and, it is due to a balance between work hardening and annealing of lattice defects.

III. **Tertiary creep.** This is the last stage before the rupture of the material. The creep-rate exponentially increases with stress as a consequence of the necking of the sample.

![Illustrative example of the variation of the elongation (ε) of a material with time (t) during a thermal creep experiment. The three different stages during creep are indicated in the figure, together with the geometrical explanation of the creep-rate at the steady-state (\(\dot{\varepsilon}_{ss}\)) [67].](image)

In a first approximation during secondary creep, the creep-rate in the steady-state (\(\dot{\varepsilon}_{ss}\)) as a function of the applied stress (\(\sigma\)) can be described using the following equation [67]:

\[
\dot{\varepsilon}_{ss} = A \cdot e^{-Q_e/kT} \cdot \sigma^n
\]  

(4)
A is a constant, $Q_c$ the activation energy of the creep process, $k$ the Boltzmann’s constant and $n$ the creep exponent.

The value of $n$ is indicative of the creep mechanism. Some examples are given below:

- $n = 5$ (but could range between 4 and 7): dislocation climb (or creep). The metal is plastically deformed by climbing of dislocations. The activation energy $Q_c$ of the creep process has often been found to be similar to that of self-diffusion.
- $n = 3$: dislocation (or viscous) glide. The metal is plastically deformed by movement of dislocations that occurs by two competing mechanism: climb and glide. This latter is slower and thus it is rate controlling.
- $n = 2$: superplasticity. The metal is plastically deformed mainly as a result of the weakening of the grain boundaries. The grains would slide each other in a mechanism called grain boundary sliding (GBS).
- $n = 1$: diffusion creep. The metal is plastically deformed via the diffusion of vacancies to the grain boundaries through the grains (Nabarro-Herring creep) or, at lower temperatures, along the grain boundaries (Coble creep).

Each mechanism occurs in a specific range of pressure and temperature. Beyond these experimental limits, eq. (4) is not more able to predict the creep-rates and when power-law-breakdown (PLB) occurs [67]. It is not uncommon that several mechanisms occur simultaneously, in that case it is possible to determine the predominant mechanism.

In the case of the V-4Cr-4Ti alloy, it has been reported that the predominant creep mechanisms are dislocation glide and climb, in the range between 100 and 300 MPa and at around 700 °C [40, 68]. Zheng et al. carried out creep tests at 700 and 750°C (Fig. 2.40) for several NIFS-Heat-2 plates treated following different thermo-mechanical routes (Table 2.6). For STD, they found that the creep mechanism below 180 MPa is dislocation climb because the estimated activation energy, $Q_c$, takes a value of 243 kJ/mol, consistent with the self-diffusion activation energy of vanadium (about 270 kJ/mol at 700-800°C) [50]. Above 180 MPa, dislocation glide is considered to operate since $Q_c$ becomes much higher: 360-580 kJ/mol for $\sigma = 220-240$ MPa [15]. A similar behaviour has been found for the SAACW sample and so its creep mechanisms are considered the same as STD. However, the creep mechanism of SACWA does not change to dislocation glide.
Table 2.6 Description of several thermo-mechanical treatments [15].

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Treatment</th>
<th>Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>STD</td>
<td>Standard</td>
<td>1000°C for 2 h</td>
</tr>
<tr>
<td>SAA</td>
<td>Solution Annealed and Aged</td>
<td>1100°C for 1 h + 600°C for 20 h</td>
</tr>
<tr>
<td>SAACW</td>
<td>Solution Annealed, Aged and Cold-Worked</td>
<td>SAA + 20% cold-working</td>
</tr>
<tr>
<td>SACWA</td>
<td>Solution Annealed, Cold-Worked and Aged</td>
<td>1100°C for 1 h + 20% cold-working + 600°C for 20 h</td>
</tr>
</tbody>
</table>

The average grain size of the alloy in SAA and STD states was about 28 μm and 18 μm, respectively.

Figure 2.40 Steady-state creep rate dependence on the applied stress at (a) 700°C and (b) at 750°C [15].

Figure 2.41 shows the results of uniaxial and biaxial creep tests for the V–4Cr–4Ti (US 832665) and V–3Fe–4Ti alloys [11]. A uniaxial test is the classical creep experiment where the stress acts in one direction. In biaxial tests the sample geometry is cylindrical and inside it a liquid or a gas under pressure is placed. That liquid/gas will exert a force against the inner walls of the tube causing its creep deformation. The advantage of biaxial tests is the possibility to simulate the expected conditions of pressure and temperature inside the pipes of a blanket cooling system in the fusion reactor. The resultant creep activation energy $Q_c$ was 299 kJ/mol, close to the self-diffusion activation energy of vanadium. These results confirm that the predominant creep mechanism in V–4Cr–4Ti at 700-800°C is dislocation glide for effective stresses ranging from 50 to 120 MPa.
2. Description of vanadium as first wall reactor material

Interstitial atoms in the lattice can increase the activation energy $Q_e$ after interactions with vacancies. Creep experiments at 100 and 150 MPa have been performed for the (NIFS-Heat-2) V–4Cr–4Ti alloy, which has a lower amount of interstitials than the (US 832665) V–4Cr–4Ti alloy, and the activation energy resulted to be 210 kJ/mol. This reduction in activation energy may be due to the lower amount of interstitials atoms in the matrix, which increase the potential barrier for the vacancy diffusion since interstitials act as a trapping site for vacancies, leading in V–Cr–Ti alloys to the formation of vacancy complexes between the Ti and the interstitial atom which could act as an obstacle for the dislocation motion [14].

Kurtz et al. [11] pointed out that at low pressures the creep mechanism could be different from dislocation creep. For the lowest stress specimens tested at 800°C the occurrence of other mechanisms such as Coble creep in conjunction with dislocation creep, cannot be excluded due to the relatively fine grain size (≈20 μm) and, especially, due to the decrease of the creep exponent to a value close to 1. Proof of a diffusional creep mechanism was provided by Gelles et al. [68]. They found that precipitate particles appeared to accumulate mainly on the grain boundaries oriented perpendicularly to the stress direction (Fig. 2.42).

![Figure 2.41 Stress dependence of the normalized effective mid-wall creep strain for unirradiated V–4Cr–4Ti and V–3Fe–4Ti, $D$ is the diffusion coefficient, $G$ the shear modulus and $b$ the burgers vector [11].](image)
Indeed, in diffusion creep, the grain boundaries oriented perpendicularly to the stress direction are those with the higher vacancies concentration, and so with the higher probability of precipitation due to the formation of Ti-vacancy complexes precursors of Ti precipitates [69].

![Figure 2.42 Precipitation at grain boundaries in the specimen tested by Gelles et al. [68].](image)

Returning to the results in Fig. 2.40, the (steady-state) creep rates ranged between $10^{-9}$ and $10^{-6}$ s$^{-1}$. These results are in accordance with the theoretical creep map proposed by Zinkle and Lucas [70]. Using the established constitutive equations of Sherby and Miller [71] of several creep mechanisms, the authors calculated the deformation map for V–4Cr–4Ti (Fig. 2.43) at two different strain rates. They assumed a grain size of 30μm, close to the typical values (18-35μm) reported in several experimental studies. The diffusion creep mechanism (Nabarro-Herring and Coble) is almost present only in the deformation map at $10^{-8}$ s$^{-1}$ since the motion of vacancies cannot drive creep at higher strain rates. Together with dislocation creep, it has a significant contribution and more experiments are suggested to define the border between the occurrences of these different creep mechanisms. Glide range does not change increasing the strain rate dislocation, but the start dislocation creep shifts at higher temperatures. If the strain rate increases, dislocation creep is sustained only if dislocations can move faster and a higher temperature is so required.
2. Description of vanadium as first wall reactor material

The effect of the alloying elements is now addressed. Figure 2.44 shows for V-Ti alloys a creep resistance peak at around 3 wt% of Ti, further addition becomes deleterious for the creep resistance. The substitutional hardening effect of Ti is overpassed by the effect of Ti over the recovery of V during creep [50] that would occur earlier due to the lowering of the melting point (Par. 2.2.2). Creep rate increases with the addition of Cr even up to 15 wt% as shown in Figure 2.45.

Figure 2.43 Predicted deformation maps for V-4Cr-4Ti at a strain rate of (a) $10^{-8}$ and (b) $10^{-4}$ s$^{-1}$ [70].

Figure 2.44 Creep exponent n dependence with Ti concentration in V [50].

Figure 2.45 Creep rates in V-Cr-Ti alloys [50].
2.5 Irradiation effects

2.5.1 Material activation

Another advantageous property of vanadium alloys for application as first-wall materials is the low activation probability when in contact with 14 MeV neutrons. Unfortunately, the low activation properties of the material are modified by the level of interstitial atoms. In Figure 2.46a the dose rate as a function of the time for the three V-4Cr-4Ti grades is shown, together with the theoretical curve for the ideal pure vanadium material. The contribution of each potential element present in the vanadium microstructure is reported in Fig. 2.46b. Co-60 provides the most dominant contribution for cooling times up to 60 years [72].

![Figure 2.46](image) (a) Dose rate as a function of cooling time for V-alloys and (b) contributions of different nuclides to the dose rate of the NIFS-HEAT-2 alloy [72].

New development efforts are required to reduce the level of active species in the matrix during the material production. Table 2.7 shows the maximum amounts allowed for two recycling mechanisms: the remote and the hands-on mechanism. In the first case, the operator can handle radioactive materials only through remote devices such as robotic arms, while in the last case the operator, with appropriate clothing protection, can handle the radioactive materials directly.
2. Description of vanadium as first wall reactor material

Table 2.7 Required impurity level (wppm) for recycling the first wall materials [72].

<table>
<thead>
<tr>
<th>Cooling time (yr)</th>
<th>Recycling mechanism</th>
<th>Co</th>
<th>Nb</th>
<th>Ag</th>
<th>Mo</th>
<th>Al</th>
<th>Ni</th>
<th>Fe</th>
<th>Ta</th>
<th>Si</th>
<th>Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>Remote</td>
<td>0.4</td>
<td>74</td>
<td>11</td>
<td>7.9E3</td>
<td>2.7E4</td>
<td>21</td>
<td>2.1E4</td>
<td>5.9E4</td>
<td>1.4E5</td>
<td>38</td>
</tr>
<tr>
<td></td>
<td>Hands-on</td>
<td>3.8E–4</td>
<td>0.07</td>
<td>0.01</td>
<td>7.8</td>
<td>27</td>
<td>0.02</td>
<td>21</td>
<td>58</td>
<td>140</td>
<td>0.04</td>
</tr>
<tr>
<td>50</td>
<td>Remote</td>
<td>0.01</td>
<td>74</td>
<td>12</td>
<td>8.5E3</td>
<td>3.6E4</td>
<td>570</td>
<td>1.3E5</td>
<td>1.3E5</td>
<td>1.3E5</td>
<td>1000</td>
</tr>
<tr>
<td></td>
<td>Hands-on</td>
<td>0.07</td>
<td>0.07</td>
<td>0.01</td>
<td>8.4</td>
<td>35</td>
<td>0.56</td>
<td>120</td>
<td>120</td>
<td>120</td>
<td>1</td>
</tr>
<tr>
<td>100</td>
<td>Remote</td>
<td>7.4E3</td>
<td>75</td>
<td>13</td>
<td>8.6E3</td>
<td>3.8E4</td>
<td>1.7E5</td>
<td>1.7E5</td>
<td>1.7E5</td>
<td>1.7E5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Hands-on</td>
<td>7.3</td>
<td>0.07</td>
<td>0.01</td>
<td>8.6</td>
<td>38</td>
<td>170</td>
<td>170</td>
<td>170</td>
<td>170</td>
<td></td>
</tr>
</tbody>
</table>

2.5.2 Irradiation hardening and embrittlement

Radiation induced precipitation

Radiation induced hardening and embrittlement occur at relatively low temperatures and in the case of vanadium alloys, there is a threshold temperature around 400°C, below which significant radiation hardening has been observed even at a radiation level of 0.1-0.5 dpa [69]. This effect may be attributed to the presence of high densities of fine defect clusters and fine Ti precipitates containing interstitials (C, O and N) after irradiation [59, 73]. Radiation induces so a phase transition (Par. 1.3) that in this case regards Ti(O, C, N) precipitation. The reduction of the interstitials is expected to improve the radiation resistance of the alloys at low temperatures [20]. The harmful effect of the impurities has been confirmed by Fukumoto et al. [74]. Fig. 2.26 shows that irradiation hardening decrease in V-4Cr-4Ti purified with a Zr-treatment [74].

Figure 2.47 shows the change of selected mechanical properties after irradiation. It is worth noting that irradiation hardening in pure vanadium does not change significantly when the metal is alloyed with 5 wt.% of Ti or Cr. However, if a slight amount of Ti is added to the V-5Cr alloy, the irradiation hardening suddenly increases. In the V-4Cr-0.1Ti and V-4Cr-0.3Ti alloys, high densities of tiny voids (5nm) were formed homogeneously in the irradiated microstructure while for V-5Cr alloy, a high density of voids (10nm) was formed under the same irradiation conditions. However, those 10nm voids were inhomogeneously distributed around the dislocations. Titanium is an oversized atom for the vanadium matrix, and disturbs the vacancy diffusion in the matrix and therefore hinders the growth of voids. Indeed, Ti has been reported to prevent irradiation swelling in vanadium alloys [75]. The main source of irradiation hardening is considered to be void formation in V-4Cr-0.1Ti and V-4Cr-0.3Ti, and Ti(O, C, N) precipitates induced by irradiation in V-4Cr-1Ti and V-4Cr-4Ti [73]. The
precipitates present a TiO type structure with a lattice parameter of 4.18Å at RT [59, 60]. The crystallographic relationship between the precipitates and the vanadium matrix was determined to be (110)precipitate// (100)matrix and <011> precipitate // <011> matrix [74]. Irradiation is so anticipating the Ti (O, C, N) precipitation that would occur from 600°C (Par. 2.3.2). This phase transformation is facilitated also by the enhanced Ti diffusion during irradiation. As Ti is oversized atom, the activation energy for a vacancy to diffuse by exchange with a Ti atom will be lower than that by exchange with a V atom. Both V and Ti, are substitutional atoms and require the coordination with a vacancy to diffuse; those generated by irradiation will preferentially interact with Ti atoms, improving its diffusion rates [75].

Figure 2.48 shows the microstructural differences between two pure vanadium specimens with different concentration of interstitials after irradiation to 1dpa. Interstitials affect the microstructural evolution of pure V after irradiation at 400°C: the void nucleation that is more predominant in the most purified samples since vacancies can move easier [20]. For alloyed V, Zr-treated V-4Cr-4Ti alloys have significantly reduced irradiation hardening at 425°C (Fig. 2.47). However, no voids and differences in microstructure, dominated by dislocation loops and Ti(O, C, N) precipitates, were observed between the untreated Zr-treated specimens, see Fig. 2.49 and Fig. 2.50.

Figure 2.47 Changes of yield stress (Δσ_y), ultimate tensile stress (Δσ_UTS), and uniform elongation (ε_u) by neutron irradiation up to 3.7 dpa for pure vanadium and selected alloys [74].
2. Description of vanadium as first wall reactor material

**Figure 2.48** TEM micrographs of pure vanadium irradiated with 4MeV Cu to a damage level of 1 dpa. The two upper images correspond to as-received vanadium containing 170 wppm O, while the bottom images are from Zr-treated highly purified vanadium containing 15 wppm O [20].

**Figure 2.49** Examples of TEM microstructures of untreated and Zr-treated V-4Cr-4Ti alloys irradiated at 425 °C and 598 °C in HFIR. B = [001], g = (110) [74] at 3.7 dpa.
2. Description of vanadium as first wall reactor material

Fukumoto et al. [74] suggested that the reduction of irradiation hardening in the V-4Cr-4Ti alloys is due to the fact that almost all the interstitials atoms have formed precipitates leaving the matrix free from them. In not Zr-treated specimen, interstitial atoms are still present in the matrix even after the precipitation. The amount of interstitial atoms in the matrix seems to play an important role as barrier against dislocation motion favouring irradiation hardening. The pinning effect of the interstitials (Par. 2.4.1) prevents dislocation loops to annihilate at the defect sinks.

About the nucleation of precipitates induced by irradiation, PAS measurements [69] detected voids rich of Ti for samples irradiated below 300°C. It is believed that O and other interstitials may reach these voids, invisible to TEM, forming an atmosphere that reacts with the Ti leading the precipitate nuclei.

**He bubble formation**

He is insoluble in metals and tends to form bubbles in the microstructure. This causes swelling and degradation of the mechanical properties of the material. The amount of He and H in V-4Cr-4Ti are of 855 and 4050 appm respectively at 15 MWy/m² [76]. The parameters characterizing the formation of helium bubbles and swelling by implanting of helium ions in vanadium alloys at 650°C are collected in Table 2.8.

Doping with titanium (from 0.1 to 10%) considerably decreases helium swelling as compared to pure vanadium. Ti has no significant effect on the density of the bubbles by decreasing the
average size of the bubbles [77]. Fe is an undersized substitutional atom in the V matrix and so it acts as a sink for interstitial helium atoms preventing their diffusion. This is most likely why the addition of 1wt.% Fe prevented the growth of the He bubbles and the corresponding swelling. However, when the iron concentration is increased the bubble size and the swelling started to grow continuously. In conclusion, the minimum bubble size and swelling are observed in the alloy with the maximum content of titanium (V-10Ti) and also in the reference V-4Cr-4Ti alloy.

Table 2.8 Parameters characterizing the formation of helium bubbles in vanadium and its alloys (\(d_{\text{max}}\), \(d_{\text{av}}\), \(d_{\text{m.l}}\) – maximum, average, and most likely bubble size, respectively; density (\(\rho\)) and swelling (\(S\%\)) [69].

<table>
<thead>
<tr>
<th>Material</th>
<th>(d_{\text{max}}) mm</th>
<th>(d_{\text{av}}) mm</th>
<th>(d_{\text{m.l}}) mm</th>
<th>(\rho), (10^4) m(^{-3})</th>
<th>(S%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>V</td>
<td>-22</td>
<td>16/8.6(^*)</td>
<td>17</td>
<td>1.4 ± 0.4/0.017 ± 0.004(^*)</td>
<td>4.5 ± 1.1</td>
</tr>
<tr>
<td>V-0.1%Ti</td>
<td>3.6</td>
<td>1.9</td>
<td>0.7</td>
<td>0.9 ± 0.2</td>
<td>0.5 ± 0.2</td>
</tr>
<tr>
<td>V-0.3%Ti</td>
<td>3.2</td>
<td>1.7</td>
<td>2.0</td>
<td>1.3 ± 0.3</td>
<td>1.1 ± 0.3</td>
</tr>
<tr>
<td>V-0.5%Ti</td>
<td>2.4</td>
<td>1.5</td>
<td>1.7</td>
<td>1.7 ± 0.4</td>
<td>0.4 ± 0.1</td>
</tr>
<tr>
<td>V-0.7%Ti</td>
<td>6.5</td>
<td>3.7</td>
<td>1.8</td>
<td>1.8 ± 0.5</td>
<td>0.7 ± 0.2</td>
</tr>
<tr>
<td>V-1%Ti</td>
<td>-3</td>
<td>2.0</td>
<td>1.5</td>
<td>1.5 ± 0.4</td>
<td>0.4 ± 0.1</td>
</tr>
<tr>
<td>V-5%Ti</td>
<td>3.6</td>
<td>1.6</td>
<td>0.8</td>
<td>1.4 ± 0.3</td>
<td>0.5 ± 0.2</td>
</tr>
<tr>
<td>V-10%Ti</td>
<td>-2</td>
<td>-1</td>
<td>0.8</td>
<td>3.3 ± 0.8</td>
<td>0.32 ± 0.08</td>
</tr>
<tr>
<td>V-4%Ti-4%Cr</td>
<td>-2</td>
<td>-1</td>
<td>0.8</td>
<td>3.6 ± 0.9</td>
<td>0.21 ± 0.05</td>
</tr>
<tr>
<td>V-1%Fe</td>
<td>-2</td>
<td>1.3</td>
<td>2.4</td>
<td>2.4 ± 0.6</td>
<td>0.3 ± 0.1</td>
</tr>
<tr>
<td>V-5%Fe</td>
<td>2.6</td>
<td>1.6</td>
<td>-2.5</td>
<td>2.9 ± 0.7</td>
<td>0.6 ± 0.2</td>
</tr>
<tr>
<td>V-10%Fe</td>
<td>7.3</td>
<td>1.7</td>
<td>3.6</td>
<td>2.9 ± 0.7</td>
<td>0.8 ± 0.2</td>
</tr>
</tbody>
</table>

\(^*\) Taking account of and neglecting the smallest bubbles.

The effect of the He bubble formation on the mechanical properties of vanadium alloys is not fully understood. According to Chen et al. [17] helium embrittlement is critical to determine the upper temperature limit of vanadium alloys. According to Kurtz et al. [78], He ion implantation plays a significant role in the reduction of the ductility at elevated temperatures. But with the subsequent neutron irradiation, the effect of He implantation seems to become insignificant. The implanted He seemed to have positive effect on creep property if small dispersive He clusters are formed in the matrix.
Swelling due to void formation

Pure vanadium presents a bcc crystal structure at RT and good swelling resistance. Experimental results on the swelling of vanadium and selected vanadium-based alloys are summarized in Fig. 2.51. Vanadium and vanadium alloys exhibit peak swelling at ~525 °C under fast neutron irradiation [79, 80]. Experiments have shown that titanium concentrations of only a few percent in the alloy greatly suppress swelling as compared to pure vanadium [79, 80]. High swelling resistance has been reported in a number of vanadium alloys. The estimated total dose for swelling of V-Cr-Ti alloys would be > 250 dpa [81]. It is worth to notice that swelling is almost totally suppressed even at very high dose in all the vanadium alloys with Ti. It happens that vacancies produced by irradiation are trapped by Ti which is oversized with respect to V. Strain-energy considerations predict indeed that vacancies will preferentially exchange with oversize solute atoms rather than agglomerate in voids [75].

Figure 2.51 Swelling of pure and alloyed vanadium caused by neutron and ion irradiation [81].
2.5.3 Irradiation creep

Creep can be induced by irradiation at temperatures where thermal creep is not significant. This would cause failure of blanket components even though creep is not expected to occur. At high temperatures radiation- and thermally-induced creep take place simultaneously [82]. Irradiation creep is therefore a critical issue to consider when selecting the structural materials for the blanket. Figure 2.52 shows experimental creep data for the V-4Cr-4Ti (US 832665) neutron irradiated in different reactors: HFIR 17J [83], ATR A1 [84, 85], HFIR 12J [86], and by Troyanov et al. [87]. Irradiation creep strain seemed to be proportional to the applied stress below 120MPa at irradiation temperatures of 400-600°C.

By subtracting the thermal creep strain from the total strain, we can derive the irradiation and the thermal contributions to the total strain. These contributions are plotted in Fig. 2.53 as a function of the applied stress for V–4Cr–4Ti irradiated at 600°C in the HFIR 17J test reactor [16]. The contribution coming from the irradiation creep is much higher than that of the thermal creep, which confirms that this was the main cause of the material deformation at that temperature. The activation energy for irradiation creep is considered to be significantly lower than the one corresponding to thermal creep [17].

![Figure 2.53](image_url) Irradiation creep data obtained for the V-4Cr-4Ti alloy irradiated with neutrons in different test reactors [16, 84-87].
2. Description of vanadium as first wall reactor material

Figure 2.53 Irradiation creep strain and thermal creep strain as a function of stress the V-4Cr-4Ti alloy irradiated to 3.7 dpa at 600°C. Thermal creep was predicted using a power-law dislocation model. Open circles represent the best estimate, while open triangles represent the upper bound estimate [16].

A more recent study of the creep of V–4Cr–4Ti alloy (NIFS-Heat-2) irradiated in the Japanese JOYO test reactor at 425–600°C to 1.8-5 dpa showed no difference with the previous US 832665 heat (see Fig. 2.54). Moreover, experiments where also carried in liquid Li and Na and no significant differences were observed between the two metallic liquids. The reason to perform creep experiments in liquid Li was to simulate the blanket conditions during operation [88].

Figure 2.54 Irradiation creep data of the V-4Cr-4Ti (US 832665) alloy, closed circles [16]; V-4Cr-4Ti (NIFS-Heat) alloy in liquid lithium, open circles [80]; V-4Cr-4Ti (NIFS-Heat) alloy in liquid sodium, closed triangles [88].
In order to study the contributions of thermal and irradiation creep to the overall creep process, several experiments have been performed with and without irradiation keeping the other experimental conditions constant (Table 2.9). In the range between 450 and 600°C irradiation creep strain was significantly larger than thermal creep, implying that it is the predominant creep during neutron irradiation at those temperatures.

Table 2.9 Results of creep tests with and without irradiation of V–4Cr–4Ti alloys in liquid sodium environment with same conditions of creep temperature, creep period and internal pressure [89].

<table>
<thead>
<tr>
<th>Creep experiment</th>
<th>Temperature (°C)</th>
<th>Creep period (h)</th>
<th>Internal pressure (MPa)</th>
<th>Effective creep strain εc (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Irradiation</td>
<td>419</td>
<td>2880</td>
<td>96</td>
<td>0.07</td>
</tr>
<tr>
<td>Thermal in Na</td>
<td>450</td>
<td>2800</td>
<td>100</td>
<td>0.02</td>
</tr>
<tr>
<td>Irradiation</td>
<td>419</td>
<td>2880</td>
<td>134</td>
<td>0.11</td>
</tr>
<tr>
<td>Thermal in Na</td>
<td>450</td>
<td>2800</td>
<td>150</td>
<td>0.06</td>
</tr>
<tr>
<td>Irradiation</td>
<td>560</td>
<td>2880</td>
<td>96</td>
<td>1.6</td>
</tr>
<tr>
<td>Thermal in Na</td>
<td>600</td>
<td>2800</td>
<td>100</td>
<td>0.03</td>
</tr>
<tr>
<td>Irradiation</td>
<td>560</td>
<td>2880</td>
<td>143</td>
<td>2.2</td>
</tr>
<tr>
<td>Thermal in Na</td>
<td>600</td>
<td>2800</td>
<td>150</td>
<td>0.13</td>
</tr>
</tbody>
</table>

Neutron dose and estimated damage level at 419 and 560 °C were respectively $2.4 \times 10^{25}$ n/m² (1.5 dpa) and $6.7 \times 10^{25}$ n/m² (4.2 dpa).

At temperatures below 500°C, the irradiation creep was found to be proportional to the square root of the damage level (Fig. 2.55) and to be linearly proportional to the stress level (Fig. 2.56). Above 500°C, the irradiation creep strain appeared to be proportional to the stress level but with a power exponent higher than the unity [89].

![Figure 2.55](image-url) A plot of the effective irradiation creep strain as a function of neutron dose for V–4Cr–4Ti alloys irradiated at 450°C [89].
2. Description of vanadium as first wall reactor material

2.6 Previous efforts to improve the mechanical properties in radiation environments

2.6.1 Tailored thermo-mechanical treatment

Several attempts have been carried out to improve the alloy resistance to thermal creep by thermo-mechanical treatments. A solution annealing plus aging (Table 2.6), SAA, seems to be the thermal treatment that provides the highest precipitation hardening [21]. Unfortunately the expected operating temperature in the fusion reactor may reach 800°C. At this temperature precipitate coarsening would occur leading to a degradation of the optimized precipitation distribution at 600°C. The precipitate coarsening may be reduced at higher temperatures through cold working after aging (SAACW, see Table 2.6). The dislocations produced by cold rolling would trap interstitial atoms and would prevent a significant precipitate coarsening during operation. Figure 2.48 shows the effect of cold working on the SAA sample during subsequent aging at 800°C. The dislocations introduced by cold work suppressed the precipitate coarsening during high-temperature aging [90]. The creep rates for different thermo-mechanical treatments have been reported in Fig. 2.40. SACWA showed the best creep resistance at the higher stresses. This sample kept dislocation climbing-assisted creep mechanism at larger stress levels than SAACW and STD. This may be due to the pinning of dislocations by the high density of fine precipitates formed along these latter [15]. At low stress levels (σ < 180 MPa), the dislocations act as vacancy sinks [91], enhancing the dislocation climb mechanism and leading for SACWA a higher creep rate than that of SAACW and STD [15].
2. Description of vanadium as first wall reactor material

Figure 2.57 The evolution of precipitate size and density with the aging time at 800°C for SAA specimens. The data in ellipses are for SAACW specimens after the creep deformations [90].

The fact that the dislocation in SACWA can be pinned by the precipitates seems confirmed from the comparison of the microstructure after and before 60h creep test at 176 MPa and 750°C (Fig. 2.58). The recovery of dislocation is not visible as in Fig. 2.59, which shows instead the microstructure evolution of a STD sample 20% cold worked, creep deformed under the same condition [92].

Regarding the characterization of the dislocation nature, it has been found that cold working induces in V-4Cr-4Ti alloys a mixture of \(a\)<100> and \(a/2<111>\) dislocation types after thermal aging. When a force is applied (creep deformation) the predominant type becomes \(a/2<111>\) [92]. Fig. 2.60 resumes the concentration of different dislocation types for several cold rolled samples while in Fig. 2.61 is provided an example of microstructure evidence from the SAACW sample. This latter has been heated at 750°C for 80h both with and without 176 MPa of applied pressure.
2. Description of vanadium as first wall reactor material

Figure 2.58 Comparison of microstructure of SA–CW–A (a) as-prepared and (b) after creep deformation at 750°C for 60 h at 176 MPa [92].

Figure 2.59 Recovery of dislocations induced by cold work during creep deformation at 750°C and 176 MPa for a STD specimen 20% cold rolled [92].
2. Description of vanadium as first wall reactor material

**Figure 2.60** Graph of the dislocation density listed by their type after aging (0 MPa) and creep test (≠0 MPa) at 750°C. Residual strain in cold worked specimen can make the dislocation analysis problematic leaving the dislocations unidentified [92].

**Figure 2.61** Microstructure of the SAACW specimen after thermal aging (0 MPa) and creep test (175 MPa) for 80h at 750°C. Using the \( g \cdot b = 0 \) invisibility criterion, the dislocations in the circles 1, 2 and 3 are attributable to the Burgers vectors \( b = \pm a[100] \), \( b = \pm a[010] \), and \( b = \pm a/2[11\pm1] \), respectively. The dislocation in circle 4, and most in the row below (creep-deformed sample), have instead Burgers vector \( b = \pm a/2[1-1\pm1] \) [92].
The a<100> type dislocation is formed by interactions of a/2<111> dislocations at different planes during cold work [90]. As sessile, the a<100> type dislocation is meant to be stable and contributes so to the suppression of precipitate coarsening. Unfortunately this dislocation type recovers leaving a/2<111> dislocations, which are glissile (capable to move by glide) and so more mobile. In order to maintain high temperature strength, it should be avoided conditions that led to the recovery of a<100> dislocations.

2.6.2 Removal of interstitials from the matrix

In order to reduce the occurrence of irradiation hardening, the amount of interstitial atoms must be as low as possible. Besides an appropriate forging to prevent impurities pick up in the heat, the amount of “free” interstitials atoms in the matrix can be reduced by precipitation during annealing [54]. Direct aging at 900°C for 1h seemed to be the best thermal treatment because the precipitation is maximised, as evidenced by the minimum in hardness (see Fig. 2.46). After irradiation, however, the hardness did not change significantly from 800 to 1000°C, implying that the levels of interstitials in solution was similar. This is probably due to the irradiation-induced dissolution of the thin precipitates [54].

![Vickers hardness as a function of the annealing temperature before and after irradiation.](image)

**Figure 2.62** Vickers hardness as a function of the annealing temperature before and after irradiation. Note that the applied load is indicated in the figure and is different in the two cases [54].

It is possible to further reduce the amount of O by introducing yttrium (Y) in the alloy [93]. The Y addition was effective to slag-out oxygen due to the formation of Y₂O₃. It also provided protection from oxygen contamination during melting [93]. Oxygen concentration in the alloys decreased linearly with increasing yttrium addition (Fig. 2.63).
2.6.3 Refined grain size microstructure with nanoparticles as strengtheners

Microstructures with a reduced grain size seem to behave better under irradiation. This is due to the high density of grain boundaries, which acts as a sink for irradiation induced defects [95]. V-Y alloys with a grain size of around 300nm have been obtained through powder metallurgical methods including mechanical alloying and hot isostatic pressing (sintering). Mechanical alloying (MA), if carried from high purity powders, is an effective method to obtain a material with a remarkable purity and reduced amount of interstitial in the matrix. The results from the sintered samples seem promising (Fig. 2.64): at 290°C and 0.25 dpa the irradiation hardening was almost non-existent. Figure 2.65 shows the absence of voids for the V–2.6Y alloy irradiated at 290°C to 0.25 dpa, suggesting that the defects have been absorbed at the grain boundaries. However, at 800°C there was an appreciable hardening effect. According to the authors, this hardening can be attributed to the precipitation induced by irradiation of Y₂O₃ and YN particles.

Figure 2.63 Dependence of oxygen concentration on the amount of Y added to the alloy [94].
2. Description of vanadium as first wall reactor material

Figure 2.64 Vickers microhardness before and after neutron irradiation in various conditions for V–1.6Y and V–2.6Y alloys,* the irradiation temperature ranged between 600°C and 800°C in 6 cycles [95].

Figure 2.65 TEM micrograph of the V–2.6Y irradiated at 563 K to 0.25 dpa [95].

The dispersion of Y nanoparticles strengthens also V-4Cr-4Ti alloys and becomes effective to improve also its mechanical properties at the higher temperatures [96]. It has been found that the high number density of Y₂O₃ nano-particles is effective to improve creep resistance of V–4Cr–4Ti–1.5Y–0.3TiC alloy under 100 MPa stopping the motion of dislocations as shown in Figure 2.66, overpassing the STD and SACWA samples [97]. Anyway at higher loads, due to the refined grain size, the creep resistance is the lowest [97].
Figure 2.66 Creep rates of 40 h MA V−4Cr−4Ti−1.5Y−0.3TiC alloy compared with those of different thermo-mechanical treated samples of V-4Cr-4Ti (table 2.2) [97].

TiC, SiC and Ti$_3$SiC$_2$ particles can be added together to Y to enhance the performance. Understand the stability and the coarsening of the added particles under thermal treatment is fundamental to predict the performance of sintered V-4Cr-4Ti components [96].
2. Description of vanadium as first wall reactor material

2.7 References

2. Description of vanadium as first wall reactor material


2. Description of vanadium as first wall reactor material


2. Description of vanadium as first wall reactor material


2. Description of vanadium as first wall reactor material


2. Description of vanadium as first wall reactor material


3. FEASIBILITY OF VANADIUM ALLOYS FOR FUSION REACTOR APPLICATIONS

In the first section, the feasibility of vanadium alloys in fusion energy is discussed in relation to the technical requirements: which ones are satisfied and which are the remaining issues. Comparisons with others candidate materials are also included. Section 3.2 describes the first trials of large production of V-4Cr-4Ti alloys, with a description of the two heats mainly reported in literature. Section 3.3 finally summarizes the remaining issues of V for fusion energy applications and where research needs to focus in the next years.

3.1 Comparisons of vanadium alloys with other fusion reactor materials

“The performance limits of the first-wall/blanket structure will be limited by both the inherent properties of the candidate structural materials and by factors imposed by the fusion system environment, such as the coolant/breeder system, the high-energy neutron environment and the magnetic field effects. Also the specific design configuration will affect the performance of the blanket [1]”

In order to consider fusion energy as a viable energy source, it needs to be economically competitive with other energy sources, and it must be public accepted as a safe and environmentally friendly energy source [1, 2]. The first wall/blanket system constitutes the key component that influences the economical performance and safety of the future fusion reactor. The development and testing of materials that can withstand the extreme conditions generated by the plasma without compromising the safety of the power plant is considered as one of the greatest materials science challenges in history [3]. Table 3.1 collects the suggested minimum requirements that a material must be able to withstand for a future fusion energy reactor, together with the performance goals of the reactor. These values are based on US estimates which were derived primarily for a tokamak configuration, but are assumed to be generic to magnetic confinement fusion devices [2, 4].

93
Several materials have been proposed for the DEMO blanket and the V-4Cr-4Ti alloy is amongst them due to their low absorption cross section for 14 MeV neutrons, high-temperature strength, good chemical compatibility with liquid lithium as coolant and good swelling resistance [5, 6, 7]. Other proposed candidate materials are the reduced activation ferritic-martensitic (RAFM) steels, oxide dispersion strengthened (ODS) steel variant of the EUROFER and SiC composites. These materials are characterized by different operating temperature windows:

1. RAFM steels are based on the experience with 8–12%Cr–MoVNb steels developed for fission reactor applications, where alloying elements such as Mo, Nb and Ni have been replaced with W and Ta to decrease the probability of producing radioactive nuclides. They are relative cheap (Tab. 3.2). They are also the best developed and characterized candidate materials up to date, and require the smallest extrapolation for use in DEMO. The test blanket modules (TBMs) to be installed and tested in ITER will be produced using RAFM steel [8]. However, their upper operational temperature limit is approximately 650°C [9].

2. ODS steels allow to increase the upper operational temperature limit up to about 750°C. This is achieved by introducing a nanoscale oxide dispersion of yttrium in the EUROFER alloy, which increases the high-temperature strength by acting as pinning points for dislocations [10–13]. These nano-particles also promote radiation resistance, since the large density of interfaces between the matrix and the oxide particles are expected to act as sinks for the irradiation-induced defects [14, 15]. However, the long-term stability of the nano-precipitates under irradiation is still an open question [16].

3. SiC composites have excellent high-temperature strength which provides an upper operational temperature of 1000-1100°C [2]. Unfortunately, these composites are brittle.
and the effect of irradiation damage on their microstructure hinders their application as blanket material.

(4) The upper operating limit of V-4Cr-4Ti is expected to be 750°C [1, 6]. Based on this fact, India and Russia have already developed two blanket projects for DEMO [17, 18]. The operating temperature window is relatively wide (400-750°C) at a neutron wall loading of 5±10 MW/m², and the power conversion efficiency is >40% [1]. Unfortunately, the vanadium technology for production of large components is still immature [3, 5], and the price to produce large amounts of vanadium alloys with low content of interstitials (Table 3.2) may prevent their extended use in future fusion reactors.

The individual challenges that a blanket material will face are discussed below with respect to the vanadium alloys, together with a comparison with other candidate materials. A discussion about the factors that affect the material’s operating temperature window is also included in the text.

Table 3.2 Cost for bulk quantities of simple plate products in year 2000 [19].

<table>
<thead>
<tr>
<th>Material</th>
<th>Cost per kg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-9Cr steels</td>
<td>≤$5.50 (plate form)</td>
</tr>
<tr>
<td>SiC/SiC composites</td>
<td>&gt;$1000 (CVI processing)</td>
</tr>
<tr>
<td>V-4Cr-4Ti</td>
<td>~ $200 (CVR processing of CFCs)</td>
</tr>
<tr>
<td>CuCrZr, CuNiBe, ODS copper</td>
<td>~ $10</td>
</tr>
<tr>
<td>Nb-1Zr</td>
<td>~ $100</td>
</tr>
<tr>
<td>Ta, Ta-10W</td>
<td>$300 (sheet form)</td>
</tr>
<tr>
<td>Mo</td>
<td>~ $80 (3 mm sheet); ~ $100 for TZM</td>
</tr>
<tr>
<td>W</td>
<td>~ $200 (2.3 mm sheet); higher cost for thin sheet</td>
</tr>
</tbody>
</table>

Neutron wall load

Table 3.3 presents a summary of the neutronic response of the V-4Cr-4Ti alloy and other candidate structural materials. As explained in section 1.3, neutron irradiation causes materials activation and displacement of atoms (dpa) which leads to material damage and embrittlement. The hardening and embrittlement of the material determines the low limit of
the operating temperature window of that material. In order to avoid crack formation in the blanket during the cooling of the reactor, the DBTT must be below RT for the total damage level expected to receive during its lifetime. Furthermore, the He and H embrittlement is very pronounced in SiC composites due to their low Z number and this compromises its feasibility as a structural material. Among the candidate blanket structural materials, vanadium alloy exhibit the lowest He and H transmutation rates; however, the effect of these products on the material properties and so to the lifetime and performance limits are still not clear [1, 6].

**Table 3.3** Neutronic response of first-wall/blanket structural materials\(^a\) [1].

<table>
<thead>
<tr>
<th>Alloy</th>
<th>dpa(^b) (15 MWy/m(^2))</th>
<th>He Transmut(^b) (15 MWy/m(^2)) appm</th>
<th>H Transmut(^b) (15 MWy/m(^2)) appm</th>
<th>Dose rate(^c) (Sv/h)</th>
<th>Decay heat(^c) (W/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Austenitic steel (316)</td>
<td>170</td>
<td>2400</td>
<td>8550</td>
<td>4000</td>
<td>3</td>
</tr>
<tr>
<td>Ferritic steel (9Cr-1Mo)</td>
<td>170</td>
<td>1800</td>
<td>7350</td>
<td>1000</td>
<td>1</td>
</tr>
<tr>
<td>Vanadium alloy (V-4Cr-4Ti)</td>
<td>170</td>
<td>855</td>
<td>4050</td>
<td>0.3</td>
<td>0.0005</td>
</tr>
<tr>
<td>SiC/SiC composite</td>
<td>135</td>
<td>19 500</td>
<td>13 350</td>
<td>0.0001</td>
<td>0.00003</td>
</tr>
<tr>
<td>Niobium</td>
<td>95</td>
<td>495</td>
<td>1725</td>
<td>4000</td>
<td>4</td>
</tr>
<tr>
<td>Molybdenum</td>
<td>95</td>
<td>525</td>
<td>5250</td>
<td>500</td>
<td>0.3</td>
</tr>
<tr>
<td>Tantalum</td>
<td>51</td>
<td>45</td>
<td>135</td>
<td>1 000 000</td>
<td>1000</td>
</tr>
<tr>
<td>Tungsten</td>
<td>45</td>
<td>51</td>
<td>135</td>
<td>1000</td>
<td>10</td>
</tr>
<tr>
<td>Copper</td>
<td>219</td>
<td>1500</td>
<td>8700</td>
<td>2000</td>
<td>1</td>
</tr>
</tbody>
</table>

\(^a\) Approximate values; actual values depend on specific design. \(^b\) Approximate values at first wall after 15 MW y/m\(^2\). \(^c\) Approximate values one month after 3 yr at 5 MW/m\(^2\).

**Surface heat flux**

A neutron wall load of 5-10 MW/m\(^2\) corresponds approximately to heat fluxes of 1 and 2 MW/m\(^2\) [1]. The resulting temperature on the FW depends on: (1) the heat flux on the wall, (2) thickness of the material, (3) the input temperature of the coolant and the thermal conductivity of the material. Fig. 3.1 shows the maximum allowed surface heat flux for the first wall of a V-4Cr-4Ti module as a function of its thickness and wall temperature, for a fixed temperature and pressure of the coolant. The solid lines indicate the structural design limits based on the ITER structural design criteria (ISDC). 3S\(_m\) is a set of rules used in the past [20]. New structural design stress criteria have been extended to include radiation-induced embrittlement and thermal creep (but not fatigue) for vanadium-base alloys [21]: the Bree limit for ductile materials, with an uniform elongation \(\varepsilon_u > 2\%\), and the \(S_d\) limit, for brittle materials \((\varepsilon_u < 2\%\)). With these new criteria, it is possible to raise substantially the heat load in the first wall. This will allow to increase the energy conversion efficiency of the plant.
3. Feasibility of vanadium alloys for fusion reactor applications

Figure 3.1 Maximum surface heat flux as a function of wall thickness for a blanket made of V-4Cr-4Ti vanadium alloy structure [1].

Energy conversion efficiency

The energy conversion efficiency depends on the coolant parameters [2]. Keeping the difference between the input and output coolant temperature as wide as possible increases the energy conversion efficiency, but at the same time increases the pressure of the coolant which introduces additional stresses on the blanket. Moreover, a high outlet coolant temperature would correspond to a high FW temperature where thermal creep effects would further compromise the device lifetime of the blanket module. The occurrence of thermal creep effects determines the upper limit of the operating temperature window: the higher the creep resistance of the material, the higher the upper operating temperature limit.

On the basis of the material properties and of a target blanket lifetime, the input and output coolant temperatures of several coolants (He, Li, PbLi) have been established, see Table 3.4. In the case of vanadium blanket the proposed coolant is liquid Li.
Table 3.4 Estimated energy conversion efficiencies for selected candidate blanket concepts [2].

<table>
<thead>
<tr>
<th>Concept</th>
<th>He/Se/Sb/FS/Be</th>
<th>H$_2$O/PbLi/FS</th>
<th>Li/V</th>
<th>He/Se/Sb/SeC/Be</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coolant</td>
<td>He</td>
<td>H$_2$O</td>
<td>Li</td>
<td>He</td>
</tr>
<tr>
<td>Coolant pressure (MPa)</td>
<td>8</td>
<td>15</td>
<td>0.4</td>
<td>15</td>
</tr>
<tr>
<td>$T_{in}$, °C</td>
<td>250</td>
<td>265</td>
<td>330</td>
<td>350</td>
</tr>
<tr>
<td>$T_{out}$, °C</td>
<td>450</td>
<td>325</td>
<td>610</td>
<td>650</td>
</tr>
<tr>
<td>Approx. gross efficiency (%)</td>
<td>28</td>
<td>35</td>
<td>46</td>
<td>49</td>
</tr>
<tr>
<td>Approx. net plant efficiency (%)</td>
<td>19</td>
<td>28</td>
<td>39</td>
<td>39</td>
</tr>
</tbody>
</table>

* Based on ARIES reactor design.
* Assumes high conductivity SiC.

Fig. 3.2 summarizes the operating temperature window of several materials which may be used to fabricate facing components. ODS steels remain the most versatile material for the blanket and so the main candidate among the advanced materials up to now.

Figure 3.2 Operating temperature windows for refractory alloys, Fe–(8–9%)Cr ferritic-martensitic steels, Fe–13%Cr oxide dispersion strengthened (ODS) ferritic steels, Type 316 austenitic stainless steels, solutionized and aged Cu–2%Ni–0.3%Be, and SiC composites. The proposed windows of temperature are based on radiation damage and thermal creep considerations. The light shaded bands on either side of the dark bands represent the uncertainties in the minimum and maximum temperature limits [19].
Magnetohydrodynamics effects

Due to the high magnetic fields generated by the magnetic coils, magnetohydrodynamics (MHD) effects are expected to be relevant for the metallic liquid used as coolant in the blanket module. These magnetic effects will cause a large pressure drop in the flowing system affecting the system pressure and the pumping power. The heat transfer in the coolant will also be degraded since the magnetic field will tend to laminarize the flow [2]. To avoid these effects, the use of electrical insulating coatings is planned: calcium oxide (CaO) and aluminium nitride (AlN), are currently the leading candidate materials for coating the Li/V system [2].

Corrosion

Liquid Li is expected to cause corrosion of the blanket material. Corrosion data of various V-Cr-Ti alloys tested in stagnant, thermal forced and convective flowing lithium showed that this alloy could be used in lithium environments at temperatures up to 700°C. This would lead to a corrosion rate lower than 7.5 μm/year [6, 22]. It is known that the corrosion of vanadium alloys in liquid lithium is highly dependent on the alloy composition and chemistry [23, 24].

Other oxidizing conditions such water, He and Na are more deleterious than Li coolants, an anti-corrosion barrier is so compulsory. A silicide coating is being developed as oxidation barrier for vanadium alloys [25, 26].

Tritium breeding ratio (TBR)

In DEMO each blanket module will act as a tritium breeding module. In order to make DEMO self-sufficient, a TBR > 1.15 is required [27]. The expected TBR for the proposed DEMO blanket project would meet this requirement [28]. Unfortunately this concept is not going to be tested in ITER [8].

Safety and environmental issues

The safety and environmental issues for future fusion reactors will be dominated by the first-wall blanket system [2]. The materials challenges are:

(1) Tritium is radioactive and its potential release is of great concern. The tritium containment in the V/Li system at elevated temperatures is an open issue.
The accepted limit of tritium dissolved in a DEMO blanked is less than 1kg [29]. Tritium inventory in V blanket changes with different types of Li coolant. Data in Fig. 3.2 show the tritium amount in equilibrium inside a 700 tons blanket of V-4Cr-4Ti at 1273°C, as function of the tritium concentration in the coolant [30]. Not pure Li coolants lead to an unacceptable amount of tritium (10 kg <<) that can be reduced lowering the tritium partial pressure in the coolant with TF (Tritium Fluoride) control [31].

![Equilibrium tritium inventory in a 700 tons V-4Cr-4Ti DEMO blanket at 1273°C for three tritium breeders as a function of tritium level in the breeders assuming self-cooled FFHR reactor [30].](image)

**Figure 3.2** Equilibrium tritium inventory in a 700 tons V-4Cr-4Ti DEMO blanket at 1273°C for three tritium breeders as a function of tritium level in the breeders assuming self-cooled FFHR reactor [30].

(2) The chemical reactivity of liquid lithium with air and water [2].

(3) The structural materials under irradiation may become active. It is important that the plasma facing materials contain low activation elements in order to limit the production of radioactive waste. Figure 3.3 compares radioactivity of four materials after their use in the first wall of a commercial fusion reactor. The full-remote and full-hands-on recycle limits are shown to indicate the guideline for recycling and reuse [32]. V-4Cr-4Ti alloy remains between both safety after 1000 years.
3. Feasibility of vanadium alloys for fusion reactor applications

Figure 3.3 Radioactive levels of four reference materials after use as first wall materials in a commercial fusion reactor: SS316LN-IG (the reference ITER structural material), F82H (a candidate RAFM steel), NIFS-HEAT-2 (a V-4Cr-4Ti alloy heat) and SiC/SiC composite assumed to be free from impurities [5].

3.2 Large scale production of vanadium components

V-4Cr-4Ti alloys would require a production route that can be adopted at industrial scale. The first experiments to develop a production route were reported in the US: during the last years of the 90s Oremet-Wah Chang of Oregon (WCA, previously Teledyne Wah Chang of Albany) produced a large ingot of 500 kg called US 832665 for the US Department of Energy for basic fusion material research [33, 34] and a second ingot called US 832864 of 1200 kg, requested by General Atomics for the DIII-D radiative divertor upgrade [35]. In 2000 the Japanese National Institute for Fusion Science (NIFS), in collaboration with the Japanese industry, announced the production of a high purity ingot of 30 kg (NIFS-HEAT-1) [36, 37], followed by other ingots with a total weight of 166 kg (NIFS-Heat-2) [38]. In Table 3.5 the chemical composition of the nominated heats is summarized [39].

The production of the NIFS-HEATs was an important achievement since it demonstrated the development of a technology capable to produce large amounts of vanadium alloys with high purity. Figure 3.4 shows the levels of Al, Nb, Ag and Mo in USHEATs, NIFS-HEATs and raw V, Cr and Ti metals used for producing NIFS-HEATs. The impurity levels are shown as relative values with respect to the recycling limit proposed by Dolan and Butterworth [28]. This figure shows that all produced heat meet the criteria for full remote recycling, and that
the NIFS-HEATs are close to meet the criteria for quasi-hands-on recycling. Thus NIFS-HEATs are considered to have demonstrated the feasibility of recycling vanadium alloys economically [39].

Following the Japanese, fabrication efforts have been in Russia (RF-VVC-2, VM-DPCh-9, ingots of 30–110 kg) in 2000–2013 [40], in China (SWIP-30, ingots of 30 kg) in 2010 [41], and in France (CEA-J57, ingots of 30 kg) in 2011 [42]. Similar and consistent fundamental properties have been obtained for these materials providing evidence that the fabrication technology has been almost standardized [25].

Table 3.5 Chemical composition of the different V-4Cr-4Ti heats [39].

<table>
<thead>
<tr>
<th>ID</th>
<th>C</th>
<th>O</th>
<th>N</th>
<th>B</th>
<th>Na</th>
<th>Mg</th>
<th>Al</th>
<th>Si</th>
<th>V</th>
<th>Cr</th>
<th>Mn</th>
<th>Fe</th>
<th>Ni</th>
<th>Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>NIFS-HEAT-1</td>
<td>56</td>
<td>181</td>
<td>103</td>
<td>7</td>
<td>17</td>
<td>&lt;1</td>
<td>119</td>
<td>280</td>
<td>Bal.</td>
<td>4.12</td>
<td>&lt;1</td>
<td>80</td>
<td>13</td>
<td>4</td>
</tr>
<tr>
<td>NIFS-HEAT-2</td>
<td>69</td>
<td>148</td>
<td>122</td>
<td>5</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>59</td>
<td>270</td>
<td>Bal.</td>
<td>4.02</td>
<td>&lt;1</td>
<td>49</td>
<td>7</td>
<td>2</td>
</tr>
<tr>
<td>US832665</td>
<td>170</td>
<td>330</td>
<td>100</td>
<td>3.7</td>
<td>0.01</td>
<td>0.17</td>
<td>355</td>
<td>785</td>
<td>Bal.</td>
<td>3.25</td>
<td>0.21</td>
<td>205</td>
<td>9.6</td>
<td>0.84</td>
</tr>
<tr>
<td>US832664</td>
<td>37</td>
<td>357</td>
<td>130</td>
<td>&lt;2</td>
<td>&lt;1</td>
<td>193</td>
<td>273</td>
<td>Bal.</td>
<td>3.8</td>
<td>–</td>
<td>228</td>
<td>–</td>
<td>&lt;50</td>
<td></td>
</tr>
</tbody>
</table>

As  Zr  Nb  P  S  Cu  Co  Ag  Sn  Sb  Ti  W  Mo  Ta
| NIFS-HEAT-1 | 1    | <10  | 1.4  | 16   | 9    | 3    | 2   | <0.05 | <1   | <1   | 4.13 | <1   | 23   | 58   |
| NIFS-HEAT-2  | <1   | 2.5  | 0.8  | 7    | 3    | 12   | 0.7 | <0.05 | <1   | <1   | 3.98 | <1   | 24   | 13   |
| US832665    | 1.4  | <46  | 60   | 33   | 33   | 0.26 | 0.30 | 0.078 | 0.24 | 0.17 | 4.05 | 25   | 315  | <19  |
| US832664    | –    | –    | 106  | <30  | –    | 4    | –   | –    | –    | –    | 3.8  | –    | <50  |

For the NIFS-HEATs metallic impurities were measured by GD-Mass analysis except Nb, Ag and Zr, which were measured by ICP analysis. (Cr, Ti: wt%, others: ppm).

Figure 3.4 Impurity levels of US-HEATs, NIFS-HEATs and the raw metals used for production of NIFS-HEATs, as relative to the hands-on recycle limits [39, 28].
3.3 Remaining challenges

The remaining scientific and technological challenges to address in order to consider vanadium alloys as the material candidate for the blanket modules of the future fusion reactors are:

- Improve the mechanical properties at high temperatures, in order to extend the upper limit of the operating temperature window of the blanket modules.
- Improve the resistance to radiation embrittlement, in order to extend the lower limit of the temperature window.
- Ensure tritium production at sufficient levels in the blanket.
- Design blankets capable of withstanding the chemical reactivity of lithium.
- Develop an economic industrial rate to produce high purified vanadium alloys with a reduced activation probability on the fusion reactor environment.
- Understand and control the He embrittlement of these alloys.
3.4 References

3. Feasibility of vanadium alloys for fusion reactor applications


3. Feasibility of vanadium alloys for fusion reactor applications


4. CHARACTERIZATION METHODS

The as received samples are described together with their preparation (4.1). Some of the main techniques implemented in this thesis are described: electron microscopy (4.2), positron annihilation spectroscopy (4.3) and hardness test (4.4).

4.1 As received sample description and preparation

All the as-received samples have been provided as plates by Goodfellow, an external company specialized in materials supply. The manufacturing method is unknown due to industrial secret but it is believed the samples have been crafted by arc melting. The nominal purity was 99.9% and it has been confirmed by atom probe tomography analysis (section 6). The concentration of Ti and Cr has been confirmed by energy dispersive spectroscopy (Par. 4.2.2), this technique is suitable for the scope since the Ti and Cr signals do not overlap among them and are thus clearly recognizable and measurable. Thermal treatments have been carried in a tube furnace in inert atmosphere of argon.

Regarding metallic samples, a polished surface is compulsory to carry on correctly several analyses like EBSD and hardness. The initial surface of a metal, as for example received from the supplier, can be very rough and present a lot of defect like scratches and holes that hide the microstructure information to the scientific instrumentation.

Grinding the samples can remove those defects and prepare a more flat and homogenous surface. In this thesis SiC foil ranging from 320 and 4000 grit has been implemented. The surface can be improved with polishing which will prepare a surface ideally free of defects and with a roughness below than μm. Polishing can be done in two ways: mechanically (grinding using submicron particles in a suspension) or chemically (dissolving the metal with an acid or basic solution). Chemical polishing, also called electropolishing, consists in applying an electric potential difference between the surface (anode) and a liquid solution (cathode) which could be acid or basic, called etching solution. In this thesis the etching solution was 60vol.% methanol – 35vol.% 2-butoxyethanol – 5vol.% perchloric acid (60%) and it was used at a temperature of -35°C.
The applied potential triggers electrochemical reactions that dissolve the metallic atoms in the solution as ions. The dissolution ideally will be faster on the spurs of the surface, leading to a homogenization of the surface topography and a consequent decrease of roughness. Fig. 4.1 is a hypothetical plot of the electrical current passing through the surface as function of the potential during electropolishing, the curve is not following an unique trend and three different situations are present in order as current rises: etching, polishing and pitting. Due to the low currents in etching, the regions with more crystal disorder will be attached first, like the grain boundaries. The resulting surface will show a microstructure where the grain boundaries are clearly visible and each grain is etched in a different way because the dissolution rate was sensible to the crystal orientation. Such condition can be achieved even without applying a potential and could be implemented just for simple optical microscope analysis.

Increasing the potential, the ideal condition of polishing is achieved in a flat region after the etching ramp. Increasing more the potential, the corrosive action of the solution will be more aggressive causing pitting, i.e. the formation of holes over the surface. When the passivation layer is locally removed, the pure uncovered metal becomes an anode, while the vast left passivation layer is cathode. The thermodynamic conditions will favor so the passage of high currents that will cause a fast dissolution of the metal under the uncovered passivation layer leaving it quite unchanged. This last condition, known as deleterious in corrosion prevention literature, should be avoided during the sample preparation. Decreasing the temperature of the etching solution is effective to lower the current and avoid pitting.

The same recipe of electropolishing can be applied to prepare metallic TEM foils by double jet thinning technique. In this procedure a disk usually of 3mm diameter and thick around 100μm is hit both sides by a jet of the etching solution. Each side of the disk is getting
thinned after the formation of a concave shaped pit. As the two pits merge together and the jets touch each other, a hole with a diameter of the order of the μm is formed. The border of that hole can be thick tens of nm, enough for electrons with 100-300 KeV energy to pass through, permitting TEM analysis. It is fundamental to interrupt the jet of solution as soon the hole has been formed, in order to avoid its enlargement and thickening of the edge that would become invisible to electrons. To stop the process in time a laser is pointed perpendicularly over one side of the disk, as soon the hole is formed the laser crosses the disk and is revealed by a detector located on the opposite side. The signal boost from the detector will trigger finally the immediate interruption of the electropolishing process.

4.2 Electron Microscopy

A detailed description of the relevant electron microscopy instrumentation implemented in this thesis is provided in section 5. Electron microscopy is a technique that permits to obtain magnified images of solid matter at magnifications orders of magnitude higher than optical microscopy, up to the atomic resolution. The resolution of a microscope is affected by the wavelength of the radiation according to the Rayleigh criterion, the shortest the best. Electron microscopes use as radiation a beam made of electrons which behave both as particles and waves, according to the wave–particle duality from quantum mechanics. The wave is described by the wave function and propagates along the vector \( \mathbf{k} \). The wavelength \( \lambda \) of the wave is function of the electron energy from the Louis de Broglie's equation. For electrons accelerated at 100 keV, \( \lambda \) has value of ~4 pm which is noticeably shorter than the 380-750 nm of the visible light adopted in optical microscopes. Resolution is also affected by the defects of the lenses such as chromatic and spherical aberration. In electron microscopy the lenses are not anymore made of glass but are constituted by magnetic fields capable to deflect incoming charged particles such as electrons. The electron beam is ideally monochromatic, i.e. all electrons travel at the same energy.

The interactions between the electrons of the beam and the atoms of the sample are the basis of what can be achieved by electron microscopy. Figure 4.2 summarises some of the main effects. If the sample is thin enough, electrons can get transmitted through the specimen forming the transmitted beam that can be divided in two parts: the direct and the scattered beam, only this latter is made of electrons that have changed their direction after interaction with the sample. The scattered electrons may have lost kinetic energy (inelastic scattering) after a collision with a nucleus or an electron of the sample. If the energy of the incident
4. Characterization methods

electron is high enough, the collided electron can escape from the attraction of the nucleus and come out from the sample surface taking the name of secondary electron (SE). In the case of elastic scattering, the beam electrons do not lose kinetic energy but their path has been deviated of an angle by the electromagnetic fields of the atoms. It may happen that the angle is > 90° and the electrons come out from the surface hit by the beam, these electrons are called back scattered electrons (BSE). Occurrence of scattering increases with the thickness of the sample, as the electron can collide with more atoms. How far the electron is deviated from the original path is related with the Z number, bigger atoms have stronger electric fields that perturb more the beam electron paths. If the sample is crystalline, diffraction phenomena will occur during the scattering from equally spaced atomic planes in a crystal due to the wave nature of electrons. Destructive wave interference will limit the number of scattered beam that will be addressed as scattered diffracted beams and those provide precious information about the crystal structure.

![Diagram of electron beam effects](image)

Figure 4.2 Summary of main effects of the incident electron beam over a sample.

Electron microscopy is divided in two fundamental modes: scanning electron microscopy (SEM) and transmission electron microscopy (TEM).

4.2.1 Scanning electron microscopy

In SEM the electron beam has energies around tens of keV and it is focused in one spot over the sample surface (Fig. 4.3). The electrons of the beam can ionize the atoms of the sample forming SE that are collected by a detector and their intensity is measured. That intensity
measure provides the value of the digital pixel related to that particular position of the beam spot. The beam is deflected and the position of the spot changes, other pixels are acquired and a (digital) image is obtained, representative of the SE intensity along the sample’s surface. Contrast is made since the SE intensity is function also of the angle of the surface with the beam and the detector. The digital image can be interpreted as a measure of the surface geography where cracks, pits and other features appear clearly. Besides the SE, an image can be formed detecting only the BSE. The intensity of the BSE is strongly dependant of the atomic number Z of the nuclei. The contrast of BSE images is indicative of the presence of different phases with different chemical elements. BSE intensity is also affected by the degree of channeling of the incident electrons through the sample crystal lattice. Different grains in the microstructure of a metallic sample will show in a BSE image different contrast as for each crystal orientation the electron channeling varies.

![Image](image.jpg)

**Figure 4.3** Schematic representation of how an SEM operates.

4.2.2 Transmission electron microscopy

In TEM the beam has higher energies (usually 100-300 keV) and it is meant to get transmitted through thin foils of the order of several tens of nm (TEM foil). The beam is
considered parallel if all electrons are hitting the sample at the same angle, or convergent if the electrons are focused in a spot (< nm) changing the beam shape to conical with an apex angle limited to tens of mrad. Convergent beam is meant for particular operating modes described later. In conventional TEM mode (CTEM) the incident (parallel) beam spot is spread over the area of interest and, as described in Figure 4.4, it can operate in two modes: imaging mode (to obtain magnified images of the sample) or diffraction mode (to obtain electron diffraction patterns), this latter mode will be addressed ahead. Using the terminology of optical geometry, in image mode the objective of the sample that will form the image is wherever the beam electrons are hitting, the transmitted beam is collected by the objective lens that divides the direct and the scattered beams focusing them on different points placed on a plane called the objective back focal plane. On that plane a physical aperture (called objective aperture) filters the scattered beam leaving only by the direct beam. It happens that the direct beam interacts with the scattering beam and viceversa, its intensity increases with the reduction of scattering events, so with the reduction of the scattering beam intensity. The transmitted beam is afterwards collected by the intermediate lens whose objective plane matches the objective lens image plane. The signal is finally spread by the projector lens over a screen fluorescent to electrons in order to make visible by eye the objective area chosen over the TEM foil. The brightness over the screen is proportional to the intensity of the direct beam which variation lead contrast. Alterations of the microstructure are revealed and are attributable for example, with a proper interpretation, to the presence of different phases or crystal defects that changes the diffraction conditions, by modifying the crystal structure. The magnified image of the sample can be stored in a digital format using a CCD (charged-coupled device) camera or in an analogic one using photographic film.

In the next sections different topics of TEM microscopy will be addressed. As diffraction phenomena occur from the electron-sample interaction, relevant data regarding the crystal structure of the sample can be obtained through the acquisition of electron diffraction patterns. If the beam is convergent, the microscope can obtain convergent electron beam diffraction (CBED) patterns that could provide a measure of the foil thickness and help to set the two-beam condition, important to analyse crystal defects such as dislocation loops (imaging structural defects). Keeping the convergence, the microscope can operate in scanning transmission mode (STEM) and carry out chemical analysis along the sample microstructure by electron energy loss spectroscopy (EELS) and energy dispersive spectroscopy (EDS).
Figure 4.4 Schematic representation not in scale of the optical geometry behind the image and diffraction modes in CTEM.
Electron diffraction

As the incident electrons behave also like a wave, they undergo diffraction phenomena after interaction with a crystalline sample in TEM leading to the formation of particular scattered beams called diffracted beams. These beams and the direct one are focused on distinct spots over the objective back focal plane, as shown in Figure 4.4. The electron diffraction pattern is formed over the screen when the objective plane of the intermediate lenses matches the objective back focal plane.

Diffraction of electrons from the lattice planes of the crystal, like the X-rays case, follows the Bragg Law and for TEM electrons the values of the Bragg angles are around tens of mrad. For every $hkl$ set of planes satisfying the Braggs Law, there will be a different scattered beam, inclined with respect to the direct beam of an angle two times the Bragg angle of that set of planes with spacing $d_{hkl}$. The construction of the Ewald Sphere (Fig. 4.5) allows understanding which set of planes, at a given crystal orientation, will reflect electrons and at which intensity. The $\mathbf{k}$ of the incident beam ($\mathbf{k}_I$) is pointing the origin of the reciprocal lattice of the crystalline sample, the origin of $\mathbf{k}_I$ is the centre of the Ewald Sphere with radius the modulus of $\mathbf{k}_I$, which is the reverse of $\lambda$. Whatever $hkl$ point of the reciprocal lattice that is intersecting the sphere surface can be linked from the centre of it by the $\mathbf{k}$ of the diffracted beam ($\mathbf{k}_D$). The change in $\mathbf{k}$ of the electron due to diffraction is:

$$\mathbf{K} = \mathbf{k}_D - \mathbf{k}_I = \mathbf{g}_{hkl} + s$$  

Where $\mathbf{g}_{hkl}$ is the diffraction vector of that $hkl$ set of planes and has as modulus the reverse of $d_{hkl}$. The deviation parameter is $s$, at the Bragg angle $s = 0$ and diffraction occurs. However diffraction occurs even when $s \neq 0$ (at lower intensity), since each point of the reciprocal lattice becomes a kind of relrod intersecting the Ewald Sphere. This in general is due to the fact that the TEM foil is much larger than thicker. Translated in the reciprocal space, each point of the lattice is affected by this surface/thickness ratio and extends along the direction perpendicular to the sample surface.
Figure 4.5 2D sketch not in scale of the Ewald sphere construction.

Figure 4.6 shows an example of diffraction pattern characterized by different spots, reflections of the focused scattered and direct beams. The brightest spot is called the direct spot since it is the reflection of the direct beam and corresponds to the origin of the reciprocal lattice \((hkl=000)\). Each \(g_{hkl}\) vector is starting from the direct spot and points the corresponding \(hkl\) spot, reflection of the focused beams that have been scattered by the \(d_{hkl}\) planes. In first approximation, the length of \(g_{hkl}\) is equal to the linear distance between the direct spot and the \(hkl\) spot, thus providing a measure of the planes spacing. The angles between different \(g\) vectors will provide sights for the determination of the crystal structure. The intensity of the diffraction spot is maximum when \(s = 0\).

Figure 4.6 Diffraction pattern of crystalline aluminium with the incident beam perpendicular to the (111) plane [1].
If we are interested to get the diffraction pattern only from a specific area of the sample, like a large precipitate, we can apply an aperture that filters the transmitted beam from the not interesting area, the diffraction pattern is called SAD (selected-area diffraction). The aperture is called SAD aperture and is located on the image plane of the objective lens. The available apertures have diameters of the order of the μm, in case the selected area has to be smaller, of the order of the nm, the nano-diffraction technique can be used. The TEM is operating in STEM mode, the incident beam is focused keeping as much as possible the parallel condition to prevent an enlargement of the diffraction spots (CBED paragraph). Once a STEM image is acquired, the position of the beam spot can be changed relating it to the image. The diffraction pattern is afterwards recorded in live mode and it changes as the spot moves in the different features measured by the image.

To record a diffraction pattern a CCD camera can be used but the danger of damage from the direct beam limits the amount of collectable signal. Where possible, photographic film should be used which does not pose any restriction of acquisition time allowing the detection of the weakest spots.

Information about the crystal lattice can be obtained also from atomic resolution images by the fast Fourier transformation (FFT) algorithm. This mathematical operation recognizes in the image the presence of periodicities of the intensity signal due to the ordered disposition of the atoms. The FFT translates these periodicities in a sort of diffraction pattern. Anyway it has to be reminded the mathematical nature of this method and that data from conventional diffraction techniques, more physical, should always be considered first.

*Convergent electron beam diffraction (CBED)*

Due to the beam convergence, the diffraction spots are spread like disks as the electrons are incident at different angles (Fig. 4.7). The diffraction cannot be described with the kinematical approximation but it has to be treated as dynamical, with the Howie-Whelan equations, where the transmitted and the diffracted beam are interacting creating a contrast that permits thickness measurements.
4. Characterization methods

Figure 4.7 Sketch of optical geometry that shows how the diffraction spots enlarge when the beam is convergent.

The variance of the incidence angle will be responsible of interesting phenomena like the appearance of the Kikuchi lines superimposed over the diffraction pattern, each of these lines is straight and related to a $g_{hkl}$ spot, the line of a particular $g_{hkl}$ spot crosses perpendicularly the middle of an hypothetical line linking that $g_{hkl}$ spot with the direct spot.

Two beam condition

The TEM foil is tilted at the two beam condition when there is only one strong diffracted beam. Diffraction contrast interpretation is made easier as it is known that the set of diffracting planes which has been perturbed is the set of planes responsible for the strong diffracted beam. In the diffraction pattern, the main diffracted beam will appear bright like the direct one, formally $s = 0$. The set up of the two beam condition is straightforward during CBED. Following Fig. 4.8, the Kikuchi line of the diffraction spot $g$ (of the strong diffracted beam) has to lie over it in the middle, the Kikuchi lines of the opposite spot $-g$ lies instead in the middle of the direct spot, which should not be crossed by the Kikuci lines of other main reflections.
4. Characterization methods

**Figure 4.8** a) Kikuchi lines over the diffraction pattern of a fcc crystal oriented in a [111] zone axis. b) The sample is tilted at the two beam condition with $g\ 02\cdot2$ as strong reflection [2].

*Measure of the foil thickness*

Every time the thickness increases of half of a length called the extinction distance $\xi_g$ the transmitted beam is depleted by destructive interference with the diffracted beam of that particular $g$. At a particular zone axis, the direct (spot) disk will usually contain concentric diffuse fringes known as Kossel-Möllenstedt (K-M) fringes, each fringe will correspond to an increase of the thickness equal to the extinction distance. Those fringes became parallel when the foil is tilted at the two beam condition (Fig. 4.9). For the appearance of the fringes the foil has to be thicker than $\xi_g$ and the convergence angle has to be wider than the Bragg’s angle of that particular zone axis.
4. Characterization methods

Figure 4.9 Parallel Kossel-Möllenstedt fringes in a CBED pattern under two-beam condition with $\mathbf{g} \ 200$ as strong reflection [1].

From the position of the Kossel-Möllenstedt fringes, the thickness $t$ can be measured together with $\xi_\mathbf{g}$. Figure 4.10 shows how the spacing of the Kossel-Möllenstedt fringes corresponds to $\Delta \theta_i$ angles, the index $i$ is an integer that rises of 1 every time with the following fringe.

![Figure 4.10 Sketch of two diffraction disks showing the $\theta$ parameters [1].](image)

The $\Delta \theta_i$ angles will be used to measure the deviation parameter $s_i$, as shown in equation (2).

$$s_i = \lambda \frac{\Delta \theta_i}{2 \theta_B d^2}$$  

(2)
Where $\lambda$ is the electron wavelength, $d$ is the spacing of the diffracting planes and $\theta_B$ is the Bragg's angle. For each $s_i$ the following equation (3) is satisfied.

$$\frac{s_i^2}{n_k^2} + \frac{1}{\xi_g^2 n_k^2} = \frac{1}{t^2}$$

Where $n_k$ is an integer that raises of 1 every time with the following fringe satisfying that $k = i + j$, where $j$ is the largest integer $< (t/\xi_g)$.

Figure 4.11 show how from equation (3) a straight line plot can be drawn using the different values of $s_i$, from the slope and the intercept the $\xi_g$ and $t$ can be measured respectively.

![Liner plot of equation (3)](image)

Figure 4.11 Liner plot of equation (3) [1].

**Scanning transmission electron microscopy (STEM)**

In STEM the beam is convergent and focused in a probe large less than 1 nm. The transmitted beam is collected by several detectors in order to measure both the direct beam and the scattered ones at different angles. As in SEM, the collected signal is translated in a digital pixel and a digital image is formed as the beam spot raster the area of interest. The HAADF (high angle annular dark field) detector is the one detecting the electrons scattered at the higher angles and its images are the most sensible to the Z contrast.

The advantage of STEM over CTEM is that the transmitted beam is not passing through any lens, preventing the issues related to lens defects. With the new technology advancements, the spherical aberration of the lenses between the electron source and the sample can be drastically reduced. As a result, the probe can have a diameter of around 0.1 nm, keeping at
the same time the current high enough to limit noise at acceptable levels. As the probe size is shorter than the atomic bond, it is possible to acquire atomic resolution images.

*Electron energy loss spectroscopy (EELS) and energy dispersive spectroscopy (EDS).*

A chemical analysis of the microstructure shown by the microscope can be conducted after two phenomena arising from the sample interaction with the electron beam.

The first phenomenon is the emission of X-rays from the sample, the chemical analysis that detects an element from the emitted X-ray wavelengths is called energy dispersive spectroscopy (EDS). The emission of an X-ray photon arises from the knock-off of an electron of an atom belonging to the sample by an electron of the beam. This knocked off electron, literally the known SE (secondary electron), has left an empty space in the electronic structure of the atom. An electron from the upper atomic levels (with higher energy) will occupy this empty space (with lower energy) through an electronic transition that can release energy under the form of an X-ray photon. The energy of that photon is equal to the difference between the initial and final atomic level of the electron. From that energy value, the atomic element can be determined. X-rays, under the name of Bremsstrahlung radiation, can also be generated when the incident electron approaches the nuclei and undergoes a substantial change of its momentum.

Fig. 4.12 shows an example of EDS spectrum with at the ordinate the energy of the measured X-ray photons (0-30 keV) and on the coordinates the intensity. After acquisition, the background consists of the noise at zero energy (strobe peak) and the Bremsstrahlung radiation, both have to be removed. Peaks denote the occurrence of electronic transitions.

![Figure 4.12 Example not in scale of an EDS spectrum.](image-url)
Precise qualitative analysis can be problematic due to the resolution of the detector and the broadening of the peaks which overlap making trivial the precise element identification. To overcome the problem, the hypothesis that a peak belongs to that element should be supported by the presence of the other peaks expected for that element at other energies. Since different electronic transitions have different cross sections, it is expected that the intensity ratio between two peaks from the EDS spectra corresponds to the ratio between the cross sections of their identified electronic transitions.

If the qualitative analysis is satisfactory, a quantitative one can be carried. From the Cliff-Lorimer equation, the concentrations ratio between element A and B is proportional to the ratio between the X-rays intensity from A and B. The constant of proportion is dependant to several factors, and can be obtained through standards of known composition. The formula works best for thin specimens (<100nm, TEM foils) as absorption effects can be neglected facilitating the interpretation.

The second phenomenon regards the energy lost by the electron from the beam after transmission through the TEM foil. These losses of energy are due to inelastic interactions with the electrons of the sample and are indicative of the type of atom and its chemical surrounding. The analysis measuring the electron loss of energy is called electron energy loss spectroscopy (EELS).

An EELS spectrum, as shown in Fig 4.13, has as ordinate the energy lost by the electron and as coordinate the occurrence of the loss. Usually three distinctive parts can be recognized. The first one is the zero-loss peak, due to the high number of electrons that have been transmitted without undergoing inelastic interactions. The second one after the zero loss peak and up to ~50 eV is the low-loss region, there are collected interactions with bound conduction and valence-band electrons which generate plasmon vibrations. The low-loss spectrum can be used to fingerprint specific elements and their chemical surrounding, different chemical compositions change the atoms electronic structure causing shifts of the low loss spectrum peaks.
Above ~50 eV there is the region of the core loss, where the beam electrons have interacted with the atoms ionizing them. The energy loss associated to this process corresponds to the ionization energy, it cannot be lower but it can be higher (with lower probability). As a result of this, from low to high energy loss, the shape of the intensity signal associated with a particular ionization becomes very sharp as the precise ionization energy is reached and after it decreases exponentially. The overall signal shape is thus asymmetric, is called edge instead of peak. The position of the edges in indicative of the chemical element present, shifts of those edges are related to the atoms chemical surrounding.

With EELS is possible to carry quantitative analysis if the background can be properly removed and it is know the ionization cross section.

**Imaging structural defects**

Dislocations lines, dislocation loops, whatever crystal defect is visible on TEM if it distorts the crystal lattice changing locally the diffraction conditions for the beam electrons. If after the lattice distortion the electron is now scattered, the direct beam intensity is lower with respect to where the lattice is undistorted. That intensity difference creates a contrast that describes the defect responsible of that lattice distortion.

Figure 4.13 Example not in scale of an EELS spectrum.
The Burgers vector \( \mathbf{b} \) of a dislocation defines the distortion of the crystal by its modulus and the glide plane by its direction. Defining \( \mathbf{b} \) is important in the description and understanding of the microstructure evolution subsequent to irradiation or plastic deformation. The contrast of the dislocation under TEM analysis is proportional to the dot product \( \mathbf{g} \cdot \mathbf{b} \), when it is equal to zero the dislocation is ideally out of contrast and so invisible. Measuring the different contrast of a dislocation at different two-beam conditions (so different \( \mathbf{g} \) vectors) will provide insights to define the \( \mathbf{b} \) vector for that dislocation. The \( \mathbf{g} \) vector lies on the plane of the image perpendicular to the incident beam, in first approximation.

The nature of dislocation loops can be of interstitial type if they are represented in the lattice as an inserted atomic plane, or vacancy type if the atomic plane is missing. The nature of edge loops larger than 30nm can be understood with the outside-inside contrast method where the dark line of the loop can appear inside the loop, or outside it (appearing larger) on the basis of the loop nature and versus of \( \mathbf{g} \) and \( \mathbf{b} \). Figure 4.14 resume the imaging condition, first of all we are not in two-beam condition as the deviation parameter \( s \) is \( > 0 \). The strain induced by the loop can bring back the diffracting planes to the Bragg condition \( (s = 0) \) leading to a peak of the contrast that could lie inside (inside contrast) or outside (outside contrast) the dislocation core. Formally inside contrast arises when \( (\mathbf{g} \cdot \mathbf{b}) s < 0 \) and outside when \( (\mathbf{g} \cdot \mathbf{b}) s > 0 \).

**Figure 4.14** Schematic representation of the outside-inside method applied for a interstitial and vacancy loop, changing the versus of \( \mathbf{g} \) (rotating so the diffracting planes) shifts the contrast peak position due to the diffracting planes back to the Bragg condition after the distorting action of the loop [1].
4.3 Positron annihilation spectroscopy

Nanoscale defects like clusters, precipitates and open-volume defects (as voids and vacancies) and their chemical surroundings can be studied non-destructively by positron annihilation spectroscopy. Positron is the anti-particle of the electron and it has positive charge; it can be created in laboratory from the decay of radioactive isotopes such as 22Na.

Figure 4.15 shows the events that follow the collision of a positron with the sample. After implantation in a material, positrons thermalize within picoseconds with a depth of about 100 μm, then diffuse through the crystal lattice (in the range of 100 nm), and finally annihilate with an electron of the sample. The annihilation process leads to the emission of two photons of exactly 511 keV in opposite directions from the center-of-mass of the electron-positron system. In this phenomenon, two aspects are relevant from the experimental point of view:

- Positron lifetime τ, i.e. the time from the birth of the positron to its annihilation
- Doppler broadening, the energy peak of the photons at 511 keV is broadened.

![Figure 4.15 Summary of the events that follow the collision of a positron (e⁺) with the sample.](image-url)
4. Characterization methods

**Positron lifetime**

Positrons are very sensitive to vacancy-type defects. The free positron in a crystal lattice experiences strong repulsion from the positive ion cores. An open-volume defect like a vacant lattice site is therefore an attractive centre where the positron gets trapped. The reduced electron density at the vacant site increases the positron lifetime. Not only vacancy-like defects form attractive potentials for positrons but also metallic clusters or layers as long as their positron affinity is higher than the surrounding material. The intensity of the emitted radiation at a determinate lifetime is indicator of the concentration of that particular defect.

**Doppler broadening**

Since the energy of the fully thermalized positron can be neglected, the momentum of the electron-positron system is determined mainly by the electron momentum which will change the measured energy of the emitted 511 keV photons. This change can be up to 2 keV. Hence, the broadening of the 511 keV (Fig. 4.16) is a direct measure of the electron momentum distribution at the annihilation site. If the positron is trapped in open-volume defects such as vacancies, the annihilation probability with core electrons strongly decreases, which leads to a lower broadening. The ratio curve from the rapport between the doppler broadening curve of a sample over a standard constituted of a pure material is indicative of where positrons annihilate. The closer of that ratio curve to the unit, the higher number of positrons that annihilate in zones where the electron density is the same of the standard material in that ratio curve.

The ratio of the area of the central part of the broadening curve over the area of the entire curve is called the S-parameter, whereas the W-parameter is the ratio of the area of the bounds of the broadening curve over the area of the entire curve (Fig. 4.16). S corresponds to positron annihilating with the valence electrons and W-parameter corresponds to positron annihilating with the core electrons. S is sensitive to open volume defects and its increase indicates presence of vacancy defects. W is instead sensitive to the chemical surrounding at the annihilation site and is so the considered zone in the ratio curves.
Figure 4.16 Example of broadening of the photons energy from the peak at 511 keV. The ratio of the curve area included in the W and S rectangles over the entire curve area provides respectively the S and W parameters.

4.4 Hardness test

The hardness of a material is a mechanical related property and is often reported to vary linearly with the tensile strength. There are different methods to measure it on the basis of the material type, for this study the Vickers method has been adopted which can be used for all metals and it has one of the widest scales among hardness tests.

Figure 4.17 Schematic representation of a Vickers indenter indenting a sample leaving a pyramidal indentation characterized by two diagonals (d₁, d₂)[credits from Wikipedia].
The measure consists of pressing the tip of a square pyramidal indenter over the sample surface for a precise duration of time in order to leave at the end a pyramidal indentation (Fig. 4.17). The indenter has to be ideally not deformable and is made of diamond; the slant angle is $22^\circ$ and comes from the previous optimization of the Brinell hardness method. The ratio of the used force ($F$) over the area of the pyramidal impression ($A$) left by the indenter is the measure of the Vickers hardness ($HV$) as stated by the following equation (4)

$$HV = \frac{F \,(kgf)}{A \,(mm^2)} \quad (4)$$

The value of $A$ can be obtained from the average $d$ of the two diagonals defining the indentation.

$$A = \frac{d^2 \,(mm^2)}{2 \sin\left(\frac{136^\circ}{2}\right)} \quad (5)$$

Vickers hardness has the enormous advantage over tensile tests to be not destructive. A proper Vickers hardness measurement should consist in the average over a statistically relevant number of indentations, surface quality affects data scattering and an indentation is considered acceptable if the difference of the two diagonals is less than the 5% of their average. An indentation should not be taken close to the edge or to another indentation in order to avoid respectively lack of interaction with the sample and interaction with the cold-worked region around the pre-existent indentation. The ASTM E384 method states that the distance of an indentation between another or the edge should be $2.5 \, d$.

### 4.5 References

Most of the text of this chapter is based from the following books


Atomically resolved chemical ordering at the nm-thick TiO precipitate/matrix interface in V-4Ti-4Cr alloy

A. Impagnatiello\textsuperscript{a,b}, D. Hernandez-Maldonado\textsuperscript{c}, G. Bertali\textsuperscript{b}, E. Prestat\textsuperscript{b}, D. Kepaptsoglou\textsuperscript{c}, Q. Ramasse\textsuperscript{c}, S.J. Haigh\textsuperscript{b}, E. Jimenez-Melero\textsuperscript{a,b}

\textsuperscript{a}Dalton Cumbrian Facility, The University of Manchester, Moor Row CA24 3HA, UK

\textsuperscript{b}School of Materials, The University of Manchester, Manchester M13 9PL, UK

\textsuperscript{c}SuperSTEM Laboratory, STFC Daresbury Campus, Keckwick Lane, Daresbury WA4 4AD, UK

Corresponding author (*):

Dalton Cumbrian Facility

University of Manchester

Westlakes Science & Technology Park

Moor Row

CA24 3HA

United Kingdom

Tel.: +44 1946 508860

Email: andrea.impagnatiello@postgrad.manchester.ac.uk
Contribution of the different co-authors

The samples were prepared by the main author A. Impagnatiello, who also analysed and interpreted the data with the valuable input of all the co-authors in their specific areas of expertise.

With regard to the data acquisition, D. Hernandez-Maldonado operated the SuperSTEM and calculated the simulated image that appears in the supplementary section of the manuscript. G. Bertali and E. Prestat operated the FEI Titan, and the collected data is shown in Fig.1. The main author was always present during the data acquisition, providing input about the regions of interest for detailed characterization.

The main author wrote the manuscript together with E. Jimenez-Melero. G. Bertalli, D. Kepaptsoglou, Q. Ramasse and S.J. Haigh provided feedback to the written manuscript before the journal submission.
Abstract
We have used advanced analytical electron microscopy to characterise the local structure and chemistry at the interface between nm-thick TiO precipitates and the V-based matrix in a V-4Ti-4Cr alloy. Our results reveal the presence of an intergrowth between the fcc TiO and bcc vanadium structures, with a repeat lattice distance that equals 2.5 times the vanadium lattice parameter along the c-axis. Our atomic resolution analysis of the interface will impact the mechanistic understanding of its interaction with interstitials and radiation-induced lattice defects, and consequently trigger the development of improved alloy structures with interfaces engineered for enhanced radiation tolerance.

Keywords: refractory metal, crystalline oxides, lattice defects, high-resolution electron microscopy, nuclear fusion reactor
Vanadium-based alloys constitute advanced structural material candidates for the first wall of future magnetically-confined fusion reactors, due to their relatively low cross section for neutron activation [1,2]. Consequently, the targeted tritium breeding ratio will be achieved without the need of an additional neutron-multiplier material such as beryllium. The high strength and creep resistance of V-based alloys, enhanced by the addition of Cr, will allow these materials to withstand temperatures up to 750°C without compromising reactor operability and safety [3]. In addition, the body-centred cubic (bcc) nature of the V matrix, with additions of Ti, provides these materials with good resistance to radiation-induced void swelling [4,5]. These considerations have led to the V-4Cr-4Ti alloy being identified as the prime V-based candidate material for fusion reactor applications [2,6,7].

However, the presence of H, C, O and N as ‘free interstitials’ in the V-matrix causes the detrimental shift of the ductile-to-brittle transition temperature from -200°C to values well above room temperature [8-10]. Ti was identified as an effective scavenger for interstitials [11], by forming plate-like oxycarbo-nitride precipitates [12-15]. The additional benefit is that the precipitate/matrix interface could potentially act as an effective sink for radiation-induced lattice defects, such as vacancies, vacancy clusters or dislocation loops, or for transmutant helium atoms [16,17]. Unfortunately, a unified view about the local structure and chemistry of these nano-precipitates is still lacking. In this paper, we have addressed this by characterizing, with atomic resolution, the chemical distribution and local structure inside the precipitates and within the precipitate-matrix interface region.

In this study we annealed V-4Cr-4Ti (wt.%) sheet material for 2h at 1200°C in an inert atmosphere, followed by water-quenching to room temperature. For transmission electron microscope (TEM) imaging and analysis discs were prepared by mechanical pre-thinning, followed by electro-polishing using an electrolyte of 60vol.% methanol – 35vol.% 2-buthoxyethanol – 5vol.% perchloric acid (60%) at a temperature of -35°C. Advanced
scanning transmission electron microscope (STEM) imaging, coupled with Energy-Dispersive X-ray Spectroscopy (EDS) and Electron Energy Loss Spectroscopy (EELS) measurements performed in a STEM microscope, was used to obtain structural and chemical information with atomic resolution. A High Angle Annular Dark Field (HAADF) detector was used to collect the Rutherford-like scattering signal while the subnanometer-sized electron probe was scanning the sample. The intensity in the HAADF images is proportional to \( Z^\nu \), where \( Z \) denotes the atomic number and \( \nu = 1.6-1.9 \) [18]. The HAADF data therefore yielded information about the atomic positions and local arrangements inside the Ti-rich precipitates present in the V-4Cr-4Ti alloy. For the chemical identification we used (1) STEM-EDS to detect elements with high atomic number, and (2) STEM-EELS suitable to detect low-Z elements, and also to determine the chemical environment of a specific element.

Fig. 1a shows a TEM bright-field (BF) image of the V-4Cr-4Ti specimen after the annealing treatment. A significant number of plate-like precipitates, with lengths of up to a few microns and only a few tens of nanometers in width, were observed in this material. The selected area electron diffraction pattern (SADP) of Fig. 1e shows the [001] zone axis of the V matrix with additional reflections due to the presence of one of the plate-like precipitates. The lattice parameter of bcc V \( (a_v) \) is \( \sim 3.02\text{Å} \). The pattern clearly shows that the plates are lying on the V{100} family of planes. Additionally, we have observed the presence of diffraction spots corresponding to a superstructure with a spacing of \( \sim 7.56\text{Å} \), which corresponds to \( \sim 2.5 \) times the lattice parameter of the matrix.

High resolution STEM imaging of the precipitates (Fig. 1) revealed a range of atomic structures within different plate-like precipitates: uniform (b), showing a superstructure through the thickness (c), or showing a superstructure localised on one (d) or both (f) long sides of the precipitates. The spacing determined in the high resolution STEM data for the superstructure corresponds to the value obtained from the SADP. Fig. 1g and 1h are the
related background-subtracted EDS spectrum images for the Kα Ti and Kα V lines, respectively. The EDS data show that the uniform area of the precipitate mainly contains Ti, whereas both Ti and V are present in the superstructure regions. Cr has not been detected in significant amounts inside any of the precipitates. Two additional cases are also reported in Fig. 1: superstructure at the short edge of the precipitates (i), and surrounding a region of uniform atomic structure (j). Interestingly, the interface between the precipitate superstructure and the matrix acts as an effective trap for dislocations present in the matrix (k).

In order to obtain further information about the local chemical distribution and the origin of the interfacial superstructure phase, we recorded the EELS core loss and low loss spectra [19] at representative locations of the matrix, the superstructure and the uniform structure of the precipitate (Fig. 2). The EELS core loss spectrum of the matrix is dominated by the L_{2,3} edges of vanadium (in the region of 440-590eV). A relatively weak L_{2,3} edge from the substitutional Cr atoms can also be observed close to 580eV. When profiling from the matrix to the superstructure of the precipitate, the vanadium edge is still visible but decreases in intensity, whereas the L_{2,3} edge of Ti starts to appear at characteristic peak energies of 457 and 462eV. The edge consists of L_3 and L_2 ‘white lines’ which originate from electron transitions from the inner 2p_{3/2} and 2p_{1/2} orbitals respectively to empty 3d orbitals of Ti [20]. Those characteristic Ti lines constitute the main feature of the EELS spectrum in the uniform structure of the precipitate. Additionally, we can also observe the appearance of the K-edge of oxygen at 530-550eV, with the most distinctive maximum located just above the edge onset at 532eV. The lower-energy features of this peak are known to originate from transitions between oxygen 1s and 2p σ* states that are hybridized with empty Ti 3d orbitals [20]. The intensity of the 532eV peak increases when moving the beam from the matrix into the superstructure and further into the uniform structure of the precipitate. We have not observed any significant signal in the EELS spectrum at around 280 and 400eV which
suggests the absence of C or N within the precipitate. These results would point to the precipitates consisting of a titanium oxide phase. To confirm this, we have also examined the EELS low loss or valence spectrum below 35eV (Fig. 2c), which is dominated by plasmon excitations. The main plasmon peak of the matrix at 21.6(1) eV can be attributed to metallic vanadium [19]. The position of the maximum consistently shifts to a value of 23.8(1)eV inside the precipitate. An equivalent peak shift is observed for the superstructure and the uniform structure in the precipitate, see Fig. 2a-II. The main plasmon peak of metallic Ti would be located at 18 eV [19], and is expected to shift to ~20 eV when forming Ti hydrides [21] and to 22-26 eV when Ti forms compounds with C, N or O [19, 20]. Our combined EELS core loss and low loss spectral data are therefore consistent with a titanium oxide phase as precipitate.

An HAADF image of one of the precipitates and surrounding matrix is shown in Fig. 3a, together with its Fast Fourier Transform (FFT) and the measured electron diffraction pattern taken at selected locations in the precipitate and the matrix. The diffraction pattern of the matrix corresponds to the vanadium bcc structure acquired along the [100] zone axis. The pattern of the uniform structure in the precipitate has been indexed based on a face-centred cubic TiO unit cell (S.G. Fm-3m) along the [110] zone axis. This titanium mono-oxide phase presents a NaCl-type fcc structure, with a reported value of its lattice parameter of 4.184Å. Its structure can host up to approx. 15% of vacancies [22, 23], and also small amounts of C and N, since both TiN and TiC are isostructural with TiO [24]. We have determined the lattice parameter of the TiO-type precipitates in V-4Cr-4Ti as 4.28Å. This value corresponds to $\sqrt{2} a_v$, where $a_v$ is the lattice parameter of V matrix. Furthermore, the TiO precipitates must be related to the V matrix by the Baker–Nutting orientation relationship: [001]$_{TiO}$ // [001]$_v$, (110)$_{TiO}$ // (100)$_v$. From these results, it is then possible to construct a proposed model for the superstructure in the precipitates, which consists of an intergrowth of the two end structures:
the ‘V bcc matrix’ and the ‘TiO fcc uniform structure, see Fig. 3b. The unit cell contains one vanadium octahedron from the V bcc structure, located between two ‘TiO layers’. The unit cell becomes elongated along the c-axis with a lattice parameter of \( c = 2.5 \times a_V \sim 7.56\text{Å} \). The orientation relationship of the superstructure with the V matrix is thus: \([001]_\text{st} // [001]_V\), \((100)_\text{st} // (100)_V\).

Fig. 4 contains a plan view representation of the proposed model along the [100] direction, together with an experimental atomic resolution HAADF image of the superstructure, and the spatial distribution of the V and Ti derived from the EELS spectra using the \( L_{2,3} \) edges of both elements. The combined interpretation of the chemical and structural data strongly supports the validity of the proposed superstructure model. The repeat distance of \( \sim 7.56\text{Å} \) corresponds to the c-axis of the simple tetragonal unit cell. The dark and bright lines observed in the HAADF images can therefore be linked to TiO and V layers respectively. Careful examination and comparison of the images and chemical information from the EELS data also suggest that it is possible to identify individual V atoms at two positions in the unit cell, i.e. \( x=0 \) and \( x=1/2 \) from the V octahedron in the intergrowth, and also interleaving Ti atoms.

Some simple diffusion considerations can be put forward to explain how the superstructure forms. When the sample is annealed at 1200°C, both Ti and O diffuse in the V bcc matrix to form the TiO precipitates. The diffusion of O interstitials is relatively fast; with a reported value of the activation energy of 119.6-122.5 kJ mol\(^{-1}\) [25-27]. Early trace diffusion experiments in binary V-Ti alloys yielded a value for the Ti diffusion coefficient of \( \sim 1.5 \times 10^{-3} \text{μm}^2/\text{s} \) at 1200°C [28]. If we assume a random walk approach for the diffusion of Ti in the V matrix, we obtain a Ti diffusion length of \( \sqrt{Dt} \sim 3.3\text{μm} \). This value is in good agreement with our experimental value for the average precipitate length in this material (\( \sim 3\text{μm} \)). A correlation factor (\( f \)) is defined as the ratio of the diffusion coefficient of a given
species, Ti in this case, to the diffusion coefficient calculated assuming randomly oriented jump vectors [29]. The reported value of this correlation value for Ti diffusion, assuming that the Ti atoms produce only a weak perturbation of the V lattice and also a vacancy-mediated mechanism, takes a value lower than but close to 1, i.e. \( f_{Ti} = 0.75-0.80 \) in the temperature range of 1100-1550°C [28]. In general, the greater the freedom of movement of the vacancy, the less important the correlation effects become, and therefore the smaller \( 1-f \) is [30]. This means that the binding energy for a Ti-vacancy is relatively low, and the random walk treatment is a suitable approach for the Ti diffusion in the V matrix. The V self-diffusion is slower than the Ti diffusion, but the V diffusivity is affected by the rate at which Ti-vacancy pairs break up. The V diffusion coefficient takes a value of \(~6.0 \times 10^{-4} \text{ μm}^2/\text{s}~\) at 1200°C [28, 31], which yields a V diffusion length of \( \sqrt{Dt} \sim 2.1\text{μm} \). V can therefore form the superstructure phase together with Ti along the precipitate-matrix interface during the annealing treatment.

The local structure and chemical distribution at the precipitate interface with the V matrix will influence the strength of the precipitates as sinks and recombination sites for radiation-induced lattice defects and He atoms [32]. Helium has a relatively low solubility in metals [33, 34], and hence the diffusion and accumulation of He at interfaces and grain boundaries can potentially form bubbles. The presence of He has also been proposed to accelerate the radiation-induced swelling, both by stabilising the void nuclei formed by clustering of the vacancy defects, and by enhancing the void growth that may lead to percolating networks [35]. The leading approach to mitigating void swelling in He-containing materials is to delay the bubble transformation into voids by nano-structuring [36, 37]. Recent work reports the role of semi-coherent fcc-bcc heterophase interfaces in delaying bubble growth in nano-layered composites, materials in which helium seems to accumulate at intersections between misfit dislocations. The spacing between those dislocation interactions
could therefore be optimised to influence the effectiveness of the interface as point defect sinks so that enhanced damage tolerance is achieved [35, 38]. In the case of the TiO(fcc)-V(bcc) system, the observed atomic ordering at the interface could effectively delay the He bubble growth, and also accommodate significant amounts of lattice defects and interstitial atoms at the interface, so that low-temperature embrittlement is minimised or delayed.

In conclusion, our atomic-resolution STEM imaging and analysis results have revealed the presence of an intergrowth of the TiO fcc and V bcc structures at the precipitate/matrix interface in the V-4Ti-4Cr alloy. The O atoms are primarily concentrated inside the nm-thick precipitates, where they seem to be homogeneously distributed, while the V/Ti superstructure atomic ordering can in some cases extend through the full thickness of the plate-like precipitates. This atomic-scale characterization of the local structure and chemistry of the interface and precipitate structure will assist the mechanistic understanding of the interaction of interstitials and radiation-induced lattice defects with the precipitate interface, and hopefully trigger the development of novel alloy structures with enhanced radiation tolerance.

We acknowledge the Engineering and Physical Sciences Research Council (EPRSC) for providing funding for this project via the Centre for Doctoral Training in the Science and Technology of Fusion Energy (http://www.fusion-cdt.ac.uk/), and also for providing access to the SuperSTEM Laboratory, the U.K. National Facility for Aberration-Corrected STEM (http://www.superstem.com/). S.J.H. would like to acknowledge EPSRC grant EP/M010619/1 as well as the defence threat reduction agency grant number HDTRA1-12-1-0013. We would also like to thank Matthew Smith for his valuable help with the FEI Titan microscope in Manchester.

References

Fig. 1. (a) TEM BF image of the V-4Ti-4Cr alloy microstructure with the plate-like precipitates viewed along the [001] zone axis. (b-d) HAADF images showing precipitates with (b) a uniform atomic structure, (c) a superstructure and (d) both uniform and superstructure regions. (e) The corresponding SADP of (a) with the V matrix and simple tetragonal (st) superstructure reflections highlighted. Precipitates with different proportions of superstructure fringes: (f) with superstructure at both long sides with the relative EDS spectrum images for (g) Kα Ti and (h) Kα V, (i) with superstructure at the short edge of the precipitates, and (j) with superstructure surrounding a region of uniform atomic structure. (k) BF image of a precipitate with dislocations pinned at the precipitate-matrix interface.
Fig. 2. (a-I) HAADF image showing a precipitate with regions of both uniform structure and superstructure and (a-II) related map of the plasmon peak. (b-I) EELS core loss and (b-II) EELS low loss spectra taken from the regions highlighted by the coloured squares in (a-I), corresponding to matrix (red), superstructure (black) and uniform precipitate (blue) structure regions. The fitted position of the main plasmon peak in the region of interest is reported in (a-II).
Fig. 3. (a-I) HAADF image showing a TiO precipitate with regions of both superstructure and uniform atomic structure. (a-II) to (a-IV) show the FFT and diffraction patterns taken from the regions outlined by the coloured squares in (a-I). (a-V) is the superimposed pattern containing the position of the spots in (a-II) to (a-IV). (b) Proposed crystal structure model relating the V bcc matrix structure to the TiO fcc (NaCl-type) precipitate and the superstructure (simple tetragonal ‘st’ of TiO with V). The lattice parameter of both TiO structures is indicated taking the lattice parameter (aV) of the V bcc matrix as reference.
Fig. 4. (a) HAADF image of the superstructure within the precipitate, (b) composite image constructed from the EELS maps generated by integrating the L2,3 edge intensity of V (red) and Ti (blue). (c) Atomic resolution detail of the region marked by the yellow rectangle in (a), with atomic positions superimposed inside the blue rectangle. (d) Crystal structure model showing two repeating units of the superstructure along the z-direction with the atomic pattern shown in (c) highlighted by the blue rectangle.
Detailed experimental conditions

We employed an FEI Titan G2 80-200 aberration-corrected S/TEM with an X-FEG and ChemiSTEM™ technology [1], i.e. four solid-state detectors for high EDS data collection efficiency. This instrument used an accelerating voltage of 200 kV and a probe current of 90 pA. The HAADF detector had a semi-angular range from 36 to 180mrad, and the EDS collection angle was 0.7 sr. We also used in this work a Nion UltraSTEM™ 100MC with C₃ Nion QO corrector, full correction up to six-fold astigmatism for high spatial resolution imaging, together with a high-energy-resolution monochromator for enhanced energy resolution [2]. For this microscope the accelerating voltage was 100 kV and the probe current after monochromation was 16-20 pA. The HAADF detector here covered a semi-angular range from 86 to 190 mrad, whereas the EELS detector covered a semi-angle of 44mrad and the dispersion was 0.02eV/channel. In both microscopes it is possible to achieve a spatial resolution < 0.08nm.


Simulation of the HAADF STEM image

The simulation has been performed using the QSTEM software package and the following input parameters: (a) beam energy 100kV, (b) convergence semi-angle 30mrad, (c) angles HAADF 80-240mrad, (d) foil thickness 18nm.

**Fig. A.1.** (a) Simulated HAADF STEM image of the precipitate superstructure, and (b) comparison with the atomic resolution experimental image in Fig. 4c of the article.
Electron diffraction patterns of the superstructure

**Fig. A.2.** Selected area electron diffraction patterns.

**Fig. A.3.** Nano-diffraction patterns.
Ti-rich precipitate evolution in vanadium-based alloys during annealing above 400°C

A. Impagnatiello\textsuperscript{ab,*}, T. Toyama\textsuperscript{c}, E. Jimenez-Melero\textsuperscript{a,b}

\textsuperscript{a}School of Materials, The University of Manchester, Manchester M13 9PL, UK
\textsuperscript{b}Dalton Cumbrian Facility, The University of Manchester, Moor Row CA24 3HA, UK
\textsuperscript{c}The Oarai Center, Institute for Materials Research, Tohoku University,

Oarai, Ibaraki 311-1313, Japan

\textbf{Corresponding author (*):}

Dalton Cumbrian Facility
University of Manchester
Westlakes Science & Technology Park
Moor Row
CA24 3HA
United Kingdom
Tel.: +44 1946 508860
Email: andrea.impagnatiello@postgrad.manchester.ac.uk
Contribution of the different co-authors

The samples were prepared by the main author A. Impagnatiello, who also analysed and interpreted the data with the assistance of all the co-authors. In particular, T. Toyama supervised his work during his stay in Japan, and taught A. Impagnatiello the operation of the PAS set-up. Atom probe tomography maps and relative FIB sample preparation were obtained with the help of K. Tomura and E. Ebisawa.

The main author wrote the manuscript together with E. Jimenez-Melero. T. Toyama provided feedback of the written manuscript before the journal submission.
Abstract

We have assessed the plate-like TiO precipitate evolution in V-4Ti and V-4Ti-4Cr alloys during isochronal annealing above 400°C, by combining Vickers hardness, positron lifetime and coincidence Doppler broadening measurements. Our results reveal the formation of additional TiO precipitates in both alloys at temperatures of 450-600°C in both alloys. The implanted positrons become trapped at the nm-thick TiO/matrix interface, and act as effective probes of the concomitant annealing of vacancies taking place inside the TiO precipitates above 550°C in V-4Ti alloy. The presence of Cr in the ternary alloy not only retards the recovery of dislocations, but also enhances the oxygen diffusivity and therefore decreases the vacancy content in the TiO precipitates. These results will impact the expected alloy stability and capacity to bind light elements in the operational temperature window of these alloys for fusion reaction applications.

Keywords: refractory metal, crystalline oxides, positron annihilation, electron microscopy, nuclear fusion reactor
1. Introduction

The future realization of magnetically-confined fusion reactors relies on the prior development and testing of reduced-activation engineering alloys for the first wall and divertor components of the reactor [1, 2]. Vanadium-based alloys stand out as promising first wall materials due to their low activation characteristics under fast neutron bombardment [3-6], in combination to their high temperature strength [6-9], void swelling resistance [10, 11] and compatibility with liquid metal coolants [12-14]. Cr is added to the material as an effective solid-solution strengthener that increases the thermal creep and oxidation resistance, while Ti enhances the void swelling resistance of the alloy [15]. The high temperature limit of ~700°C for safe operation of V-based alloys in fusion reactor conditions is controlled mainly by the material’s resistance to thermal creep and helium embrittlement. On the other hand, the low temperature limit is currently considered to lie at ~400°C, due to the significant low-temperature hardening and embrittlement caused by the presence of small amounts of O, C, and N and/or radiation-induced lattice defects in the matrix [9, 16, 17]. Furthermore, relatively high amounts of Cr + Ti (>10wt.%) also lead to additional embrittlement at low temperatures [18]. V-4Cr-4Ti is therefore widely considered as the reference vanadium alloy for structural applications in future nuclear fusion reactors [18, 19].

The presence of Ti in the material triggers the formation of ultra-fine Ti(C,O,N) precipitates during the thermo-mechanical processing of the material, and therefore improves the material’s resistance to low-temperature hardening and embrittlement, and also the workability and weldability of V-4Cr-4Ti [20, 21]. The precipitate density can be maximised by cold working prior to annealing, and the best impact properties are achieved by annealing at 900-950°C [22]. Welding V-based plate materials can dissolve part of the Ti-rich precipitates, and a post-weld heat treatment is recommended to recover the precipitate distribution and, consequently, the pre-weld values of the ductile-to-brittle transition
temperature [19]. Recent work on the low-temperature behaviour of V-4Cr-4Ti reveals the formation of additional Ti(C,O,N) precipitates below 400°C in the vicinity of radiation-induced dislocation loops [23]. This radiation-induced precipitation allows the optimal temperature window during annealing prior to irradiation to be extended up to 1000°C [24].

Despite the intensive efforts to optimise the precipitate characteristics for improved properties at low temperatures, limited information is available about the behaviour of those precipitates at intermediate temperatures, i.e. within the accepted temperature window (~400-700°C) for use of the V-4Cr-4Ti alloy in fusion reactor applications, and how any potential changes would affect mechanical properties and radiation resistance of this material. In this paper, we performed micro-hardness tests to monitor the microstructural changes above 400°C in this material containing Ti-rich precipitates, in combination with positron annihilation spectroscopy studies, since positrons are reported to present a relatively high affinity for the Ti-rich precipitates in the V-4Cr-4Ti alloy [23]. The potential influence of Cr on the structural stability is assessed by comparing the results for the V-4Ti and V-4Cr-4Ti alloys. This study constitutes the stepping stone to assess the precipitate stability at relevant reactor temperatures and radiation doses, and the consequences for the radiation tolerance and structural integrity of these low-activation materials.

2. Experimental

V-4Ti and V-4Cr-4Ti materials, named ‘V4Ti’ and ‘Val’ respectively, were solution annealed at 1100°C for 2 hours in inert atmosphere, followed by water quenching to room temperature. The resultant microstructure was characterized by combining scanning and transmission electron microscopy, and also atom probe tomography (APT) of selected precipitates. For transmission electron microscope (TEM) imaging and analysis discs were prepared by mechanical pre-thinning, followed by electro-polishing using an electrolyte of 60 vol.% methanol–35 vol.% 2-buthoxyethanol–5 vol.% perchloric acid (60%) at a temperature
of −35°C. We used the FEI Tecnai G2 F30 (FEG TEM) microscope operating at an accelerating voltage of 200kV. Needles with a tip diameter less than 100nm for APT were prepared using 30 keV Ga⁺ focused ion beam (FIB) milling [25]. The needles were prepared from cross section lamellae taken from the surface of electro-polished samples and lifted with an omniprobe device. The APT data was collected using the AMETEK-CAMECA LEAP 4000X HR equipment at a temperature of -223°C, with a pulse mode with UV laser at 50pJ and a pulse fraction of 200 kHz. The software program IVAS from Cameca Instruments Inc. was used to analyse the APT data.

Afterwards, samples of both alloys were isochronally annealed for 1.5 hours at selected temperatures between 200°C and 900°C, and subsequently quenched in water to room temperature. We measured the Vickers micro-hardness of the annealed samples using a load of 0.5kg and duration of 5s. Samples annealed at temperatures in the range of 500-700°C of both alloys, together with the reference room temperature condition, were also studied using Positron Annihilation Spectroscopy (PAS). For this experiment, positrons were emitted from a $^{22}$Na source having an activity of ~1MBq and sealed in Kapton foil. The source was placed between two equivalent vanadium samples. The positron lifetime spectra were obtained using a fast digital oscilloscope and two BaF$_2$ scintillator detectors, with a time resolution of ~180ps at full width at half maximum. For each spectrum we collected ~2.5-4 × 10$^6$ coincidence events. The data was corrected for the background and source contributions, and analysed using the PALSfit software package [26]. We also recorded the Coincidence Doppler broadening (CDB) spectra of the positron annihilation radiation using two high-resolution Ge detectors in coincidence. This arrangement enhances the signal to noise ratio by three orders of magnitude, as compared to the single-detector approach. We were therefore able to assess, using the high-momentum region of the CBD spectra, the positron annihilation with the core electrons of atoms in the vicinity of the positron trapping
site [27]. The overall momentum resolution was $\sim 4 \times 10^{-3} m_0c$, where $m_0$ denotes the electron/positron rest mass and $c$ is the speed of light. The CDB spectra for each sample were taken for 80k s with a total number of counts of $\sim 800k$, whereas the counting time for reference Ti and SiO$_2$ materials was 420k s, with a total number of counts of $\sim 40M$. From the recorded CBD spectra, we derived the line shape parameters, namely the S- and W-parameter, by taking the ratio of the low momentum ($|p_L| < 4 \times 10^{-3} m_0c$) and high momentum ($10 \times 10^{-3} m_0c < |p_L| < 18 \times 10^{-3} m_0c$) region of the spectrum to the total region, respectively. We also obtained the CDB ratio curves by normalizing the momentum distribution of each spectrum to that of a reference sample of either well-annealed Ti or SiO$_2$. The high momentum region of the CBD ratio curves manifests the presence of either Ti or O close to the positron trapping site [27-29].

3. Results

3.1. Initial microstructure

The room-temperature microstructure of both V-4Ti and V-4Cr-4Ti materials, after annealing at 1100°C for 2 hours, contains a relatively high density of precipitates. Fig. 1a show an SEM image of plate-like TiO precipitates present inside the grains of the V matrix. The interface between those precipitates and the matrix is characterised by a superstructure (Fig. 1b), which in some cases even extends through the full thickness of the precipitate (Fig. 1c). Our recent aberration-corrected STEM/EELS results revealed the atomic ordering of the V and Ti at the precipitate/matrix interface (Fig. 1d). This superstructure was interpreted in terms of the intergrowth of the TiO fcc and V bcc structures [30]. In addition to the plate-like precipitates, we have also observed the presence of a high density of cuboidal-shaped precipitates, which are mainly decorating the grain boundaries of the V matrix, see Fig. 2a. The chemical analysis of those precipitates using APT (Fig. 2b) confirms the TiO nature of these GB precipitates. However, they also contain relatively high amounts of C,
together with N in smaller quantities. Cuboidal-shaped precipitates were also observed inside the grains in the V matrix, but mainly in the vicinity of grain boundaries.

3.2. Behaviour during annealing

Fig. 3 shows the hardness values of both V-4Cr-4Ti and V-4Ti as a function of the annealing temperature. At room temperature, in the ‘as-quenched’ condition after the initial annealing at 1100°C for 2 hours, the hardness of the ternary alloy is higher due to the presence of Cr atoms in the matrix. The hardness remains constant up to 300°C in both materials. At higher temperature, the hardness in V-4Ti decreases, and only recovers the room temperature value when 500°C is reached. On the contrary, the hardness in V-4Cr-4Ti remains constant until 400°C, and above that temperature the hardness gradually increases and attains a maximum at 600°C. The V-4Ti alloy also presents a maximum in hardness at 600°C. However, this alloy presents a smaller increase in hardness with respect to the room temperature value, as compared to the ternary alloy. At temperatures higher than 600°C, the hardness in both materials gradually decreases, reaching values at 900°C even lower than at room temperature. This decrease in hardness is especially noticeable in the V-4Ti alloy.

In order to gain further insight into the processes taking place in both alloys during annealing in the temperature range of 500-700°C, we performed positron lifetime and CBD measurements at selected temperature in that range, and also at room temperature for both alloys and pure V as reference. Fig. 4 shows the values of the lifetime (τ) and line shape S-parameter for the studies samples. The lifetime values of the alloy samples lie in the range of 116-128ps, in close vicinity of the measured τ value for V of 117ps. Both the τ and S-parameter for the room temperature, 500°C and 550°C samples in the V-4Ti alloy are significantly higher than for the V-4Cr-4Ti samples, and shift to lower values when the annealing temperature is 600°C or higher. In contrary to the behaviour observed for the binary alloy, the values of both positron parameters remain closer to the values for V, and do
not reveal any clear trend with temperature. We have extracted additional information about
the positron local environment from the CDB data, by deriving the W-parameter from the
high-momentum region of the 511keV peak and the ratio curves with respect to Ti and SiO₂,
see Fig. 5 and 6 respectively. The data collected in both figures reveal that the values of the
W-parameter and the CBD ratios lie closer to Ti and SiO₂ in the case of V-4Ti, and shift
toward the ternary alloy and the V sample with increasing annealing temperature.

4. Discussion

V-4Ti and V-4Cr-4Ti alloys present an equivalent microstructure at room temperature,
after the initial solution annealing at 1100°C for 2 hours. Their microstructure contains a fine
dispersion of Ti-rich precipitates, with two types of morphologies and spatial distributions:
cuboidal-shaped precipitates [31] decorating or in the vicinity of the grain boundaries of the
V matrix, and plate-like precipitates [30, 32, 33] distributed within the grains of the V matrix.
The interface of the latter precipitates with the matrix is characterised by an intergrowth of
the bcc V and fcc TiO structures [30]. Both types of precipitates are primarily TiO, but
contain small amounts of C and N. These precipitates may have formed during cooling from
1100°C down to room temperature, by the transformation of the high temperature β-TiO to
α-TiO [34].

Despite the similarities in the starting precipitate characteristics and distribution of
both alloys at room temperature, the hardness dependence on the annealing temperature up to
900°C shows significant differences. The hardness in the V-4Ti alloy decreases in the
temperature range of 300-450°C. This reduction in hardness is not observed in the V-4Cr-4Ti
alloy. Previous work on the recovery and recrystallization of V samples with varying nitrogen
and oxygen levels showed that the dislocation-impurity interaction in vanadium is overcome
at 300°C or higher temperatures [35]. Therefore the softening observed in V-4Ti can be
attributed to an additional recovery of pre-existing dislocations at 300-450°C. However, in
V-4Ti-4Cr, the Cr atoms present in the matrix exert an effective pinning effect on the movement of dislocations [36, 37], and can therefore delay the recovery and the corresponding alloy softening at those temperatures. Furthermore, the presence of extra O atoms in the V matrix, due to O intake during the material’s processing or from the Li-based coolant during reaction operation, is expected to precipitate as plate-like TiO [32], and therefore induce additional hardening to these alloys. The diffusion of O interstitials in the V matrix is relatively fast; with a reported value for activation energy of 119.6-122.5 kJ mol\(^{-1}\) [38-40]. The presence of Cr in the matrix reduces the activation energy for oxygen diffusion by 10-15% [40]. Ti atoms tend to decorate dislocations in V-Ti alloys, and therefore experience an enhanced mobility due to pipe diffusion along dislocations, prior to the formation of Ti-rich precipitates [23, 34]. The increase in hardness in both alloys at temperatures of ~400-600°C can therefore be attributed to the additional formation of Ti-rich precipitates. Further increase in temperature above 600°C leads to the precipitate coarsening destabilization and subsequent dissolution.

Once implanted in the sample and thermalized, the positron can become trapped by existing open volume lattice defects. The reduced electron density at the trapping site increases the positron lifetime with respect to the bulk lifetime. Not only vacancy-like defects form attractive potentials for positrons but also metallic clusters or precipitates, as long as their positron affinity for those is higher than for the surrounding material. In the case of the V-Cr-Ti system, the positron affinity for Cr is lower than for either V or Ti, and has recently been reported to be relatively high for the Ti-rich precipitates [23, 41]. In our study, the measured positron lifetime in each of the studied samples remain close to the value for the V sample of \(\tau = 117\) ps [42]. We have only detected one component in the lifetime spectrum, which could be the average value of positrons annihilating in the bulk V matrix and in open volume defects. The lifetime of positrons trapped in vacancy cluster is higher than in the bulk,
and its value increases with the number of vacancies in the cluster [29]. Our results yield values for the positron lifetime that are in all cases higher, but relatively close to the value for vanadium. This means that a fraction of the positrons are annihilating at mono-vacancies. This is confirmed by the higher values of the S-parameter encountered in the samples of both V-4Ti and V-4Cr-4Ti. The fcc structure of TiO-type precipitates can host up to approx. 15% of vacancies [43, 44] and also small amounts of C and N [45]. Therefore, a significant fraction of the implanted positrons will be annihilating at vacancy-type defects present either in the TiO layer of the precipitate/matrix interface or inside the precipitates. The decrease in both the positron lifetime and the S-parameter in V-4Ti when the temperature is higher than 550°C can be attributed to the annealing of vacancies associated with the TiO precipitates [34].

The decrease in the S-parameter takes place simultaneously with an increase in the W-parameter that characterises the high-momentum region of the CDB spectrum. This region of the spectrum, together with the CBD ratio with respect to reference materials such as Ti or SiO₂, contains additional information about the nature of the atoms surrounding the positron trapping side [28, 46]. The results in Fig. 5 and 6 reveal that the local environment of the positron trapping site has a higher fraction of Ti and O in the binary alloy, and shifts towards a higher presence of V atoms with increasing temperature. The values derived for the ternary alloys at the studied annealing temperatures are all closer to the values of the V sample. The relative positron affinity for the mono-vacancies in the fcc TiO layer and for the bcc V-type layer, both forming the intergrowth in the plate-like precipitates, lead to the observed trends in the W-parameter and CBD ratios. The vacancy content in TiO depends on the annealing temperature, and also on the O diffusivity that is enhanced in the presence of Cr atoms in the V matrix [34]. The decrease in the S-parameter and the concomitant increase in the W-parameter observed in the V-Ti alloy with increasing annealing temperature is not clearly
observed in the V-4Cr-4Ti, most likely due to the enhanced O diffusivity and therefore lower vacancy content in the TiO precipitates.

5. Conclusions

We have studied the evolution of the Ti-rich precipitates present in V-4Ti and V-4Cr-4Ti alloys during isochronal annealing, by combining Vickers hardness, positron lifetime and coincidence Doppler broadening measurements. Our results reveal that the local atom probe characteristics of the implanted positrons are suitable to monitor the annealing of vacancies in plate-like TiO precipitates, esp. at the interface with the surrounding matrix. The presence of Cr in the material both retards the recovery of pre-existing dislocations in V-4Cr-4Ti and enhances the O diffusivity, and consequently increases the oxygen content in the precipitates. Additional precipitate formation takes place in both alloys materials above 400°C, whereas the annealing of vacancies, present in the TiO precipitates, above 550°C is observed only in the V-4Ti alloy.

Acknowledgements

We acknowledge the Engineering and Physical Sciences Research Council (EPRSC) for providing funding for this project via the Centre for Doctoral Training in the Science and Technology of Fusion Energy (http://www.fusion-cdt.ac.uk/). The work described was supported in part by the Dalton Cumbrian Facility Project, a joint initiative of The University of Manchester and the Nuclear Decommissioning Authority. A.I. would also like to thank the Tohoku University for the travel grant to perform PAS experiments at its facilities.

References


Fig. 1. (a) SEM image of the plate-like precipitate distribution in V-4Cr-4Ti alloy, TEM HAADF image of (b) superstructure and uniform regions inside the precipitates, and (c) superstructure region extending through the thickness of the precipitate, (d) composite image constructed from the EELS maps generated by integrating the L2,3 edge intensity of V (red) and Ti (blue). Data in (b)-(d) taken from ref. [30].
**Fig. 2.** (a) SEM image of V-4Cr-4Ti alloy showing the distribution of cuboidal-shaped precipitates at the grain boundaries of the V matrix, and (b) atom probe tomography maps for different elements and relevant compounds of a selected cuboidal-shaped precipitate.
Fig. 3. Variation of the Vickers hardness with annealing temperature for both V-4Cr-4Ti and V-4Ti alloys.
Fig. 4. CDB line shape S-parameter as a function of the positron lifetime (τ) for V-4Cr-4Ti and V-4Ti alloys annealed at different temperatures, together with the room-temperature values for a reference V sample.
Fig. 5. (a) W-S plot containing data for V-4Cr-4Ti and V-4Ti alloys annealed at different temperatures, together with data for reference V, Ti, Cr and SiO₂ samples, (b) enlarged view of the V-containing samples.
Fig. 6. CBD ratio curves for V-4Cr-4Ti and V-4Ti alloys, both at room temperature and after annealing at 700°C for 1.5 hours, taken as a reference material (a) pure Ti and (b) SiO2. The inset show the high-momentum region of the curves.
Monolayer-thick TiO precipitation in V-4Cr-4Ti alloy induced by proton irradiation

A. Impagnatiello\textsuperscript{a,b,*}, S.M. Shubeita\textsuperscript{b}, P.T. Wady\textsuperscript{b}, I. Ipatova\textsuperscript{a,b}, H. Dawson\textsuperscript{a}, C. Barcellini\textsuperscript{a,b}, E. Jimenez-Melero\textsuperscript{a,b}

\textsuperscript{a}School of Materials, The University of Manchester, Manchester M13 9PL, UK

\textsuperscript{b}Dalton Cumbrian Facility, The University of Manchester, Moor Row CA24 3HA, UK

**Corresponding author (\#):**

Dalton Cumbrian Facility
University of Manchester
Westlakes Science & Technology Park
Moor Row
CA24 3HA
United Kingdom
Tel.: +44 1946 508860
Email: andrea.impagnatiello@postgrad.manchester.ac.uk
**Contribution of the different co-authors**

The samples were prepared by the main author A. Impagnatiello. S.M. Shubeita and P.T. Wady set up the required instrumentation to perform the proton irradiations of the V samples, and supervised the process together with the experimental officers for the ion accelerator A.D. Smith and N. Mason. Additional assistance during the irradiation experiments was provided by I. Ipatova, H. Dawson and C. Barcellini.

The main author wrote the manuscript together with E. Jimenez-Melero. S.M. Shubeita, P.T. Wady and H. Dawson provided feedback of the written manuscript before the journal submission.
Abstract

We have characterised with atomic resolution the mono-layer thick TiO-type precipitate induced by proton irradiation in V-4Cr-4Ti alloy at a dose of 0.3dpa and a temperature of 350°C. Its formation coincides with the coarsening radiation-induced interstitial a/2⟨111⟩ dislocation loops that are already present at 300°C. The dislocation network induced by prior cold work is mostly recovered at 300°C and 0.3dpa, and is therefore expected to exert a minimal effect on the precipitate formation. This monolayer-thick precipitate constitutes an early stage in the radiation-induced aging process of V-4Cr-4Ti at low temperatures, and can potentially absorb additional light elements in reactor environments.

Keywords: refractory metal, precipitation, lattice defects, high-resolution electron microscopy, nuclear fusion reactor
Vanadium-based alloys currently constitute advanced candidate materials for the first wall of future fusion reactors such as DEMO [1, 2]. In particular, V-4Cr-4Ti alloy offers an outstanding combination of high-temperature strength and radiation resistance [3-5], coupled with low neutron activation [6, 7] and corrosion resistance to liquid metal coolants [8-10]. However, the presence of relatively small amounts of light atoms in the matrix can drastically increase the ductile-to-brittle transition temperature, and consequently also the minimum temperature for safe use of this alloy in structural components of the reactor [11, 12]. Ti acts as an effective scavenger for light elements, by forming Ti(O,C,N) precipitates during the material’s processing [13]. Cold working prior to annealing can be used to minimise the coarsening of the precipitates and increase the thermal creep resistance of the alloy [14]. Additionally, the interface of those nano-scale precipitates with the matrix can act as an effective sink for mobile lattice defects [15, 16]. Therefore, the radiation–induced hardening and embrittlement that take place in V-4Cr-4Ti below 400°C and at dose levels as low as 0.1-0.5dpa can be reduced.

Neutron irradiation of V-4Cr-4Ti alloy at temperatures below 275°C induces the formation of a high density of faulted dislocation loops with a Burgers vector of $a/2 \angle 110$ and an average size of ~3nm. These small dislocation loops present a barrier strength lower than the Orowan value for impenetrable obstacles during dislocation gliding, and facilitate the formation of 50nm-wide cleared dislocation channels on {110} slip planes at those low temperatures. This channel formation causes a pronounced loss of strain capability and uniform elongation in the V-4Cr-4Ti alloy. At higher irradiation temperatures, $a/2 \langle 111 \rangle$ unfaulted dislocation loops predominate in the microstructure. They attain a larger average size of ~200nm, whereas their density is reduced to $< 10^{20}/m^3$ [17]. In parallel to the occurrence and evolution of dislocation loops with temperature, recent positron annihilation results revealed the presence of Ti-vacancy complexes in the vicinity of the radiation-induced
dislocation loops below 300°C [18]. These complexes may act as precursors for the formation at higher temperatures of Ti-rich Radiation-Induced Precipitates (RIPs). The growth of the additional precipitates induced by radiation may occur by changing their morphology from sphere to platelet, and also the O/Ti ratio [19]. And enhanced V content has also been reported in some of these RIPs [20]. Despite the key role of the RIPs in improving the radiation resistance of V-4Cr-4Ti in the low temperature regime, a detailed characterization of their structure and elemental content, especially at the interface with the surrounding matrix, is still required to improve the alloy resistance in radiation environments. The potential effect of pre-existing dislocations due to prior cold working on the precipitate formation should also be assessed. In this paper, we address these points by using proton irradiation as a surrogate to neutron damage, in combination with high-resolution electron microscopy to characterise both the RIPs and the presence of dislocation structures in the matrix. This study provides a comparison of proton irradiated microstructures with and without prior cold work. Generally speaking for other types of materials, the presence of dislocations due to cold work would favourably increase radiation resistance at relatively low dpa levels, since the dislocations would trap and slow down the diffusion of radiation-induced point defects [21, 22]. Cold work can also be induced during the manufacturing of the reactor components, so understanding the effect of cold work on materials that will be under irradiation becomes even more important.

Equivalent V-4Cr-4Ti (wt.%) samples were solution-annealed (SA) at 1100°C for 2 hours and afterwards water quenched to room temperature. Some of the material was afterwards 10% cold rolled (SACW). The sample surface was ground to 4000 grit SiC paper, and then electro-polished using an electrolyte of 60vol.% methanol – 35vol.% 2-buthoxyethanol – 5vol.% perchloric acid (60%) at a temperature of -35°C. After that, the samples were irradiated with a 1.4MeV proton beam produced using the 5 MV tandem ion
accelerator of the Dalton Cumbrian Facility [23]. The beam current deposited on the samples was \( \sim 28 \mu A \), and the damage rate was \( 3 \times 10^6 \text{ dpa/s} \). We achieved a particle fluence of \( \sim 1.6 \text{ protons/m}^2 \), which is of the same order of magnitude of the neutron fluence expected in the first wall of the DEMO reactor. The temperature during irradiation (either 300 or 350°C) was monitored both with welded thermocouples on the sample surface adjacent to the irradiated area, and also with a non-contact pyrometer. For transmission electron microscope (TEM) imaging and analysis discs were prepared by mechanical pre-thinning, followed by electro-polishing using the same electrolyte and temperature as mentioned before. In order to characterise the damaged structure, we used a FEI Tecnai T20 with LaB\(_6\) crystal and an FEI Titan G2 80-200 aberration-corrected S/TEM with an X-FEG and ChemiSTEM\textsuperscript{TM} technology [24], both microscopes operating at 200 kV. The thickness of the disc area studied by TEM was derived from the fringes spacing of the convergent beam electron diffraction pattern, the interstitial or vacancy nature of the defects using the inside-outside method, and the Burgers vector from the \( \mathbf{g} \cdot \mathbf{b} = 0 \) invisibility criterion [25, 26]. Vickers hardness measurements were taken using a load of 0.025 g, resulting in an indentation depth of \( \sim 8 \mu m \), which is close to the 60% of the Bragg peak position from the irradiated sample surface.

The initial (SA) microstructure contained a fine dispersion of plate-like Ti(O,C,N) precipitates [27], together with a number of cuboidal Ti-rich precipitates decorating the grain boundaries of the matrix. Fig. 1a shows a scanning electron micrograph of the cross section of the SA sample surface irradiated at 350°C. The large plate-like precipitates formed during prior annealing treatment are clearly visible in the image. A relatively bright line at \( \sim 15 \mu m \) below the sample surface can be observed passing through two neighbouring grains of the matrix. The position of this bright line agrees well with the Bragg peak position of 14 \( \mu m \) calculated using the SRIM software [28], see Fig. 1b. In the region of the Bragg peak, the lattice is mostly damaged, the channelling of electrons is more impeded and therefore the
BSE signal increases. We have prepared TEM discs of the irradiated samples at a depth of 60% of the Bragg peak position from the sample surface. This corresponded approximately to an 8 μm depth from the surface and a damage dose of 0.3 dpa in the studied samples.

Fig. 2 shows the TEM images of the SA and SACW samples, both before and after having been irradiated up to 0.3 dpa at a constant temperature of 300°C. Before irradiation and cold work, the prior annealing at 1100°C led to a microstructure free from the dislocation networks and other defects that are instead present after 10% cold work. After irradiation, dislocation loops are present in the SA sample with a density of ~1.1×10²²/m³. The majority of these loops have a Burgers vector of a/2 (111) and their average size is 12 nm. A slightly lower density of dislocation loops is present in the SACW sample after irradiation, namely ~0.9×10²²/m³, and their average diameter of 14 nm is close to the value for the SA sample. It is remarkable that the pre-existing dislocation network in the SACW sample is mostly recovered after irradiation.

The damaged microstructure of the SA sample after irradiation up to 0.3 dpa at 350°C is shown in Fig. 3a. Interstitial a/2(111) dislocation loops are also present in the microstructure. They are characterised by a larger average diameter of 86 nm and a lower density of ~2.1×10²¹/m³, as compared to the dislocation loops observed at 300°C. However, at 350°C we also observed new plate-shaped RIPs, oriented along the {100} planes of the V matrix. They appear with an average length of 56 nm and a density of ~1.5×10²¹/m³. Fig. 3b and c show a higher-resolution image of the RIPs. The precipitates seem to be composed of only one atomic layer. Chemical analysis using energy-dispersive spectroscopy confirmed the presence of Ti. These results suggest that these observed RIPs correspond to TiO-type precipitates with lattice parameter of 0.42 nm [27, 29] and the Baker–Nutting orientation relationship with the matrix [30]: [001]_{TiO} // [001]_{V}, (110)_{TiO} // (100)_{V}. Assuming that the
RIPs own that crystal structure, it allows us to propose in Fig. 3e-f a crystal model of the plate-like precipitates that is consistent with the atomic resolution TEM data of Fig.3c-e.

Table 1 summarises the microstructure of the irradiated samples in terms of average size and density of RIPs and dislocation loops, together with the change in hardness due to irradiation. The number of dislocation loops in the SACW sample is somewhat lower than in the SA at 300°C. The dislocation network in SACW has not completely recovered after irradiation, and may have reduced the mobility of the radiation-induced point defects that eventually form dislocation loops. As reported for cold-worked irradiated steels, a significant reduction of the initial dislocation network is required for the development of observable dislocation loops [31]. Irradiation at higher doses would be required to understand the evolution of pre-existent dislocations and the conditions to achieve their full recovery at the relatively low temperature of 300°C. In this alloy recovery occurs during annealing above 400°C in absence of irradiation [32]. Furthermore, the hardness values of the SA and SACW samples after irradiation lie very close. This is due to their dislocation structures after irradiation being also very similar. Taking into account that the cold work raised the hardness of the material before irradiation, the hardness change after irradiation seems to decrease with the amount of cold work prior irradiation. In conclusion it appears that initial 10% cold work does not affect significantly the final hardness of the alloy after irradiation.

Dislocation loops found in all the irradiated samples were of interstitial nature, consistent with previous work on neutron irradiated V-4Cr-4Ti in this temperature range [17]. They are unfaulted and the predominant Burgers vector is \( \frac{a}{2} \{111\} \). Faulted dislocation loops with a Burgers vector of \( \frac{a}{2} \{110\} \) was reported for temperatures below 300°C in neutron-irradiated samples. Molecular dynamic simulations previously showed that this latter type of dislocation loops has a relatively high formation energy and become unstable at high temperatures [33]. The increase in irradiation temperature from 300°C to 350°C causes a
reduction in the density of dislocation loops and an increase in the average size of the loops. As a consequence, the irradiation-induced hardening of the alloy diminishes with increasing temperature above 300°C. A higher density of loops at 300°C implies more obstacles to the motion of dislocations and, as a consequence, an enhanced irradiation hardening [17].

The appearance of Ti-rich RIPS at a radiation dose of 0.3 dpa occurred between 300°C and 350°C, in agreement with previous neutron irradiation experiments [18]. In non-irradiated conditions, the formation of plate-like Ti(O,C,N) precipitates is induced above 500°C by climbing dislocations during recovery [35]. Proton irradiation at lower temperatures has triggered the formation of dislocation loops, and at 350°C also the formation of additional plate-like TiO-type precipitates. The radiation-induced mobile vacancies would increase the diffusion of substitutional Ti atoms, and the occurrence of Ti-vacancy complexes close to the dislocation loops, where the additional TiO-type precipitates form [17, 18]. The crystal structure model in Fig. 3e describes the precipitate platelet as a fcc TiO monolayer, whose interface with the V matrix is coherent along the sides of the platelet. This monolayer platelet could evidence that the proposed Ti spherical clusters [19] evolve to a platelet Guinier-Preston (GP) zone visible with TEM techniques. The GP zone would finally evolve to a thicker plate as the dose is increased. The thickness of these TiO-type plates has been reported to be ~1-3 nm at a neutron radiation dose of 4 dpa and a temperature of ~510°C [36]. This precipitation sequence is similar to the precipitation behaviour observed in Al-Cu alloys during annealing at 130°C, where monolayer, bilayer and multilayer Cu-rich plate-like precipitates correspond to different stages of hardening during aging [37]. Therefore, the initial Ti-vacancy clusters, the monolayer platelet reported in this work, and the multilayer TiO-type precipitates characterize different stages of radiation-induced precipitation hardening in the V-4Cr-4Ti alloy.
In conclusion, our results on proton-irradiated V-4Cr-4Ti alloy lie in accordance with the nature and evolution of dislocation loops observed in the same alloy irradiated with neutrons at equivalent temperatures. Our TEM data also revealed that the dislocation networks induced by prior cold work are mainly recovered at 300°C and a radiation dose of 0.3 dpa. Therefore those pre-existing dislocations exert a minor effect on the formation of radiation-induced TiO-type plate precipitates observed at 350°C. Our high-resolution TEM data allowed us to characterise the monolayer-thick TiO precipitate. This precipitate constitutes an early stage in the radiation-induced aging process of V-4Cr-4Ti at relatively low temperatures, and therefore possesses the capacity of absorbing additional light elements in fusion reactor operation conditions.

We acknowledge the Engineering and Physical Sciences Research Council (EPRSC) for providing funding for this project via the Centre for Doctoral Training in the Science and Technology of Fusion Energy (http://www.fusion-cdt.ac.uk/). The work described was supported in part by the Dalton Cumbrian Facility Project, a joint initiative of The University of Manchester and the Nuclear Decommissioning Authority. We would also like to thank A.D. Smith and N. Mason for their assistance during the irradiation experiment.

References


Fig. 1. (a) SEM (BSE, 30keV) image of the cross section of the solution-annealed V-4Cr-4Ti alloy irradiated up to 0.3 dpa at 350°C, and (b) simulated damage profile using the SRIM software and the total current deposited on the sample during the irradiation experiment. The asterisk locates the depth equal to 60% the Bragg peak position, and denotes the region in the sample from where TEM foils were prepared.
Fig. 2. TEM images of the microstructure of the solution annealed (SA) and SA+10% cold worked (CW) samples, before and after proton irradiation up to 0.3 dpa at 300°C. The arrows show the g 200 direction.
Fig. 3. (a) Microstructure of the solution-annealed sample after undergoing proton irradiation up to 0.3 dpa at 350°C, (b) detail from (a) of Ti-rich radiation induced precipitates aligned along the [100] direction of the vanadium matrix, together with a number of dislocation loops, (c) atomic-resolution image of the region outlined by the square in (b), (d) atomic-resolution detail of the region outlined by the square in (c) where the position of the Ti and V atoms are indicated by blue and red circles, respectively, (e) upper and (f) 3-D view of the crystal structure model of the plate-like precipitate shown in (c) and (d). (a) was obtained in TEM mode, whereas the (b-d) were collected in STEM mode. In all images, B = [001] and g 200 lies parallel to the scale bar.
Table 1. Average size and density of the dislocation loops and irradiation-induced Ti-rich precipitates observed in the irradiated V-4Cr-4Ti samples, together with the initial hardness value (HV<sub>i</sub>) and the change in hardness due to proton irradiation (ΔHV<sub>irr</sub>).

<table>
<thead>
<tr>
<th>Sample condition</th>
<th>HV&lt;sub&gt;i&lt;/sub&gt;</th>
<th>T&lt;sub&gt;irr&lt;/sub&gt;(°C)</th>
<th>dose (dpa)</th>
<th>ΔHV&lt;sub&gt;irr&lt;/sub&gt;</th>
<th>Dislocation loops</th>
<th>Irr. induced Precipitates</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>average size(nm)</td>
<td>density ( \times 10^{21}/m^3 )</td>
</tr>
<tr>
<td>SA</td>
<td>196±8</td>
<td>300</td>
<td>0.3</td>
<td>130±19</td>
<td>12</td>
<td>11</td>
</tr>
<tr>
<td></td>
<td>196±8</td>
<td>350</td>
<td>0.3</td>
<td>90±18</td>
<td>85</td>
<td>2.1</td>
</tr>
<tr>
<td>SA + 10%CW</td>
<td>217±13</td>
<td>300</td>
<td>0.3</td>
<td>104±26</td>
<td>14</td>
<td>9.0</td>
</tr>
</tbody>
</table>
8. CONCLUSIONS

The formation and structure of TiO-type precipitates has been studied in the V-4Cr-4Ti alloy, together with the precipitate stability and evolution at high temperatures and under radiation fields. The structure and local chemistry of plate-shaped precipitates larger than 1μm in length and less than 100nm in width are addressed for the first time with atomic resolution. The results reveal the presence of an ordered intergrowth of the fcc TiO and the bcc V structures at the precipitate(matrix interface. In some cases the intergrowth extends through the full thickness of the plate-like precipitates.

These precipitates can contain a large number of vacancies that may prove useful to trap interstitials from the matrix and therefore improve the mechanical properties of these alloys under irradiation. The presence of vacancies in those precipitates has been confirmed by positron annihilation spectroscopy in samples annealed at different temperatures. This phenomenon has been observed primarily above 550°C and in the V-4Ti alloy. The presence of Cr in the V-4Cr-4Ti alloy enhances the O diffusivity, and consequently increases the oxygen content in the precipitates and fills most of the pre-existing vacancies.

Cr also retards the recovery of initial dislocations in the V-4Cr-4Ti alloy. However, the dislocation networks induced by prior cold work are mainly recovered after proton irradiation up to a dose of 0.3 dpa and at a constant temperature of 300°C. The increase in irradiation temperature to 350°C leads to the formation of radiation-induced plate-like TiO precipitates of ~50 nm in size. Atomic resolution images of those precipitates are provided for the first time. The precipitates form in the vicinity of a/2 <111> dislocation loops, induced by irradiation even at the lower temperature of 300°C. In the absence of irradiation, positron annihilation spectroscopy and micro-hardness measurements detected the formation of additional TiO-type precipitates at temperatures higher than 400°C.
FURTHER STUDIES

Phase diagrams (section 2.2.2) provide sights for different interpretation of the addressed phenomena that are worth to investigate. The Ti-O system shows a very complex situation at higher temperatures around 50 at. % of Ti. During annealing is so possible that the crystal structure and stoichiometry of the TiO undergoes to changes which should be investigated by transmission electron microscopy or X-ray diffractometer with heating stage in-situ. For example, the increase of hardness at 500°C can be related to the crossing of the eutectic line at 465°C. The appearance of V oxides at higher temperature is suggested by the V-Ti-O phase diagram. They have crystal structures very similar to the Ti oxides and their coexistence with these latter would play an important role in the formation of the V-Ti intergrowth present at the nm-thick TiO precipitate/matrix interface.

Future studies with proton and neutron irradiation over samples with and without this intergrowth will aim also to investigate if this novel feature can act as an effective sink for radiation-induced lattice defects and transmutant H/He atoms, and therefore enhance the radiation tolerance of the V-4Cr-4Ti alloy, as candidate material for the reactor of DEMO.