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Significantly Improving the Oxidation and Spallation Resistance of a MCrAlY Alloy by Controlling the Distribution of Yttrium

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Abstract

The NiCoCrAlY alloy with uniform yttrium distribution was fabricated via powder milling and spark plasma sintering. After powder milling, yttrium was uniformly distributed in the alloy in the form of Ni-Y precipitates (50 to 150 nm) and nano-sized Y₂O₃ particles (5 to 30 nm). It was found that the uniform yttrium distribution could: 1) lower thermally grown oxides (TGO) growth rate; 2) reduce the growth stress in the TGO; 3) suppress S segregation to the interface and the formation of interfacial imperfections (e.g. oxide intrusions, pores). Consequently, the oxidation and spallation resistance of the TGO was significantly improved.

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1. Introduction

MCrAlY (M=Ni, Co) alloys are widely used as the protective coatings for superalloy components due to their exceptional oxidation and corrosion resistance at high temperature [1, 2]. Such application relies on the capability of the coatings to form a continuous, adherent and slowly growing alumina scale. Upon cooling, high levels of residual stress develop in the thermally grown oxide (TGO), primarily because of its thermal expansion misfit with the metal substrate. The large stress and the associated strain energy in the TGO could motivate spallation once a certain thickness is reached (the elastic strain energy scales with the TGO thickness) [3]. Meanwhile, the MCrAlY/TGO interfacial toughness decreases with thermal exposure, mainly induced by detrimental sulfur segregation to the interface and the growth of imperfections (e.g. pores and oxide intrusions) [4, 5]. In this regard, reducing the TGO growth rate and improving the interfacial adhesion are crucial to increasing the durability of the TGO.

It is well established that the oxidation performance of MCrAlY alloys is substantially affected by the minor additions (<1 wt%) of reactive element (RE) Y, i.e., so called reactive element (RE) effect [6-9]. The primary mechanisms of RE-effect are elaborated as follows: (1) Y actively reacts with and ties up sulfur, which prevents the interfacial segregation and slows down the degradation of interfacial toughness [10-13]; (2) The outward transport of Al is suppressed due to the “block effect” induced by segregation of Y to the TGO grain boundaries, thus lowering the TGO growth rate [12]. Therefore, it is expected that a uniform yttrium distribution in the MCrAlY alloys is desirable for maximizing such beneficial effect. Nevertheless, it is extremely difficult to obtain a uniform yttrium distribution in the MCrAlY alloys using conventional processing techniques [7, 8, 14]. The localized enrichment of Y in the MCrAlY alloy promotes the formation of second-phase precipitates (primarily as

Ni-Y precipitates) due to the low solubility of yttrium [7, 8, 14]. The presence of the Ni-Y precipitates increases the number of Y-Al oxides incorporated into the TGO, as well as Y-enriched oxide intrusions at the TGO/substrate interface [2, 7, 15], resulting in a couple of detrimental effects. Firstly, the Y-Al oxides provide short-circuit paths for inward oxygen transport, thereby accelerating the TGO growth [2, 7, 8, 16, 17]. The fast growing TGO increases the driving force, i.e., elastic energy, for TGO spallation. Secondly, the oxide intrusions could be the preferable nucleation sites of initial interface delamination. When the oxide intrusions at the interface reaches to a critical size, cracks would initiate and propagate along the interface [15, 17, 18].

To date, only a few attempts have been made to alleviate the incorporation of Y-Al oxides into the TGO or suppress the growth of Y-rich oxide intrusions at the TGO/metal interface. It was reported that deposition of a platinum (Pt) over-layer on a NiCoCrAlY bond coat could inhibit the formation of oxide intrusions, resulting in an increase of coating lifetime [19]. Nevertheless, the mechanism is not clear yet and the industrial applications of this method are limited due to the high cost of Pt. Recently, it was reported that the excessive incorporation of Y-Al oxides into TGO can be suppressed when Y is uniformly distributed in the MCrAlY alloy in the form of fine, sub-micron Y-enriched oxides [7]. While the low TGO growth rate is observed, the underlying mechanism is not well understood. On the other hand, it has been reported that a small β -NiAl grain size ($< 3 \mu\text{m}$) is helpful to reduce the number of oxide intrusions at initial oxidation stage (< 1 hour) [20]. Nevertheless, this beneficial effect is undercut during the subsequent long term oxidation, as the β -NiAl grains will inevitably coarsen during the thermal exposure [15]. Based on the discussion above, the distribution and form of Y in the alloy are of great importance to TGO growth and interface adhesion. Understanding this point can help develop a high performance coating for thermally loaded components.

In this contribution, we report a simple and effective approach to improve the oxidation performance of a MCrAlY alloy by controlling the Y distribution. The

uniform Y distribution was achieved by powder milling and spark plasma sintering (SPS). It will be demonstrated that compared with the counterpart prepared from the pristine powder, the NiCoCrAlY alloy prepared from the milled powder exhibits a significantly lower oxidation rate and a much longer TGO spallation lifetime. Extensive characterization of the TGO microstructure, growth rate, stress, composition and spallation lifetime is conducted to understand the effect of Y distribution on oxidation in great details. The mechanisms of the improved oxidation performance of the NiCoCrAlY alloys are discussed in relation to the distribution and form of Y.

2. Material and methods

2.1 Sample preparation

Commercially available NiCoCrAlY (Ni-23Co-17Cr-12Al-0.5Y in wt. %) powder (Amdry 365-2, Sulzer Metco) was used as the starting material. Ball milling of the powder was performed at a rotation speed of 400 rpm for 24 hours in an argon atmosphere. The milling was interrupted every 20 min to minimize the temperature increase. The milled and as-received powder were subsequently sintered by SPS at 1050 °C for 10 min under a pressure of 50 MPa in vacuum (10^{-3} Pa), with a heating rate of 100 °C/min.

2.2 Oxidation test

The alloys were cut into $10 \times 10 \times 3 \text{ mm}^3$ square plates using a SiC abrasive cutting blade in a precision cut-off machine (Accutom 5, Struers). All the samples were ground with SiC abrasive papers and polished using 0.05 μm colloidal alumina. Prior to oxidation, all samples were ultrasonically cleaned in acetone and dried subsequently. The polished samples were cyclically oxidized at 1100 °C using a chamber furnace in a laboratory atmosphere. Each cycle consisted of 12 hours “hot time” at 1100 °C followed by air cooling for approximately 10 min.

Isothermal mass gains tests were performed using a thermogravimetric analyzer (TG, SETARAM, K/SETEVO16-1A) at a temperature of 1100 °C for 100 h. The alloys were cut into $2 \times 6 \times 12 \text{ mm}^3$ rectangular plates. All the samples were ground with SiC abrasive papers and polished using 0.05 μm colloidal alumina. Then the samples were placed in an alumina crucible hung up in the hot zone of the TG chamber. The heating and cooling rate were all 20 °C/min, and the recorded data began from the dwelling time.

2.3 Characterization

Scanning electron microscopy (SEM, FEI Nova Nano 230, Netherlands) was employed to characterize the microstructure of the samples. Chemical and phase analyses were executed using energy dispersive X-ray spectroscopy (EDS, Oxford Instruments) and X-ray diffraction (XRD, Ultima IV, Rigaku, Japan). An electron backscatter diffraction (EBSD, Oxford Aztec HKL Max) system fitted in the SEM was employed to measure the grain size. EBSD data was analyzed and processed by HKL Channel 5 software.

In order to examine the distribution and form of Y within the alloy prepared from the milled powder in greater details, thin lamellae of the alloy was prepared by a focused ion beam (FIB, GAIA3, Tescan, Czech Republic) and was analyzed using a transmission electron microscope (TEM, TALOS F200X, FEI, USA) equipped with an EDS system (XIS Ultra DLD, Kratos, Japan). The details of TEM sample preparation can be found elsewhere [21].

The quantitative depth profiles of elemental composition through the TGO to the metal substrate near the interface were determined by radiofrequency glow discharge optical emission spectroscopy (GD-OES, GDA750HP, Germany). The concentration of every single element of interest was quantified by comparing the measurement results of the alloy samples with those of the certified calibration samples that were

commercially available. The measurements were performed using argon gas plasma with a radiofrequency power and pressure of 20 W and 2.5 hPa, respectively.

The residual stress in the TGO was measured using the photoluminescence piezospectroscopy (PLPS) technique based on a Raman microscope (LabRAM HR, Horiba Jobin Yvon, France). Nd:YAG laser with a wavelength of 532 nm was used as the excitation source. The laser beam was focused on the surface of the TGO through a $\times 50$ lens with a spot size of $\sim 3 \mu\text{m}$. The spectra were fitted using mixed Gaussian-Lorentzian functions (Labspec software) to obtain the peak positions. The reference sample (stress free) was spalled TGO debris.

3. Results

3.1 Microstructures of the NiCoCrAlY powder before/after milling

The morphologies of the NiCoCrAlY powder before and after milling are shown in Fig. 1. Most of the as-received powder exhibits a spherical shape and has a particle size ranging from 46 to 85 μm ($d_{50} = 62 \mu\text{m}$), as presented in Fig. 1a. The as-received powder mainly contains two phases (Fig. 1c), identified as the face-centered cubic (fcc) γ -phase (a solid solution of Ni, Co and Cr) and the body-centered cubic (bcc) β -phase (aluminum rich NiAl) [22]. After powder milling (Fig. 1d), the powder morphology changes from spherical to irregular shape. The initially smooth surface become relatively rough. A direct comparison between Fig. 1c and Fig. 1f shows that the volume fraction of the β -phase is significantly lower in the powder after milling.

Fig. 1 Backscattered electron (BSE) images of the NiCoCrAlY powder before and after milling: (a) morphology of the as-received powder; (b) polished cross-section of the as-received powder; (c) high magnification image of (b) showing the two-phase microstructure; (d) morphology of the milled powder; (e) polished cross section of the milled powder; (f) high magnification image of (e) showing the grain structure. The polished samples were etched using a mixture of 50 vol. % HCl, 50 vol. % ethanol with 5 wt. % CuCl_2 dissolved [12].

Fig. 2 XRD patterns of (a) milled powder; (b) as-received powder; (c) alloy prepared from the milled powder and (d) alloy prepared from the as-received powder.

Fig. 2 presents the XRD patterns of the NiCoCrAlY powder before and after milling, as well as the corresponding alloys prepared from these two different types of powder. Two significant differences in XRD patterns could be identified between the as-received powder and the milled powder. One is the peak broadening of the γ -phase in the milled powder, probably due to the grain size refinement and non-uniform internal strain induced by the milling[22, 23]. The other difference is that the β -phase peaks in the milled powder almost disappear, suggesting dissolution of the β -phase

into the γ -matrix. The severe plastic deformation in ball milling process could lead to this phenomenon [22, 24]. However, after SPS, the β peaks re-appear from the bulk alloy, which is caused by the re-precipitation of the β -phase from the supersaturated γ -matrix [22]. In addition, the γ peaks of the alloys become much sharper compared with those of the milled powder, as a result of recovery, recrystallization and grain growth during high temperature exposure [22].

3.2 Microstructures of the NiCoCrAlY alloys prepared by SPS

Fig. 3 shows the microstructure of the alloys prepared from the as-received powder and the milled powder, respectively. The as-sintered alloys exhibit a two-phase structure, consisting of γ -Ni phase (light contrast) and β -NiAl phase, in agreement with the XRD results (Fig. 2). Both alloys are fully dense and no apparent pores are observed. Based on the elemental maps, a remarkable difference in the distribution of Y is observed in the alloys prepared from the two types of powder. Y is predominantly in the form of Ni-Y precipitates (300 to 700 nm) in the alloy prepared from the as-received powder. The Ni-Y precipitates are mainly situated at the grain boundaries, which is associated with the low solubility of Y in the major phases in NiCoCrAlY, e.g., γ -Ni and β -NiAl [7, 8, 25]. However, the Ni-Y precipitations are not detected in the alloy prepared from the milled powder. The distribution and form of Y in the alloy prepared from the milled powder will be investigated in detail in the following section.

Fig. 3 BSE images of the alloys prepared from (a) the as-received powder and (b) the milled powder. Corresponding EDS maps of Ni, Co, Cr, Al, Y and O are also presented alongside with the BSE images;

3.3 Distribution and form of Y in the alloy prepared from the milled powder

To examine the distribution of Y in the alloy prepared from the milled powder, a FIB was used to etch the polished surface and reveal the microstructure in greater details, as shown in Fig. 4. Fine, nanoscale Ni-Y precipitates (indicated by the white arrows) at the grain boundaries of the alloy. However, the size of the Ni-Y precipitates (50 to 150 nm) in the alloy prepared from the milled powder is much smaller compared with that of the Ni-Y precipitates (300 to 700 nm, Fig.3a) in the alloy prepared from the as-received powder.

TEM is employed to explore the reason for the decrease in the size of the Ni-Y precipitates in the alloy prepared from the milled powder, as shown in Fig. 5. The lamella milled by FIB is presented in Fig. 5a, together with the bright-field TEM image (Fig .5b) and high-angle annular dark-field image (Fig .5c). The EDS maps of

Ni, Al, and Co (Fig. 5d, 5e, and 5f) indicate clearly that the Ni, Al enriched phase is β -phase (grey contrast) and Co enriched phase is γ -phase (light contrast), as shown in Fig. 5c. To verify the form of Y, the EDS maps of Y and O are presented in Fig. 5g, 5h, and 5i. These results clearly show that apart from Ni-Y precipitates, nanoscale Y_2O_3 particles (5 to 30 nm) are also present in the alloy. As displayed in Fig. 5c, the Y_2O_3 particles are primarily situated at the γ/β grain boundaries, as well as in the γ and β grains. These fine Y_2O_3 particles were believed to form during the ball milling process, due to the high chemical activity of Y [26]. Ajdelsztajn et al [27] found similar fine phases within a NiCrAlY bond coat fabricated from cryomilled powder. In short, the powder milling significantly improved the uniformity of Y distribution in the SPS alloy.

Fig. 4 High magnification BSE image of the alloy prepared from the milled powder after FIB etching.

Fig. 5 TEM analysis of the alloy prepared from the milled powder. (a) thin lamella milled by FIB; (b) bright-field (BF) TEM image; (c) high-angle annular dark-field (HAADF) STEM image; (d, e, f, g and h) EDS maps of Ni, Al, Co, Y and O, respectively and (i) superimposed map of Y and O.

3.4 Grain size measurement of NiCoCrAlY alloys by EBSD

As reported in previous studies [22, 28], the powder milling can refine the grain size to nanoscale, which will significantly increase the grain boundary density. The nano-sized grains can promote the formation of a uniform α -Al₂O₃ scale, which is attributed to the faster aluminum diffusion along the grain boundaries[22, 23], thereby improving the oxidation performance of NiCoCrAlY. Therefore, it is worthwhile to measure the grain size of the alloys prepared from the two types of powders.

Fig. 6 shows the EBSD phase contrast and orientation maps of two NiCoCrAlY alloys prepared from the as-received and the milled powder, respectively. Both samples are composed of the γ and β phases. No texture can be found in both samples (Fig. 6e and 6f). Although the grain size of the alloy prepared from the milled powder (1~7 μm) is a bit smaller than that prepared from the un-milled powder (2~10 μm), they are generally in the same order of magnitude.

It should be noted that plenty of twins are found in the alloy prepared from the milled powder (Fig. 6c and 6d.), predominantly in the fcc- γ phase. The twins are always observed in the fcc phase, due to the low stacking-fault energy of the structure [29]. In principle there are two types of twins: deformation and annealing twins. As reported previously [29, 30], deformation twins are formed in the alloy related to severe plastic deformation condition (e.g. powder milling), but the annealing twins are formed due to recrystallization and grain growth during thermal exposure (e.g. SPS). Therefore, the twins in the alloy prepared from the milled powder can be either deformation twins or annealing twins or a mixture of two. The effect of the slightly decreasing grain size and twins on oxidation behavior of the NiCoCrAlY alloy will be evaluated in the section of discussion.

Fig. 6 EBSD analysis of the NiCoCrAlY alloy samples. (a, c) phase contrast map the alloy prepared from the as-received powder and the milled powder, respectively. The yellow and blue areas in the phase contrast maps are the β and γ phases, respectively. (b,d) inverse pole figure (IPF) color map of the alloy prepared from the as-received powder and the milled powder, respectively. The color in Fig.6b and d represents the crystallographic directions of the γ and β -grains parallel to the surface normal direction. The red and black lines in the IPF color maps are twin boundaries and grain boundaries (γ/γ or β/β), respectively. (e, f) color contoured pole figures show the

distribution of the $\{1\ 1\ 1\}$ poles of the γ -grains with respect to surface normal of the alloy prepared from the as-received powder and the milled powder, respectively. The color legend denotes the $\{111\}$ pole density of the γ -grains.

3.5 Cyclic oxidation behavior

Fig. 7 compares the cross-sectional microstructure of the TGO between the alloys prepared from the as-received powder and the milled powder after oxidation for 96 hours. For the alloy prepared from the as-received powder, the TGO is highly non-uniform in thickness, varying from 4.5 to 8.5 μm , with complex, multiphase microstructure ($\alpha\text{-Al}_2\text{O}_3$ matrix with a larger number of Y-Al oxide inclusions). On the contrary, for the alloy prepared from the milled powder, TGO is thinner ($\sim 4.5\ \mu\text{m}$) and highly uniform in thickness. The TGO is predominantly $\alpha\text{-Al}_2\text{O}_3$, except for a tiny amount of nanoscale Y-Al oxide inclusions. Meanwhile, the TGO/substrate interface is flat and smooth.

Fig. 7 Cross-sectional BSE images of the TGO formed on the alloy prepared from (a) the as-received powder and (b) the milled powder after oxidation at 1100 $^{\circ}C$ for 96 hours.

Fig. 8 Fractured cross-sectional BSE images of the TGO formed on the alloy prepared from (a) as-received powder and (b) milled powder after cyclic oxidation at 1100 °C for 96 hours.

Fig. 8 compares the fractured cross-sectional microstructure of the TGO between the alloys prepared from the as-received powder and the milled powder after oxidation for 96 hours. For the alloy prepared from the as-received powder, the TGO shows two different microstructures. In the areas where Y-Al inclusions are absent, the TGO consists of an equiaxed outer layer and a columnar inner layer. The duplex structure

of the TGO results from the concurrent inward oxygen diffusion and outward aluminum diffusion [3, 12]. In the areas where relatively large Y-Al inclusions are present, a thicker TGO and a mixed structure of equiaxed and columnar grains are identified. For the alloy prepared from the milled powder, the TGO shows a uniform thickness and duplex microstructure (outer equiaxed grains and inner columnar grains) over the entire alloy surface, as shown in Fig. 8b. Nanoscale Y-Al oxide precipitates are observed at the TGO grain boundaries, which is in agreement with the observations in Fig. 7b. Additionally, the average grain sizes of TGO (defined by the average grain width of columnar grains) for the alloys prepared from the as-received powder and the milled powder are estimated to be 0.73 μm and 0.64 μm , respectively [31]. The slight difference in the average grain sizes of TGO plays a negligible role on the TGO growth rate. In the areas of mixed structure for the alloy prepared from the as-received powder, the change of the TGO microstructure is related to the TGO growth mechanism, which will be discussed in Section 4.1.

Fig. 9 presents the XRD results of two alloy samples (prepared from the as-received powder and the milled powder, respectively) after oxidation for 12 hours, 48 hours and 96 hours. The Y-Al oxides were identified as YAlO_3 (YAP). For the alloy prepared from the as-received powder, it should be noted that the amount of YAP incorporated into TGO increases with an increase of oxidation time. In contrast, almost no YAP can be detected in the alloy prepared from the milled powder, probably due to its low concentration.

Fig. 9. The XRD patterns of the alloy samples (prepared from the as-received powder and the milled powder, respectively) after oxidation at 1100 °C for 12 hours, 48 hours, and 96 hours, respectively.

Fig. 10 presents the luminescence spectra of Al_2O_3 and the evolution of $\theta\text{-Al}_2\text{O}_3$ content with the oxidation time. The peaks at $14,402\text{ cm}^{-1}$ and $14,432\text{ cm}^{-1}$ belong to $\alpha\text{-Al}_2\text{O}_3$, and the peaks at $14,575\text{ cm}^{-1}$ and $14,645\text{ cm}^{-1}$ belong to $\theta\text{-Al}_2\text{O}_3$. The amount of $\theta\text{-Al}_2\text{O}_3$ can be roughly estimated using the following relationship [32]:

$$C_{\theta} = \frac{A_{14575} + A_{14645}}{A_{14402} + A_{14432} + A_{14575} + A_{14645}} \quad (1)$$

where A is the peak area and the subscript represents the peak frequency. After oxidation for 10 min, both α -Al₂O₃ and θ -Al₂O₃ were formed on the two types of the alloy samples. However, the content of θ -Al₂O₃ in the alloy prepared from the milled powder ($\sim 25\%$) is significantly higher than that in the alloy prepared from the as-received powder ($\sim 7\%$). The content of θ -Al₂O₃ gradually decreases with increasing oxidation time and after 30 min, no θ -Al₂O₃ is detected on either sample (Fig. 10d).

As pointed out by previous studies [33, 34], RE ions, such as Y, Zr or Hf, could inhibit the θ to α transformation of Al₂O₃ on β -NiAl alloys. Also, it has been reported that a uniform distribution of REs (e.g., Lu) in a β -NiAl alloy could have a stronger inhibiting effect on θ -Al₂O₃ to α -Al₂O₃ transformation [12]. The uniform Y distribution achieved by powder milling might lead to the slow θ to α transformation of the TGO on the alloy prepared from the milled powder.

Fig. 10 The PLPS spectra of the TGO on the alloy samples prepared from the as-received powder and the milled powder, respectively, after oxidation at 1100 °C for:

(a) 10 min, (b) 20 min and (c) 30 min, and (d) shows the evolution of θ - Al_2O_3 content with the oxidation time.

3.6 The TGO spallation behavior

The TGO spallation degree of two alloys as a function of oxidation time is plotted in Fig. 11. For the alloy prepared from the as-received powder, the TGO suffers severe spallation. About 20 % spallation occurred after 480 hours oxidation, and more than 90% after 720 hours. As shown in Fig. 13a and b, the exposed metal surface and the residual alumina/Y-Al oxide islands suggest that the TGO delamination occurred primarily at the TGO/substrate interface and in the TGO around the thickness imperfections associated with the Y-Al oxide intrusions [17]. Furthermore, pores at the TGO/substrate interface observed in Fig. 13b and c are probably associated with the fracture of TGO. In contrast, the TGO on the alloy prepared from the milled powder is dense and thinner with a smooth interface, after oxidation for 480 hours (Fig. 13d).

Fig. 11 The TGO spallation degree (defined by the ratio of the spalled area to the whole area of the TGO) as a function of oxidation time at 1100 °C. The inserted images show the surface morphology of the alloys: (a, b, c) prepared from the as-received powder after 240 hours, 480 hours, and 720 hours oxidation, and (d, e, f) prepared from the milled powder after 240 hours, 480 hours, and 720 hours oxidation.

Surprisingly, almost no TGO spallation (~0.1 %) occurs on the alloy prepared from the milled powder during cyclic oxidation, even after 720 cumulative hours (Fig. 14a). The spalled interface presented in Fig. 14b shows that only a few small oxide intrusions remain on the exposed alloy surface. The TGO away from the spalled regions is still intact after 720 hours (Fig. 14c and d).

Fig.13 BSE images of the alloy samples after cycle oxidation for 480 hours at 1100 °C: (a) general topview of the surface after TGO spallation on the alloy prepared from the as-received powder, (b) microstructure of remaining oxide intrusions on the alloy prepared from the as-received powder; (c,d) cross-sectional microstructure of the TGO on the alloy prepared from the as-received powder and the milled powder, respectively. The insets in Fig.13c and d present the enlarged TGO microstructure.

Fig. 14 BSE images of the alloy prepared from the milled powder after cycle oxidation for 720 hours at 1100 °C: (a) general top-view of the surface with two small TGO spallation regions; (b) microstructure of the metal surface after TGO spallation; (c) overview of the TGO cross-sectional microstructure and (d) a high magnification TGO cross-sectional microstructure.

3.7 Oxide growth kinetics

Fig. 12 shows the area specific mass gain of two samples (prepared from the as-received powder and the milled powder, respectively) after during isothermal oxidation for 100 hours at 1100 °C. As shown in Fig. 11a, the alloy prepared from the milled powder exhibits a mass gain of 0.69 mg/cm², only about 60 % of that (1.13 mg/cm²) of the alloy prepared from the as-received powder. It clearly indicated that a lower TGO growth rate was achieved by powder milling. Assuming that TGO growth

follows the parabolic law, the parabolic rate constant for oxidation, k_p , is expressed in terms of the area specific mass gain (Δm) and the oxidation time (t) [8]:

$$\Delta^2 m = 2k_p t \quad (2)$$

Based on the linear fit to the TG data presented in Fig. 11b, the parabolic rate constant k_p of the two samples are 1.9×10^{-6} (as-received) and $7.2 \times 10^{-7} \text{ mg}^2 \text{cm}^{-4} \text{s}^{-1}$ (milled), respectively. This suggests that powder milling significantly reduces the parabolic rate constant (a ~62% reduction). It has been reported by Hejrani [8] that the parabolic rate constant ($6.1 \times 10^{-6} \text{ mg}^2 \text{cm}^{-4} \text{s}^{-1}$) at 1100 °C of a CoNiCrAlY alloy produced by high-velocity atmospheric plasma spraying (HV-APS) was lower than that of a CoNiCrAlY alloy produced by low pressure plasma spraying (LPPS). However, compared to the values reported by Hejrani, the parabolic rate constant of the alloy prepared from the milled powder in our work is still one order of magnitude lower.

Fig. 12 (a) Area specific mass gain (Δm) of two samples (prepared from the as-received powder and the milled powder, respectively) during the 100 hours isothermal oxidation at 1100 °C; (b) The linear fit to the TG data in (a) based on the parabolic law[7]. (c) The area specific mass gain (Δm) of the two samples during the initial 1 hour isothermal oxidation at 1100 °C.

As displayed in Fig. 10, a higher amount of $\theta\text{-Al}_2\text{O}_3$ was found in the TGO on the alloy prepared from the milled powder within the first 1 hour oxidation, which is expected to contribute to a higher TGO growth rate at the initial oxidation stage [12]. However, the specific mass gains of the alloy prepared from the milled powder during

the initial 1 hour oxidation presented in Fig. 11c remain lower than that of the alloy prepared by as-received powder. The reasons for this difference will be discussed later.

3.8 Sulfur impurity segregation

As reported in previous studies [35, 36], the intrinsic impurities such as sulfur in alloys can segregate to the alloy/scale interface during oxidation, which results in degradation of the interface. It has been claimed that Y could getter S and suppress the interfacial segregation. To examine this effect, the elemental profile through the TGO thickness to the alloy substrate was evaluated using GD-OES, which is a powerful tool for quantitative elemental depth profile analysis of multilayer materials [37].

The concentration–depth profiles of corresponding elements for the two different types of the alloys after 48 h cyclic oxidation are presented in Fig. 15. The sputtering depth at the TGO/substrate interface is roughly equal to the TGO thicknesses. It is presented clearly that in both alloys S segregates not only to the TGO/substrate interface, but also in the inner layer of TGO. As shown in Fig. 15a, the concentration of S increases rapidly from TGO surface to the inner part of the TGO, reaching a peak value at the TGO/substrate interface, and then slowly decreases with increasing sputtering depth. This result indicates that S primarily segregates to the TGO/substrate interface for the alloy prepared from the as-received powder. However, this phenomenon is not observed in the alloy prepared from the milled powder. Instead, S segregates to the TGO layer and the concentration of S increases from the TGO/substrate interface to the TGO/gas interface, rather than segregating to the TGO/substrate interface (Fig. 15b). In summary, Sulfur segregation to the TGO/substrate interface is significantly suppressed after powder milling. Furthermore, Sulfur is primarily detected in the inner layer of the TGO for the alloy prepared from the milled powder.

Fig. 15 The quantitative depth profiles of various elements in the alloys after cyclic oxidation at 1100 °C for 48 hours (a) the alloy prepared from as-received powder and (b) the alloy prepared from the milled powder. The depth profile of Y is not showed in the graph, due to the lack of the certified calibration sample. Each element is listed with a corresponding scaling factor, e.g. S*100 means that the S concentration is 100-times lower than what is displayed in the graph.

3.9 TGO stress measurements

Since the spallation of the TGO is driven by stress, it is of necessity to investigate the difference in the TGO residual stresses between the two different alloys. The TGO residual stress at room temperature mainly comes from two sources: one is the thermal expansion mismatch (CTE) between the substrate and the TGO, the other is the TGO growth stress [38]. In this study, the residual stress in the TGO was evaluated using PLPS technique, by [38, 39]:

$$\Delta\nu = 5.07 \overline{\sigma} \quad (3)$$

where $\Delta\nu$ is the peak shift of R2 line, and $\overline{\sigma}$ is the biaxial stress in the TGO. The peak shift was obtained using the spalled TGO as stress free reference.

The theoretical thermal mismatch stress, σ_{CTE} , between the TGO and the substrate is represented by [12, 40]:

$$\sigma_{\text{CTE}} = \frac{E_{\text{ox}}}{(1 - \nu_{\text{ox}})} (\alpha_{\text{ox}} - \alpha_{\text{m}}) \Delta T \quad (4)$$

where E is the elastic modulus at room temperature, ν is Poisson's ratio, α is the CTE, and ΔT is the temperature drop from oxidation temperature to room temperature. The subscripts “ox” and “m” represent the TGO and substrate, respectively. With the values in Table 1, the average CTE stress can be estimated as -3.6 GPa.

Table 1 Material properties of the TGO and NiCoCrAlY substrate.

Material	Poisson's ratio, ν	Elastic modulus at room temperature, E (GPa)	Elastic modulus at 1100 °C, E (GPa)	CTE, α ($10^{-6}/\text{K}$)
TGO	0.2	380	340	8 [38]
NiCoCrAlY	0.3	200	/	15 [17]
YAlO ₃	0.2	316	/	6~7 [41]

Fig. 16a presents the evolution of the TGO residual stress with the oxidation time. Two features are noteworthy. First, the TGO stress is almost independent of oxidation time. Second, the TGO residual stress of the alloy prepared from the as-received powder is about 0.9 GPa higher than that of the alloy prepared from the milled powder. It should be noted that the effect of YAP on the thermal mismatch stress can be neglected. For a rough estimation, assuming that the TGO consists of pure YAP, the average CTE stress is estimated as -3.4 GPa, which is only 0.2 GPa lower than that for pure Al₂O₃. In this study, the content of YAP in the TGO is less than 10%. Additionally, the Y₂O₃ (<1%) in the alloy prepared from the milled powder is expected to have little effect on the CTE of the alloy. Thus it is reasonable to neglect

the influence of YAP in the TGO and Y_2O_3 in the alloy on the thermal mismatch stress. The difference in the TGO stress between the two alloys is only caused by the different growth stress.

Assuming there is no stress relaxation due to the rapid cooling, the growth stress, σ_{growth} , in the TGO at the oxidation temperature can be evaluated from the room temperature stress data based on following equations[12, 38, 40]:

$$\sigma_{\text{growth}} = \frac{E_{\text{ox}}^T}{1-\nu_{\text{ox}}} \left[\frac{\sigma_{\text{ox}}(1-\nu_{\text{ox}})}{E_{\text{ox}}} - \frac{(\alpha_{\text{ox}} - \alpha_{\text{m}})\Delta T}{1+R} \right] \quad (5a)$$

$$R = \frac{E_{\text{ox}}(1-\nu_{\text{m}})h_{\text{ox}}}{E_{\text{m}}(1-\nu_{\text{ox}})h_{\text{m}}} \quad (5b)$$

Where h_{ox} and h_{m} are TGO thickness and substrate thickness, respectively. E_{ox}^T represents the elastic modulus of TGO at oxidation temperature.

Based on Eq. (5), the growth stress in TGO as a function of oxidation time is plotted in Fig. 16b. The growth stress has the same variation trend as the total residual stress. The TGO growth stress of the alloy prepared from the as-received powder reaches to -1.0 GPa, about 0.8 GPa higher than that of the alloy prepared from the milled powder. The reasons for this difference will be discussed as following.

Fig. 16 TGO residual stress (a) and growth stress (b) of the alloy prepared from the as-received powder and the milled powder as function of the oxidation time at

1100 °C. The dash lines represent the CTE mismatch stress and the error bars are the standard deviation of 500 measurements.

4. Discussion

The findings of this work clearly demonstrate that compared to the NiCoCrAlY alloy prepared from the as-received powder, the NiCoCrAlY alloy prepared from the milled powder has a significantly lower oxidation rate, a lower TGO residual stress and an significantly improved inhibiting effect on sulfur segregation to the interface and interfacial imperfections growth, thereby resulting in a much longer spallation life.

As presented in Fig. 6, the smaller grain size and twins in the γ phase for the alloy prepared from the milled powder can increase the grain boundary density, which will facilitate θ -Al₂O₃ to α -Al₂O₃ transformation [21]. However, the transformation rate of θ -Al₂O₃ to α -Al₂O₃ for the alloy prepared from the milled powder at the initial oxidation stage is slower. This slower transformation rate can be attributed to the uniform distribution of Y in the alloy prepared from the milled powder, as discussed in the section of Fig. 10. In other words, the contribution of Y distribution to phase transformation rate of TGO exceeds that of grain boundary density at the initial oxidation stage. As displayed in Fig. 11c, the higher θ -Al₂O₃ content in TGO for the alloy prepared from the milled powder does not result in a higher TGO growth rate in the early oxidation stage. The oxygen affinity of Y is higher than Al and thereby Y diffuses faster than Al under the same oxygen partial pressure and temperature [26]. For the alloy prepared from the as-received powder, a large amount of Ni-Y enriched precipitates segregates on the surface of sample (Fig. 3a). Upon exposure to high temperature, the fast oxidation of Y will be inevitable and thereby significantly increases the oxidation rate in the early oxidation stage (Fig. 11c). For the alloy prepared from the milled powder, the uniform distribution of yttrium can lower the content of Y enriched oxides in TGO. Furthermore, the θ -Al₂O₃ content is much lower than that of α -Al₂O₃ and constantly decreases with the oxidation time (Fig. 10). Thus

the contribution of oxidation of Y to the early oxidation kinetics (<20 min) exceeds that of θ - Al_2O_3 content. In short, the excessive incorporation of Y enriched oxides into TGO rather than the relatively lower θ - Al_2O_3 content in TGO is a major contributing factor to the higher TGO growth rate for the alloy prepared from the as-received powder (e.g., Fig. 7 and 8). Therefore, in the following, we will devote to discuss the role of the uniform yttrium distribution on the TGO growth rate, the residual stress, segregation of S to the interface and the spallation of the TGO.

4.1 Effect of the uniform distribution of yttrium on the TGO growth rate

Failure of the TGO is driven by the elastic strain energy stored in the TGO, which is proportional to the TGO thickness. Consequently, the TGO growth rate plays a crucial role on the spallation. The high growth rate of the TGO on the alloy prepared from the as-received powder could be attributed to the following reasons. Firstly, the large YAP inclusions incorporated into the TGO can provide short-circuit paths for the inward diffusion of oxygen [17], as oxygen diffuses faster through YAP than θ - Al_2O_3 and α - Al_2O_3 [26]. Secondly, the mixed structure of equiaxed and columnar grains shown in Fig. 8a indicates that the outward diffusion of aluminum may be the dominant TGO growth mechanism in these areas, which will accelerate the TGO growth [12]. In contrast, the fine Ni-Y precipitates and Y_2O_3 particles in the alloy prepared from the milled powder suppress the excessive incorporation of YAP into TGO. As shown in Fig. 8b, the segregation of fine YAP particles to the growing Al_2O_3 grain boundaries on the alloy prepared from the milled powder will effectively block the outward diffusion of aluminum. Thus the oxidation after powder milling is dominated by inward oxygen diffusion, as confirmed by the characteristic columnar grains, which contributes to a lower TGO growth rate.

4.2 Effect of the uniform distribution of yttrium on the TGO stress

As discussed in Section 3.9, the higher TGO stress in the alloy prepared from the as-received powder is associated with the higher growth stress. The presence of Y or YAP at the Al_2O_3 grain boundaries increase the creep strength of the TGO, leading to a higher growth stress [42]. Additionally, the higher growth stress also probably derives from the volume expansion related to the reaction [7]: $\text{Y}_2\text{O}_3 + 2\text{Al} + 3\text{O} \rightarrow 2\text{YAlO}_3$. Based on the change of the molar volumes from yttria ($44.9 \text{ cm}^3/\text{mol}$) to YAP ($30.6 \text{ cm}^3/\text{mol}$), the reaction produces a ~36% volume expansion, which introduces a higher compressive growth stress in the TGO [6, 7]. For the alloy prepared from the milled powder, there are fine Ni-Y precipitates and most Y in the form of Y_2O_3 is tied up in the alloy. The amount of YAP in the TGO is much lower, leading to a lower growth stress and thus a lower residual stress at room temperature.

4.3 Effect of the uniform distribution of yttrium on the S impurity segregation

It is accepted extensively that the TGO/substrate interfacial toughness decreases rapidly as S segregates to the interface. As presented in Section 3.8, the S segregation to the TGO/substrate interface is inhibited after powder milling and most S is detected in the TGO. It has been reported by Molins et.al [36] that the TGO/substrate interface can accommodate only finite amount of S. Once the interface is saturated at high temperature, S will segregate into the growing TGO layer. It has been also reported by previous studies [12, 35, 36], the S preferentially segregates to the Al_2O_3 grain boundaries and the surface of interface pores. As presented in Fig.13, large interfacial pores and cracks are observed at the TGO/substrate interface after 480 hours oxidation for the alloy prepared from the as-received powder. Thus it is likely that the nucleation and growth of interfacial pores and cracks have been already occurred after 48 hours oxidation. The S will prefer to segregate to the surface of these detached interfaces and further coarsens these interfacial imperfections [43]. Furthermore, the columnar grains microstructure of the TGO is hardly detected due to the presence of

large YAP inclusions, where the amount of the Al_2O_3 grain boundaries is reduced (Fig. 8a). The decrease in the number of the Al_2O_3 grain boundaries results in less diffusion paths for S segregating to the inner layer of TGO [35]. Thus the S primarily segregates at the TGO/substrate interface for the alloy prepared from the as-received powder (Fig. 15a), which severely degrades the interface adhesion. However, for the alloy prepared from the milled powder, the TGO/substrate interface is clean and smooth and no interfacial defects can be found due to the uniform yttrium distribution (Fig. 13). Thus only minor quantity of S segregates to the interface. Additionally, the slower depletion of yttrium resulting from oxidation can guarantee enough yttrium concentration in the underlying alloy to obtain the beneficial RE effect. Meanwhile, the uniform columnar grains microstructure introduces more diffusion paths for the S segregation to the inner layer of TGO (Fig. 8b). Therefore the S primarily segregates to the inner layer of TGO for the milled sample (Fig. 15b). Similar observations for the S segregation to the inner layer of TGO were also reported in the reactive element Lu doped NiAl alloy [12]. Nijdam et al [20] also suggested that the uniform distribution of Y within the MCrAlY alloy may be more effective to prevent the S segregation to the interface. However, the form of S in the inner layer of TGO is unknown yet and needs further investigation. In general, the uniform yttrium distribution in the alloy prepared from the milled powder can effectively suppress the segregation of S to the TGO/substrate interface, which is responsible for the enhanced interfacial toughness.

4.4 Mechanisms of enhanced the TGO spallation

It is well known that the TGO spallation is driven by the strain energy in the TGO and resisted by the interfacial toughness [18]. Therefore, the role of yttrium distribution on the TGO spallation can be understood in terms of strain energy in the TGO and the interfacial toughness. The elastic strain energy in the TGO can be expressed as [18, 44]:

$$G = \frac{\sigma^2 h_{ox}(1 - \nu_{ox}^2)}{2E_{ox}} \quad (6)$$

where h_{ox} , ν_{ox} and E_{ox} are the thickness, Poisson' ratio and Young' modulus of the TGO, respectively. From Fig. 11 and Fig. 16, both the growth rate and the residual stress in the TGO are significantly lower for the alloy prepared from the milled powder. This indicates that a uniform yttrium distribution could lower the driving force for TGO spallation.

In terms of interfacial toughness, two factors, one is the sulfur segregation to the interface, the other is the interfacial imperfections (e.g., oxide intrusions or pores), will exert influence. The impurities in the alloys, such as S, segregate to the TGO/substrate interface during thermal exposure, weakening the interfacial adhesion. REs, such as Y, Hf, Zr, can effectively suppress such segregation [12, 45]. For the alloy prepared from the as-received powder, sulfur primarily segregates to the TGO/substrate interface, which leads to rapid degradation of interfacial toughness [4, 35, 46]. However, for the alloy prepared from the milled powder, sulfur segregation to the TGO/substrate interface is inhibited and sulfur is primarily detected in the TGO. The absence of sulfur segregation to the TGO/substrate interface in the alloy prepared from the milled powder is beneficial to the interfacial adhesion.

Besides sulfur segregation, imperfections (e.g., oxide intrusions or pores) at the TGO/substrate interface also affect the TGO adhesion. For the alloy prepared from the as-received powder, the oxide intrusions are the primary imperfections at the spalled interface (Fig. 13a), which might be the sites for initial TGO spallation. Based on the discussion in Section 4.3, the interfacial toughness will degrade rapidly, which is induced by S segregation to the interface. Furthermore, the TGO thickens quickly due to the excessive incorporation of YAP into TGO, as discussed in Section 4.1. Thus the oxide intrusions are crucial to the initial TGO spallation with the degradation of interfacial adhesion, when they form and enlarge quickly because of the intrinsically

faster oxygen diffusion rate. Above a critical size, the tensile stresses at those imperfections could lead to cracks or interfacial separation [18]. In addition, the interfacial pores (Fig. 13b and c) are also responsible for the adhesion loss [47]. However, the uniform yttrium distribution in the alloy prepared from the milled powder could significantly reduce the amount of interfacial imperfections, which is also beneficial to the TGO adhesion. Based on the discussion above, the uniform yttrium distribution in the alloy contributes to the lower driving force for TGO spallation and the enhanced interface adhesion, thereby improving the TGO spallation life.

5. Conclusions

In this work, a method to fabricate highly oxidation and spallation resistant MCrAlY alloy via powder metallurgy approach was presented. It is found that compared with the alloy prepared from the un-milled powder, the alloy prepared from the milled powder exhibits a significantly lower oxidation rate (with the parabolic growth rate constant reduced by 62 %), a dramatic improvement in the TGO spallation life (e.g., >90% spallation for un-milled powder vs. almost no spallation for milled powder after 720 hours oxidation at 1100 °C).

The powder milling promotes the formation of nanoscale Y_2O_3 particles (5 to 30 nm), resulting in a uniform yttrium distribution in the alloy. Consequently, the formation of YAP in the TGO is suppressed, leading to a lower oxidation rate and a lower TGO growth stress. It is clearly indicated by GD-OES that the sulfur segregation to the TGO/substrate interface is inhibited after powder milling, which results from the uniform yttrium distribution in the alloy. In addition, the uniform yttrium distribution can inhibit the formation of interfacial imperfections (e.g., oxide intrusions or pores) and prevents sulfur segregation to the TGO/substrate interface, thereby improving the TGO adhesion. Due to the lower TGO spallation driving force and the enhanced adhesion, the alloy prepared from the milled powder exhibits a superior oxidation

performance to the counterpart. The findings obtained in this study offer an alternative approach to fabricate oxidation resistant NiCoCrAlY alloys simply by manipulating the yttrium distribution, rather than changing the chemistry.

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