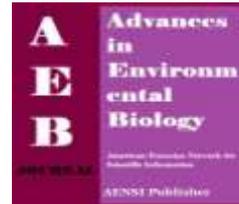




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Effect of Grain Size on the Isothermal Oxidation of Superalloys

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ABSTRACT

The oxidation behavior of two different grain sizes of superalloys is discussed. The present paper focused on the isothermal oxidation of Fe-33Ni-19Cr alloy at temperatures of 700 °C exposed in dry air for 500 hours. Different grain size of alloy was made of solution annealing treatment at different temperatures, namely, 950 °C and 1200 °C for fine and coarse grain, respectively. The results showed that the average grain size increased with increase in solution annealing temperature that was significantly affecting the oxidation kinetic of the materials. Optical microscopy, scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS) and X-ray diffraction (XRD) were employed in this study to analyze the oxidation behavior of solution-annealed samples. Results indicate that fine grain samples recorded the slow oxidation rate as compared to coarse grain samples. The analysis indicates that the fine grain sample resulting in an enhanced Cr diffusivity to form Cr rich oxides. The fine grain solution-annealed sample is an effective approach, which possess a better oxidation resistance and reduced oxidation rate.

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INTRODUCTION

Superalloy is an alloy developed for elevated temperature service, where good mechanical properties, good surface stability and high temperature oxidation and corrosion resistant are required. Superalloys are heat resistant alloys of nickel, iron-nickel and cobalt that frequently operate at temperature exceeding 538 °C. Superalloys are widely used in industrial applications where their high temperature strength and/or corrosion resistance is required. These applications include steam turbine power plants and steam generator in nuclear reactor plants [2].

Nickel (Ni)-based superalloys are used in nuclear reactors, electrical-resistance heaters, gas turbines, petrochemical, aerospace, and heat-treating industries, due to their favourable strength and excellent resistance to oxidation (and many other aggressive environments) at elevated temperatures [1]. Ni-based superalloys has the ability to form protective surface oxide scales at high temperatures that provides them with resistance to further high temperature corrosion [1,3].

Based on its advantages, these alloys are widely used in many applications as high temperature structural materials [6,4]. The chromium in the alloy imparts resistance to oxidation and corrosion. The high nickel content maintains an austenitic structure so that the alloy is ductile. The nickel also contributes resistance to scaling, general corrosion and stress corrosion cracking. The iron content provides resistance to internal oxidation.

Cr₂O₃ is an oxide with relatively crack-free and pore-free scale properties that afford their corrosion resistant of high temperature alloy. However, such oxides become prone to cracking and spalling, especially during thermal cycling. Oxidation processes are sensitive to alloy microstructure and surface treatment. Surface deformation decreases the alloy grain size by recrystallization at temperature [8]. This affects both the scale

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morphology and the kinetics of scale development by providing rapid-diffusion paths via grain boundaries for chromium to the alloy surface [8,7,5,11].

The present paper focused on the oxidation behavior of fine and coarse grain samples prepared by solution annealing process exposed in dry air at temperature of 700 °C with respect to oxidation kinetics.

MATERIALS AND METHODS

The materials used in this study was commercial Incoloy alloy 800H with the measured chemical composition (in wt%): 32.51 Ni, 18.9 Cr, 0.078 C, 0.053 Al, 0.489 Ti, 0.001 S, 0.315 Si, 0.556 Mn, 0.007 P, 0.082 Cu and balance Fe. Test samples with fine and coarse grains structure were made of different solution annealing temperatures. The solution treatments were carried out on superalloys at two different temperatures, namely, 950 °C, and 1200 °C. The samples were soaked for 3 hours during solution annealing followed by water quench.

The oxidation test samples were rectangular coupons with nominal dimensions of 10mm x 10mm x 3mm. Before oxidation test, all samples surface were ground to P600 grit surface finish, and were ultrasonically cleaned with acetone. The isothermal oxidation tests were investigated by means of discontinuous testing. The samples were tested for exposure duration of 500 hours with samples being removed at intervals of 50 and 100 hours for analysis. The weight of each sample was measured using a Metler AT400 analytical balance with a resolution of 0.1 µg.

Microstructure of solution-annealed specimens was observed by optical microscopy. Surface morphology and cross-section of the oxidized specimens was observed by scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS). Phase analysis of the oxidized samples was characterized by X-ray diffraction (XRD).

RESULTS AND DISCUSSION

Microstructures of solution annealed samples:

The optical micrographs of two solution-annealed samples were shown in Figure 1. The microstructure of all samples shows a matrix austenite phase and small amounts of precipitates such as titanium nitrides, titanium carbides, and chromium carbides (Tan *et al.*, 2008, Tan *et al.*, 2006). Results indicate increasing in solution annealing temperature were increase the grain size of the samples. Sample with solution annealed temperature of 950 °C shows a fine grain structure with average size of 50.04 µm as shown in Figure 1 (a). Figure 1 (b) shows a coarse grain structure of sample solution-annealed at 1200 °C with the average grain size of 104.62 µm. The commercial alloy has a mean grain size greater than ~70 µm in diameter [9].

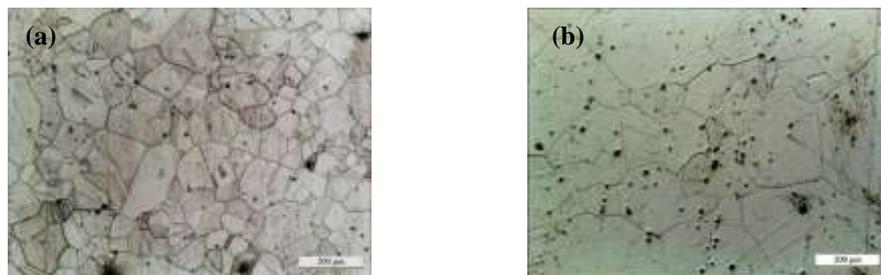


Fig. 1: Optical micrograph of solution annealed sample; (a) fine grain and (b) coarse grain.

Oxidation Kinetics:

Figure 2 illustrates the weight changes of two solution-annealed samples oxidized at 700 °C for 500 hours at dry air. The curves indicate the trend of the weight gain as a function of exposure time for fine grain and coarse grain samples. Fine grain samples exhibited the lowest weight gain and hence the superior corrosion resistance, while coarse grain samples exhibited the highest weight gain. The oxidation kinetics at different grain size follows different trend in time. The weight gain data of fine grain samples approximately follows a logarithmic rate law. Exposures of samples at working temperature were oxidizing very rapidly at start, but after a few hours' exposure, the rate decreases to a very low value.

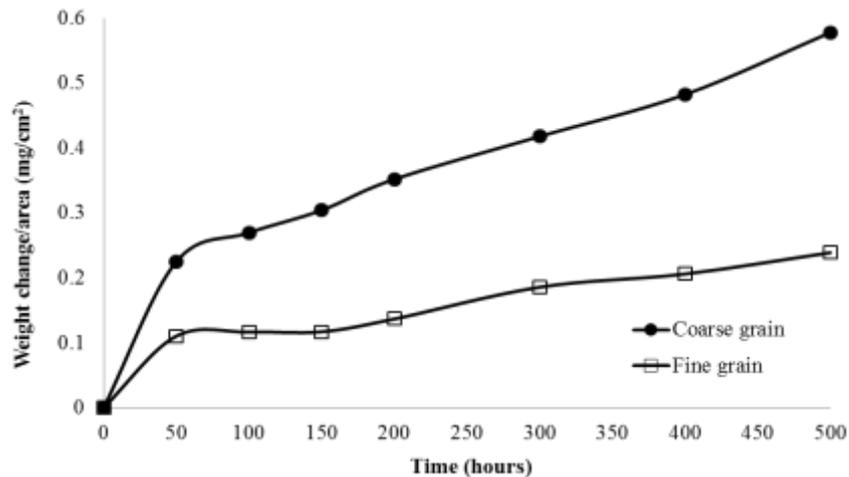


Fig. 2: Weight change of the fine and coarse grain samples subjected to isothermal oxidation at 700 °C exposure for 500 hours.

The fine grain samples indicate a lower oxidation rate that shows that the fine grains promotes the higher grain boundary path that was act as a diffusion path of ion across the metal-gas surface. The higher the diffusion ion provides rapid oxide layers growths that protect the alloys surface.

Weight gain increased sharply with short time exposure at 50 hours that is 0.1103 mg/cm². After a few hours exposure, the oxidation rate decreases to a very low value recorded a small increasing of weight gain until exposure at 150 hours. After 200 hours exposure, the oxidation rate mildly increased due to the possible of oxide cracking that develops the unprotected surface that were generated an oxide growth at that area. Prolong the exposure time were recorded a stable oxidation rate.

In contrast, the weight gain of coarse grain size gradually increased due to oxide growth during expose to working temperature. As shown in Figure 2, the oxidation of coarse grain samples follows the parabolic law which represents diffusion controlled oxide growth rate. Up to the first 50 hours, the coarse grain samples recorded a high weight gain that is 0.2248 mg/cm² followed with steady weight gain until 500 hours. These higher weight gain due to the possible continuous oxide growth that developed a protective layer at the alloys surface.

Surface Morphology:

Oxide morphology of alloy oxidized at 500 hours, analyzed with SEM corresponding secondary electron image (SEI) is shown in Figure 3. The low magnification SEI of Figure 3 (a) shows a continuous layer of oxide with distinct facets formed on fine grain samples. Another observed phenomenon in the images is that the thick oxide layer was formed at the grain boundary, revealed grain boundary oxide topographies as shown in area A of Figure 3 (b). This is most probably because of the grain boundary providing the diffusion path for ion movement across the metal-gas surface, which results the higher oxide growth rate at this region. In contrast, observed phenomenon in the images in Figure 3 (c) in area B is that the oxide topography of serration layer was recorded at the matrix phases. Prolong the exposure time, assumed to develop a uniform protective oxide layer at the matrix alloy surface.

To further study the oxidation behavior difference along the surface of fine grain samples in term of composition, EDS were employed. EDS analysis of area A resulting the major element of O and Cr detected, that indicates the Cr-rich oxide formed along the grain boundary, and thicken around the boundaries area. The microstructure of the oxide scale on the fine grain samples is dominated by Cr-rich oxides compared to that on the coarse grain samples. This analysis shows that the grain boundaries were act as a diffusion path of Cr ion to react with oxygen gas to form protective Cr oxide layer. The difference in the oxide microstructure mainly results from the grain size effect on the Cr flux since Cr has the highest diffusion coefficient in this system (Tan *et al.*, 2008). In contrast, EDS analysis at the area B detected the element of O, Fe, Ni, and Cr that indicates the element of austenitic matrix of superalloys.

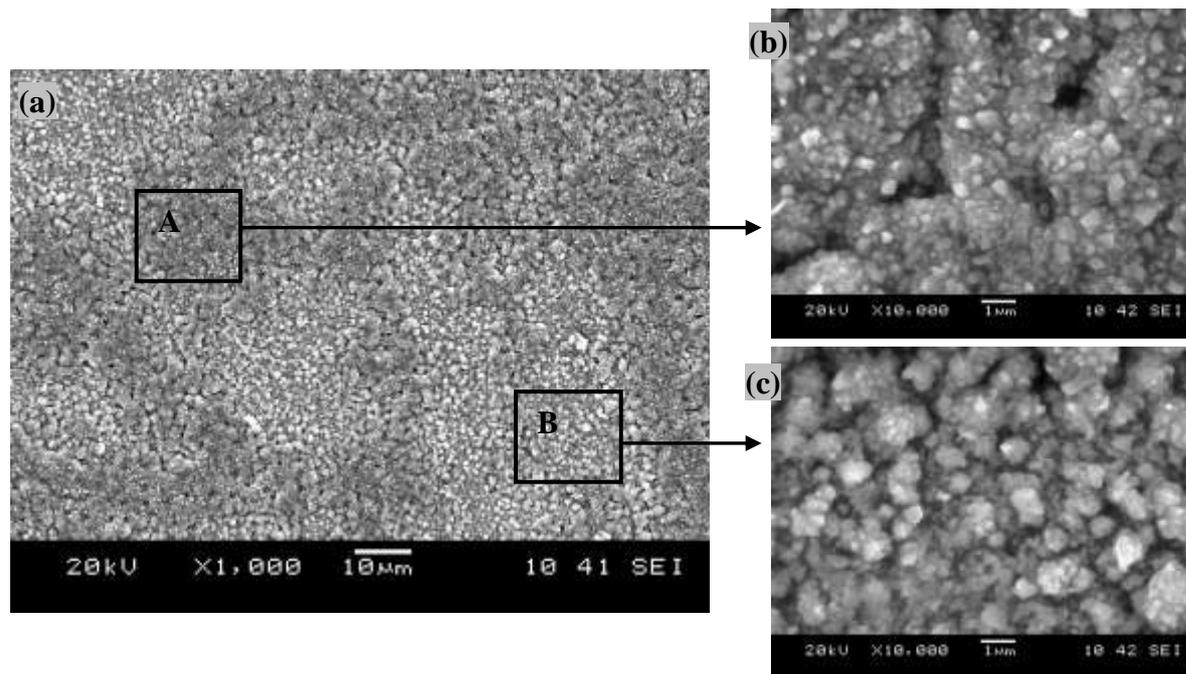


Fig. 3: Secondary electron of SEM images of the surface morphology of fine grain oxidized samples for 500 hours: (a) Oxidized sample at 1000x, (b) Area A of (a) and (c) Area B of (a).

The surface morphologies of the coarse grain oxidized samples at 500 hours exposure were shown in Figure 4. The low magnification SEI of Figure 4 (a) shows a continuous oxide layer with serration and mild undulation oxide formed on the matrix phases mixed with discrete oxide islands at the oxide layer. Figure 4 (b and c) shows a high magnification of SEI for coarse grain samples. Figure 4 (b) shows a discrete oxide islands layer that growth in distinct area on the alloy surface. The image in Figure 4 (c) shows a mild undulation with some porous oxide layer. The observed morphology was explained the oxidation kinetic of coarse grain samples that shows high oxidation rate. This phenomenon was probably results in the oxide layer to continuously growth until the unprotected layer were seal.

To further study the oxidation behavior along the surface of coarse grain samples in term of composition, EDS were employed. EDS analysis of area C resulting the major element of O and Cr detected, that indicates the Cr-rich oxide formed at the distinct area at the alloy surface. The grain boundary of coarse grain sample didn't act efficiently as a diffusion path that promotes the formation of Cr oxide layer because of less grain boundary area. This is most probably because of the diffusion path of ion movement is less compared to the fine grain size that have more grain boundary. This phenomenon were formed the discrete Cr oxide islands layer at the alloy surface. While analysis in area D shows the element of O, Fe, Ni and Cr were detected that indicates the austenitic matrix of superalloys.

Phase Analysis:

Figure 5 shows the surface X-ray diffraction patterns of the fine and coarse grain samples after exposure for 500 hours at 700 °C. The four major diffraction peaks are identified that is the austenite peaks, chromium rich oxides peaks, hematite peaks, spinel peaks and titanium rich oxides peaks. The most intense peaks correspond to the base alloy austenite phases. However chromium rich oxides peaks of Cr_2O_3 and $\text{Cr}_{1.3}\text{Fe}_{0.7}\text{O}_3$, hematite (Fe_2O_3) as well as spinel phase peaks of NiFe_2O_4 and titanium rich oxides peaks of CrTiO_3 are also identified.

The formation of Cr-rich oxides, such as Cr_2O_3 and $\text{Cr}_{1.3}\text{Fe}_{0.7}\text{O}_3$ and hematite (Fe_2O_3), mostly detected at the fine grain samples, improved not only the oxidation resistance but also the oxide exfoliation resistance because of the small difference in volume thermal expansion coefficients between the oxides and the metal [9]. Another observed pattern was the absence of magnetite (Fe_3O_4) on the samples surface that has a large difference in volume thermal expansion coefficients between the oxides and the metal.

Analysis also shows the present of Ti rich oxides, mainly on the fine grain samples, that can mitigated the Cr volatilization. Cr containing oxides becomes a problem at high temperatures because of Cr volatility that may have occurred during the cyclic oxidation testing, even though Cr oxide is a protective layer. As reported by Tan *et al.*, [8], who studied shot-peening effects on the oxidation of alloy 800H to supercritical water, the grain refinement samples with high concentration of Ti in Ti rich oxides mitigated the Cr volatilization.

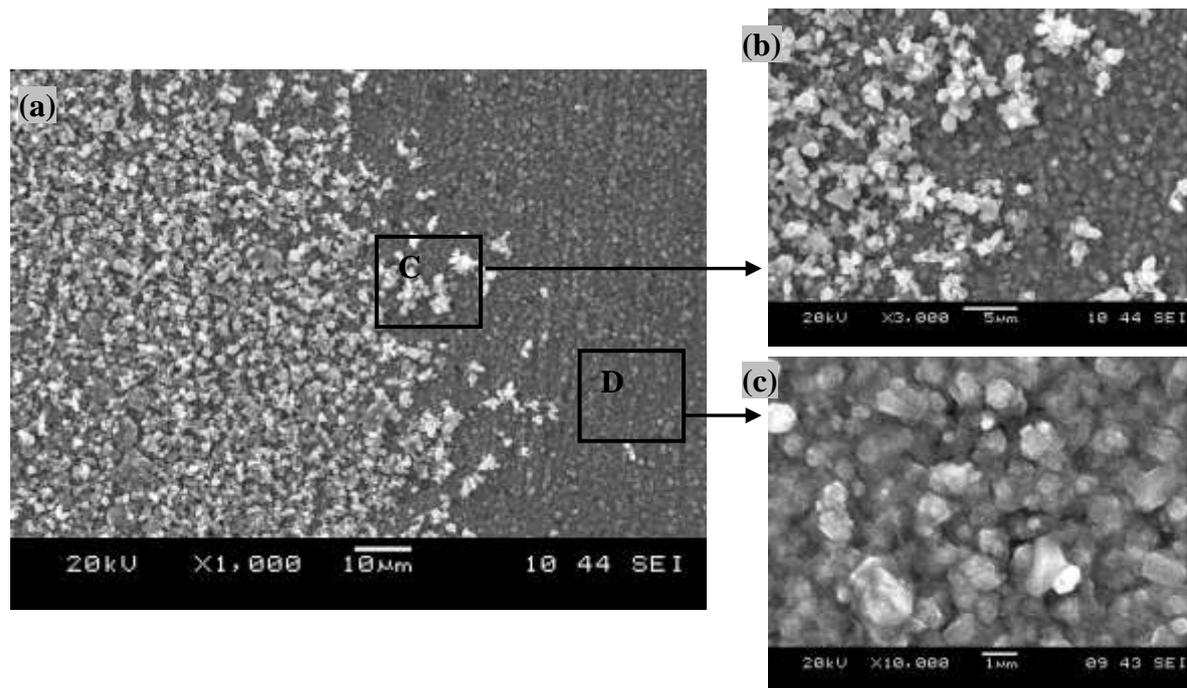


Fig. 4: Secondary electron of SEM images of the surface morphology of coarse grain oxidized samples for 500 hours: (a) Oxidized sample at 1000x, (b) Area C of (a) and (c) Area D of (a).

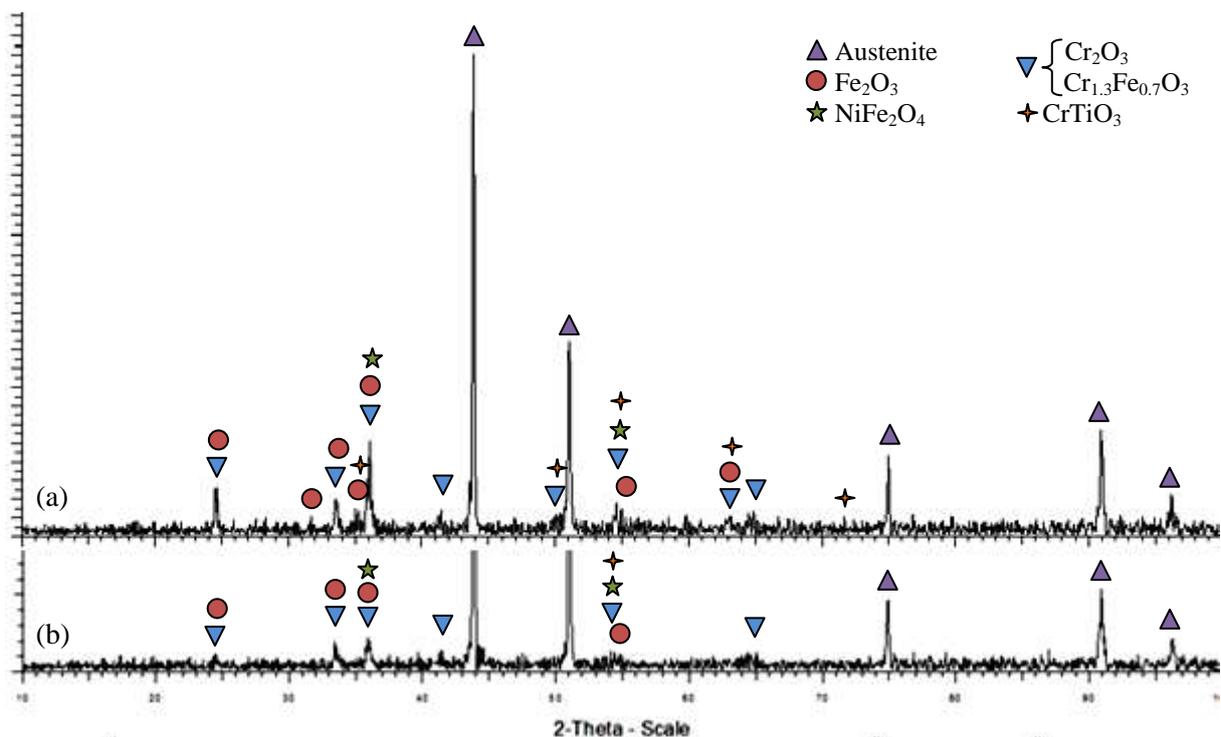


Fig. 5: A comparison among the X-ray diffraction patterns of the samples surface after 500 hours exposure time at 700 °C: (a) Fine grain sample and (b) Coarse grain sample.

Conclusion:

Solution heat treatment was applied to superalloys to alter the grain size of the alloy to improve protective oxidation behavior. Solution-annealed samples were exposed in dry air at 700 °C for 500 hours. It was found that the fine and coarse grain size was produced by the solution annealing treatment on superalloys. The oxidation rate of the fine grain was slower compared to the coarse grain. The fine grain samples tend to follow

the logarithmic rate law, while the coarse samples follow the parabolic rate law. The fine grain increased the population of grain boundaries resulting in an increased Cr diffusivity to assist in the formation of Cr-rich oxides. The fine grain samples show a continuous oxide layer with distinct facets growth evenly at the matrix phases, while coarse grain samples indicate the undulation surface with present of pore at the oxide layer surface.

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