

Full Length Research Paper

High temperature oxidation behaviour of a Ni based superalloy produced by mechanical alloying

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In this study, Ni based superalloy powders (75% Ni, 20% Cr, 4% Al₂O₃, 0.6% Ti and 0.4% Y₂O₃), were mechanically alloyed for up to 8 h and were compacted and sintered at 1200°C. Sintered samples were hot-deformed at 1200°C for various amounts and secondary recrystallisation was applied at 1325°C for 1 h. Isothermal oxidation tests were conducted at 1000°C for up to 100 h in air. Surface morphology, fractured surface and chemical composition of the samples were analyzed by using x-ray diffraction (XRD) and scanning electron microscopy (SEM). Cr₂O₃ film formed on the surface of the samples after exposure in air. Weight change results indicated the samples gained a small weight by increasing the exposure time. All samples exhibited sub-parabolic oxidation behavior.

Key words: Mechanical alloying, powder metallurgy, oxidation, microstructure, superalloy.

INTRODUCTION

Since conventional high temperature materials lose their strength and resistance to corrosion and oxidation at elevated temperatures, considerable research effort has enabled the production of numerous Ni and Fe based oxide dispersion strengthened (ODS) superalloys using a unique mechanical alloying (MA) process (Immarigeon, 1981; Cama, 1994). Because of their favorable strength and excellent resistance to oxidation and creep at elevated temperatures, nickel based superalloys are used in nuclear reactors, gas turbines, petrochemical, aerospace, and heat-treating industries, nuclear reactor tubings and other applications (Barnard et al., 2010; Suryanarayana et al., 2001; Dreshfield and Gray, 1984). The excellent high temperature strength of these materials is due to the presence of fine, stable and homogeneously distributed oxide particles which provide direct strengthening by acting as barriers to dislocation motion (Whitehouse et al., 1998). Besides, their presence also results indirectly in the growth of coarse grains with irregular grain boundaries during the secondary

recrystallization process. This type of coarse grains reduces grain boundary sliding at elevated temperatures and slows down the high temperature creep properties (Türker, 1999).

High oxidation behavior of these materials results from the formation of a slow-growing, homogeneous, adherent and with low defect concentration Cr₂O₃ oxide film (Obigodi-Ndjeng, 2011). For high temperature application, slow growing highly adherent and thermodynamically stable oxide film is preferred. Cr₂O₃ film is protective for temperature lower than 950°C. However, it loses protective properties at higher temperatures due to the evaporation problem (Wright and Wilcox, 1974; Jedlinski, 1989).

The primary aim of the present investigation is to characterize the oxidation behavior of nickel based superalloy produced by mechanical alloying techniques.

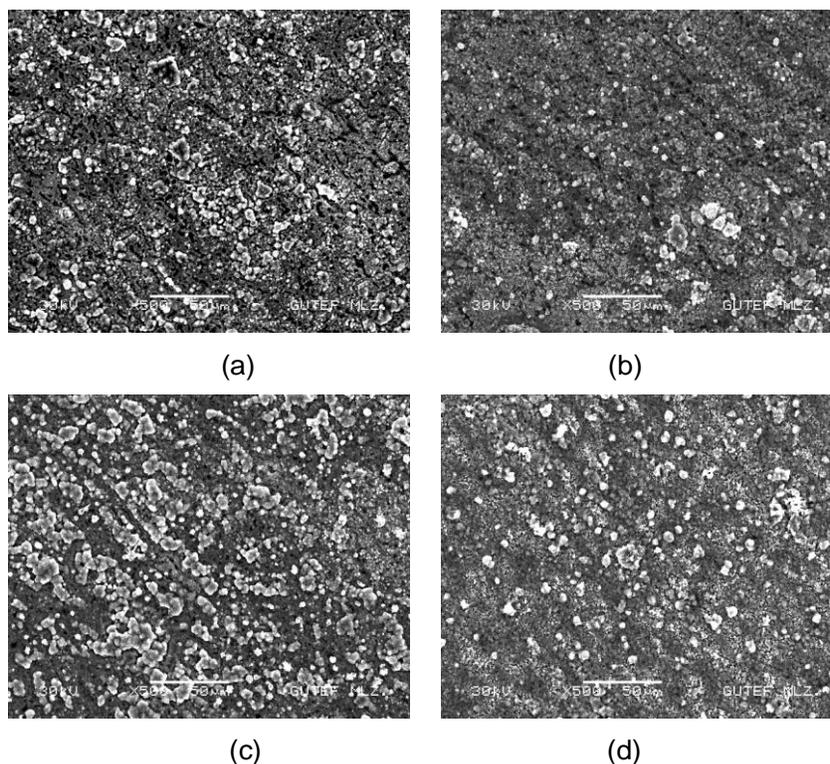
MATERIALS AND METHODS

The chemical composition of the powders used for this experimental study is shown in Table 1. Mixed powders were mechanically alloyed at 450 rpm for 8 h with the ball/powder ratio of 10/1 before compacting. MA was performed in a Szegvari type attritor which had 2 L capacity. Sintering was carried out at 1200°C

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Table 1. Chemical composition of the powders used for mechanical alloying.

Element	Ni	Cr	Al ₂ O ₃	Ti	Y ₂ O ₃
Wt (%)	Balance	20	4	0.6	0.4

**Figure 1.** SEM images of the oxidized sample surface for various duration: (a) 1, (b) 10, (c) 50 and (d) 100 h.

and then samples were deformed by 75%. After cutting the samples by using an electro erosion device, secondary recrystallization process was applied at 1325°C for 1 h. The surface area of sample was grinded and polished before calculating the surface area and then the sample was weighed with the accuracy of 10^{-5} g.

Isothermal oxidation tests were conducted at 1000°C for 1, 10, 50 and 100 h in air. After removal from the furnace, the weight change of each sample, which eventually includes losses due to spalling, was measured using a Sartorius balance with the accuracy of 1/10000. In order to obtain reliable results, all samples were weighed at least three times and the mean weight was calculated. For scanning electron microscopy (SEM) analysis, samples were fractured in liquid nitrogen.

To preserve the integrity of the brittle oxide layer on the surface of the samples during the metallographic processes and for the purpose of determination of the oxide thickness, the material surfaces were electroplated with Ni to a thickness of about 10 µm. To facilitate the nucleation process, each sample was sputter coated with a layer (about 40 nm) of gold in order to assist in the nucleation of the deposit on the insulating oxide film. Metallographic mounts of the sample were performed using standard metallographic techniques and then the samples were etched with Marbel solution. Characterization of the surface appearance of the samples after oxidation test was performed using JEOL JSM-6060

LV scanning electron microscope and XRD analyses were done by Bruker D 8 Advance device.

RESULTS AND DISCUSSION

Oxidation behavior

The structure of surface topology of the samples, exposed during 1, 10, 50 and 100 h, is shown in Figure 1a to d, respectively. After 1 h exposure (Figure 1a), a very thin oxide layer consisting of fine particles appeared. Increasing the exposure time to 10 h (Figure 1b), more oxide particles covered the surface when compared to the sample exposed for 1 h. Increasing the exposure time to 50 h (Figure 1c), oxide film covered the entire surface with coarse oxide particles. Further increase in the oxidation time to 100 h (Figure 1d) caused the oxide particles to cover the entire surface and some particle coarsening (1 to 10 µm) at the surface also occurred. Furthermore, the oxide film formed on the surface was

Table 2. Values obtained after oxidations.

Exposure time (h)	1000°C
1	ΔW : 0.1×10^{-3} g $\Delta W/A$: 0.0031452 mg/cm ² Area: 31.79364 cm ² Oxide thickness: 2-3 μ m
10	ΔW : 1×10^{-3} g $\Delta W/A$: 0.0312940 mg/cm ² Area: 31.954915 cm ² Oxide thickness: 8 μ m
50	ΔW : 1.7×10^{-3} g $\Delta W/A$: 0.0531594 mg/cm ² Area: 31.97982 cm ² Oxide thickness: 12 μ m
100	ΔW : 2.1×10^{-3} g $\Delta W/A$: 0.0656060 mg/cm ² Area: 32.00923 cm ² Oxide thickness: 12-13 μ m

ΔW : Weight change. A: oxidized area.

more homogeneous in appearance after 100 h.

Oxidation kinetics

After exposure, the weight change of all samples was determined with 10^{-5} sensitivity. The results obtained after oxidation tests were shown in Table 2. The oxidation graph ($\Delta W/A$) of sample indicates that samples show a sub-parabolic oxidation behavior (Figure 2a). It is a diffusion-controlled oxidation in which weight increases with increasing the oxidation time (Türker et al., 1995). This mechanism is typical of non-steady-state diffusion-controlled reactions.

The ionic diffusion flux is inversely proportional to the thickness of diffusion barrier, and the change in scale thickness or weight is likewise proportional to the ionic diffusion flux (Fontana, 1986). The oxide formed is assumed to be dense, adherent and non-porous. These features are preferred for high temperature applications. In order to evaluate the oxidation behavior of Ni based ODS superalloy, parabolic rate law is applied to the data given in Figure 2a. The parabolic rate equation is given by;

$$(\Delta W/A)^2 = k_p \cdot t$$

Where k_p denotes the parabolic rate constant, t is time (h), and $\Delta W/A$ is the oxidation rate (mg/cm²). Diffusion-controlled parabolic oxidation kinetics is determined by k_p

which is defined as parabolic rate constant. k_p has parabolic oxidation kinetics. k_p is gained by the ratio of the square of the increase in weight per unit area of the sample to the duration of oxidation. k_p indicates that surface protective oxide layer avoids the reactive gathering and oxidation rate decrease related with time. In order to determine the parabolic rate constant, k_p , the graph of $(\Delta W/A)^2$ against exposure time is drawn and the slope in Figure 2b is obtained.

The working life's of high temperature materials are strongly dependent on the rate of oxidation. Hence, the estimation of long term behavior, which is of great importance in the practical application of the materials at elevated temperatures, requires an accurate knowledge of growth kinetics. The short term oxidation kinetics of some ferritic superalloys was found to be essentially parabolic (Ramanarayanan et al., 1988; Nickel and Quadackers, 1991; Hendrich, 1988) whereas the long term oxidation behavior of these alloys is controversial (Bennett and Houlton, 1990). However, most of the oxide dispersion strengthened (ODS) alloys exhibit parabolic oxidation behavior. Since these alloys are designed to be used at elevated temperature for a long time, sub-parabolic oxidation behavior is desired compared to parabolic one.

Rapid oxidation rate accelerates the Cr or Al depletion of the matrix. When the depletion of protective scale forming elements such as Cr or Al reaches a critical value, the materials behave essentially as a chromium bearing ferritic alloys and subsequent exposure will produce an external scale of less protective oxide layer or a spinel (Mikkelsen, 2003; Obigodi-Ndjeng, 2011). This behavior may then result in breakaway oxidation after a short time.

In case of slow oxidation rate such as sub-parabolic oxidation rate, breakaway oxidation or dropping the oxidation elements to a critical level takes time which results in longer service life. That is why sub-parabolic oxidation kinetic is preferred for high temperature applications (Türker, 1999). Gonzales et al. (1999) exposed the Ni based ODS alloys between 900 to 1200°C for up to 100 h to determine the oxidation kinetics and the weight change results has shown that sample exposed at 900°C exhibited parabolic oxidation kinetics while the other samples exposed at higher temperature showed sub-parabolic oxidation behavior. Another work has been carried out on Ni based superalloys 900 and 1000°C for 5, 10, 50 and 100 h and all samples exhibited parabolic oxidation kinetic (Evin, 2003).

Other investigators (Suryanarayana et al., 2001) have studied the effect of surface quality on the oxidation behavior of MA 956 and found that sample with good surface quality showed continuous weight gain and consistent increase in oxide thickness together with homogeneous oxide film. Furthermore, sample with good surface quality had parabolic oxidation kinetic whereas sample with rough surface had sub-parabolic oxidation

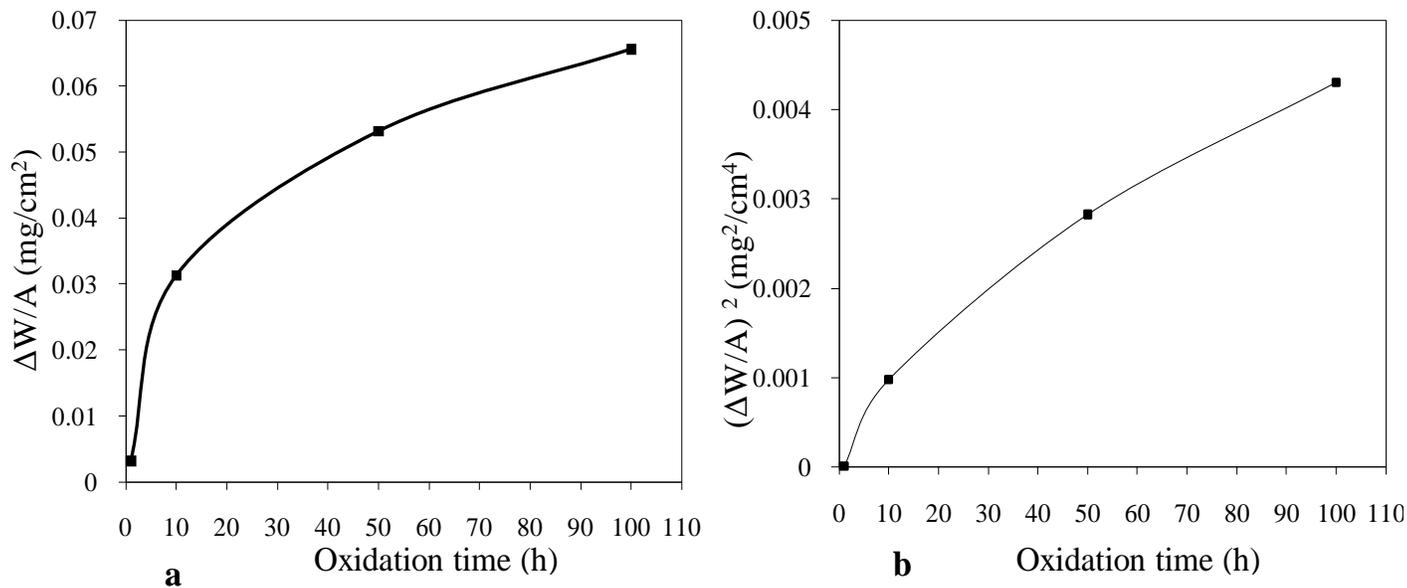


Figure 2. (a) Effect of exposure time at 1200°C on weight change, (b) Weight gain squared against exposure time.

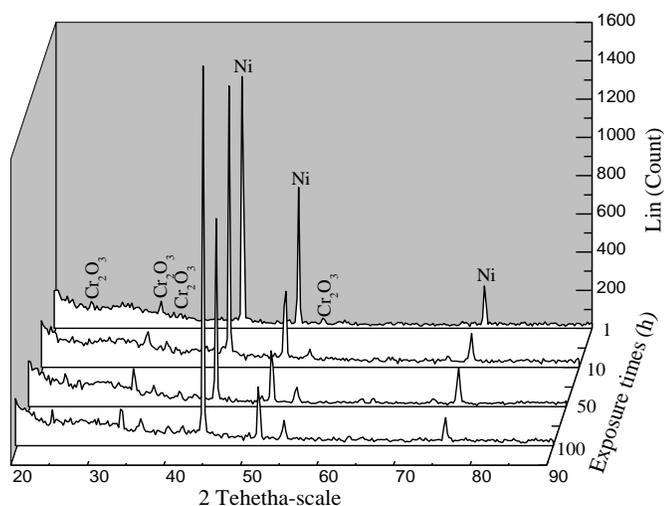


Figure 3. XRD results of the oxidized samples for various exposure times.

behavior.

Another work has been carried out on extruded Ni based IN 718 and exposed to oxidation at 1100°C for up to 180 h and showed Nb rich Cr_2O_3 film on the surface. Oxide thickness and weight gain were detected through the oxidation process up to 160 h. An increase in micro hardness has also been detected from surface to the matrix (Geng et al., 2007). Ni based alloy oxidized at 950°C for 128 h and showed parabolic oxidation behavior whereas it did not obey the parabolic rate when oxidized at 1000°C for 140 h (Zhao et al., 2004). In order to increase the isothermal and cyclic oxidation behavior of

IN 100, Wang et al. (2002) coated the alloy with 10 μm thick NiCrAlY and heat treated at 950 to 1050°C in a vacuum atmosphere for 2 h. Isothermal and cyclic oxidation tests were applied to the coated samples at 900 to 1000°C. During oxidation, all samples exhibited parabolic oxidation behavior (Wang et al., 2002).

X-ray diffraction (XRD) results

XRD results of the sample are given in Figure 3 after various oxidation durations (1, 10, 50 and 100 h). As shown in Figure 3, a small amount of protective oxide layer of Cr_2O_3 is formed on the surface after 1 h exposure. Cr_2O_3 generally grows on the surface of Ni based super alloys. The intensity of the Cr_2O_3 peak increased with increasing the oxidation duration (10 h). Increasing the oxidation duration to 50 h resulted in thicker oxide film causing a more intensive peak formation. The intensity of the Cr_2O_3 XRD peaks increased with increasing the oxidation duration (100 h), indicating the gradual increasing of thickness of oxide layer.

Evin (2003) has studied the oxidation behavior of Ni based superalloy at 900 and 1000°C in pure oxygen for 5, 10, 50, 100 h and detected some NiCrO_3 and NiCrO_4 on the outer surface of the samples. Similar studies have been carried out for Inconel 740 at 950°C for 128 h and 1000°C for 140 h and some oxide layers of Cr_2O_3 , (NiCo) Cr_2O_4 and TiO_2 α - Al_2O_3 (Zhao et al., 2004) were found. Wand et al. (2002) studied the oxidation behavior of NiCrAlY coated Ni based IN100 at 900°C and found some protective α - Al_2O_3 and Cr_2O_3 film on the surface.

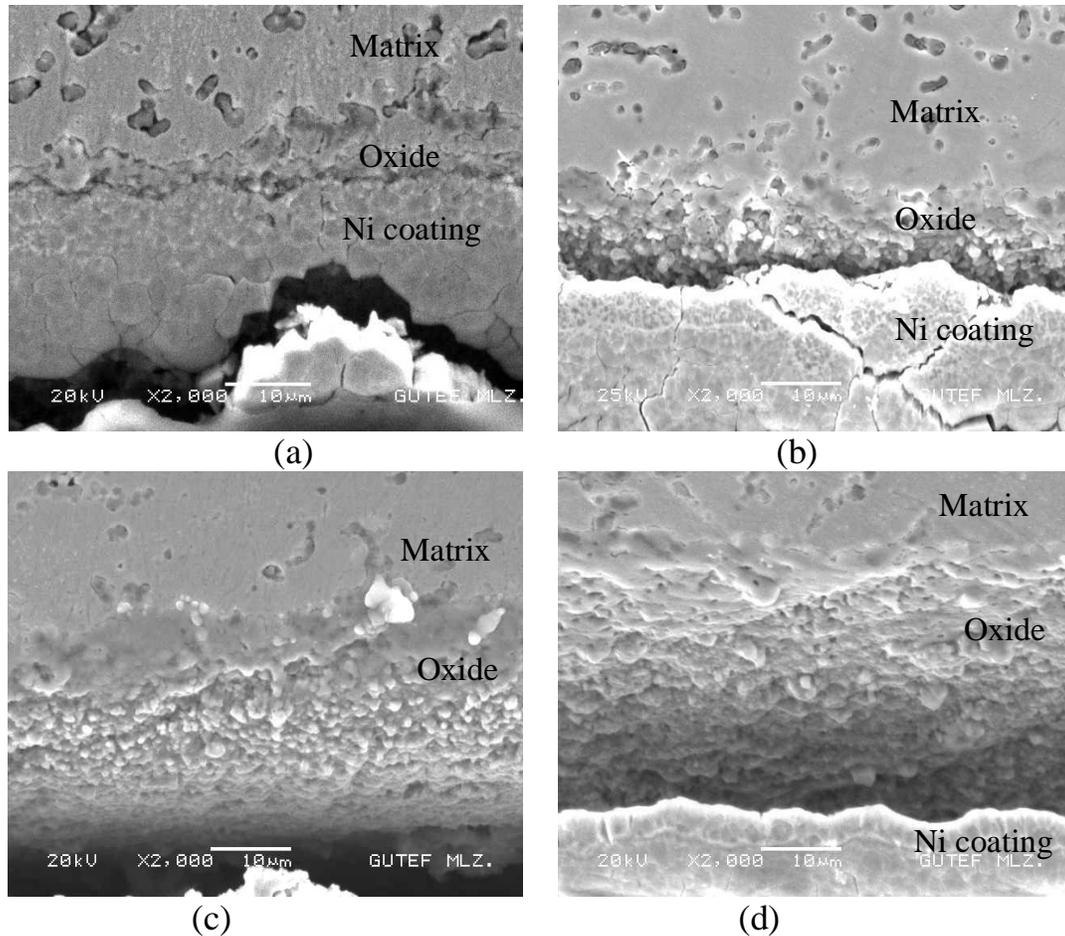


Figure 4. SEM micrographs of oxidized and polished surfaces: (a) 1, (b) 10, (c) 50 and (d) 100 h.

SEM analysis

Polished surface

SEM images of the polished section are seen in Figure 4a to d. Sample exposed for 1 h shows an oxide layer with the thickness of 3 μm although some 1 to 2 μm thick areas are also visible. The results indicate that in the early stage of oxidation, homogeneous oxide film does not form on the sample which is also non-protective. SEM investigation shows (Figure 1a) some local oxide formation on the surface. Figure 4b shows SEM micrographs of polished section of the sample with about 8 μm oxide layer covering almost the entire surface after exposure for 10 h.

The results in the foregoing indicate that even though the thickness of oxide layer is enough for the protection of the materials, the density is not enough. Figure 4c shows the SEM micrograph of the surface oxide layer after exposure for 50 h. The thickness of oxide is about 12 μm which is compact and cover the surface uniformly. It indicates that the density and thickness of oxide increase with increasing the exposure time. Figure 4d

shows the SEM image of the oxide layer after exposure for 100 h. These results indicate that the thickness of the oxide layer of the samples exposed for 50 and 100 h is almost the same. The thickness of the oxide layer is about 12 to 13 μm after 100 h, but it is more compact and adherent than 50 h exposed sample. The dense oxide layer positively affects the weight gain. Furthermore, this oxide layer was found to be bonded to the matrix via longitudinal keys. It is suggested that numerous oxide protrusions form mainly around the rare-earth containing second phase particles in the alloy at the oxide scale interface, and they are instrumental in pinning the oxide scale to the underlying metal (Stott et al., 1979). This results in the strengthening of the metal-oxide interface and increasing of the life time of the materials.

In order to determine the oxidation kinetics of Ni based superalloys, Evin (2003) exposed samples in pure oxygen at 900 and 1000°C for up to 100 h and oxide layer thickness (0.4 to 52.7 μm) was found to be dependent on the oxidation durations and oxidation temperature. Another study was carried out on Inconel 740 at 950 and 1000°C for 128 to 140 h and the thickness of the upper and lower surface of the material

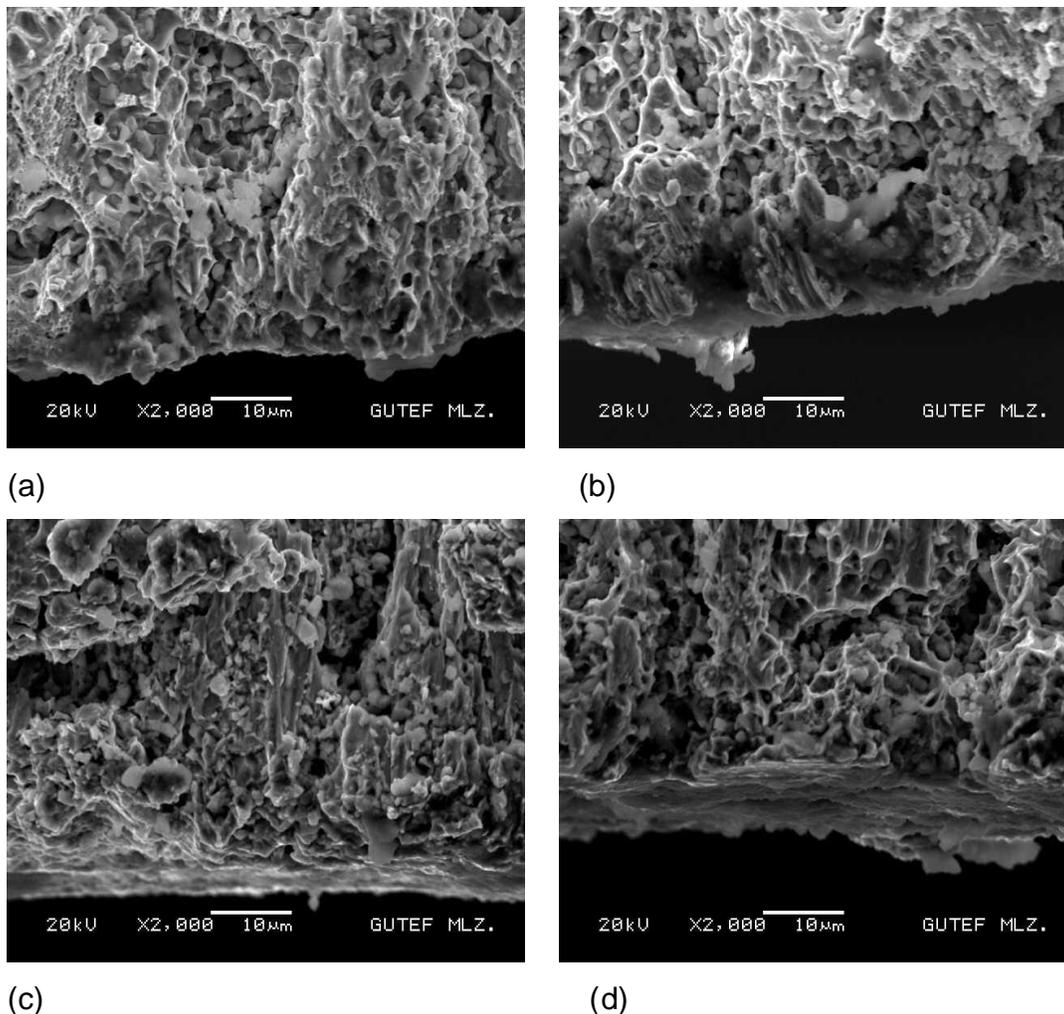


Figure 5. SEM images of the fracture surface for various exposure times: (a) 1, (b) 10, (c) 50 and (d) 100 h.

was found to be different (Geng et al., 2007).

Fracture surface

SEM micrographs of the fractured surface are seen in Figure 5a to d. Sample exposed for 1 h shows very fine surface oxide layer, laying on the edge of the materials (Figure 5a). On the contrary to matrix materials, which contain some dimples, the oxide layer exhibits smooth, sharp and brittle fracture. Increasing the exposure time to 10, 50 and 100 h, the thickness of surface oxide increased. Fractured surface clearly indicates that longer exposure time results in more dense, smoother surface with sharp edges on the oxide film that indicates brittle fracture mode (Figure 5b, c and d).

Conclusions

Ni based superalloy was produced by MA techniques and

oxidized at 1000°C for up to 100 h and the following results were obtained:

1. The thickness of the oxide film formed on the surface of metal increased with increasing the exposure time and showed good homogeneity and adherence with the underlying matrix material.
2. In this experimental work, all samples showed sub-parabolic oxidation behavior. These types of oxides are preferred for high temperature applications.
3. XRD results indicate that all samples showed Cr_2O_3 film on the surface after exposure for 1, 10, 50 and 100 h, and the intensity of chromium peak increased with increasing the exposure time.

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