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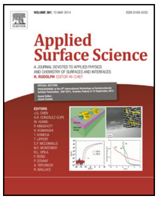

Formation of multilayered scale during the oxidation of NiAl–Mo alloy

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ABSTRACT

We have studied the oxidation behavior of a hypereutectic NiAl–Mo alloy. This alloy showed an initial rapid mass loss followed by a relatively steady state behavior. The oxide scale formed during the oxidation process was seen to have a multilayered structure comprising of NiO, $NiAl_2O_4$, $NiMoO_4$ and Al_2O_3 with minor amounts of MoO_2 in the sub-scale region. The oxidation behavior is influenced significantly by the formation and stability of the constituent oxides, especially $NiMoO_4$. Hence the decomposition behavior of $NiMoO_4$ in the 1100–1200 °C was studied as well. The thermal decomposition of the $NiMoO_4$ was slow at 1100 °C, but accelerated at 1200 °C, resulting in the formation of NiO, which remained in the oxide scale, and MoO_3, which volatilized away.

1. Introduction

Nickel aluminides have been extensively studied as prospective high temperature oxidation resistant intermetallic compounds [1,2]. Pettit's work showed that β-NiAl to be an extremely oxidation resistant compound due to its high aluminum content [3]. He showed that the oxidation of this compound was characterized by the formation of a slow growing Al_2O_3 scale and the absence of NiO and $NiAl_2O_4$ over a long oxidation period. Kuznetsov investigated the ternary Ni–Al–O equilibrium at 1000 °C and explored the formation of various oxides and demonstrated that the $NiAl_2O_4$ spinel can exist in thermodynamic equilibrium with NiO, Al_2O_3 and Ni, but not with NiAl [4]. Trumble and Rühle studied spinel formation in diffusion bonded Ni/Al_2O_3 at 1390 °C [5]. From these studies, it was apparent that the β-NiAl could exist in thermodynamic equilibrium with only Al_2O_3 but not the spinel. On the other hand, the spinel exists in thermodynamic equilibrium with NiO, Al_2O_3 and the Ni rich solid solution.

The formation of $NiAl_2O_4$ spinel during high temperature oxidation in ambient atmosphere is an interesting phenomenon, given that previous studies have shown that spinel formation on bulk β-NiAl is a strong function of the oxygen partial pressure (p_{O_2}). So far, the reports indicate that $NiAl_2O_4$ can be formed on bulk β-NiAl only at very low values of p_{O_2} [6,7]. On the other hand, studies on oxidation of Ni–Al alloys having either relatively low Al content, or a ternary alloying addition, or both, have shown the formation of the spinel phase. For instance, Kuenzly and Douglass studied the oxidation of a $Ni–Ni_3Al$ alloy with and without yttrium additions in the temperature range of 900–1200 °C. It was seen that NiO formed a part of the oxide scale. The $NiAl_2O_4$ spinel was also observed to form in the alloys containing 0.5 wt% yttrium [8]. Tjong studied the oxidation of a high activity β-NiAl coating on a γ phase Inconel 625 superalloy [9]. TEM studies following the oxidation at 1200 °C for as low as 250 s revealed the presence of a highly oriented NiO, $Ni(Al,Cr)_2O_4$ and α-$(Al,Cr)_2O_3$. The base Inconel alloy was presumably the source of chromium in the oxide scale. Strawbridge et al. studied the oxidation of dilute Ni base alloys and observed the formation of NiO in the scale as well [10]. Hindam and Smeltzer studied dilute Ni–Al alloys with low Al content (<6 wt% Al) and reported the formation of NiO and $NiAl_2O_4$ [11]. $NiAl_2O_4$ spinel can form by counter-diffusion of Ni and Al ions when Al_2O_3 and NiO are heated in contact with each other.

While oxidation of nickel aluminides generally result in an adhesive, slow growing protective Al_2O_3 scale, oxidation of molybdenum results in the formation of a volatile product, MoO_3, although MoO_2 can also form at low oxygen partial pressures [12,13]. Unlike nickel aluminides, where the steady state oxidation process is largely diffusion controlled, resulting in parabolic kinetics and low mass gain [1], oxidation of Mo is much more aggressive and follows linear kinetics, with significant mass loss [14]. Brenner studied the oxidation behavior of a binary Ni–Mo alloy and reported a formation of a triple layered structure, with NiO forming externally, $NiMoO_4$ forming in the middle layer and MoO_2 forming at the subscale region [15]. However, presence of high Al content has been known to suppress the formation of NiO in pure nickel aluminides resulting in an exclusive alumina scale [1,3]. Brenner's work suggested that alloys containing more than 20.6 at.% of Mo results in catastrophic oxidation. Our prior work on the isothermal kinetics

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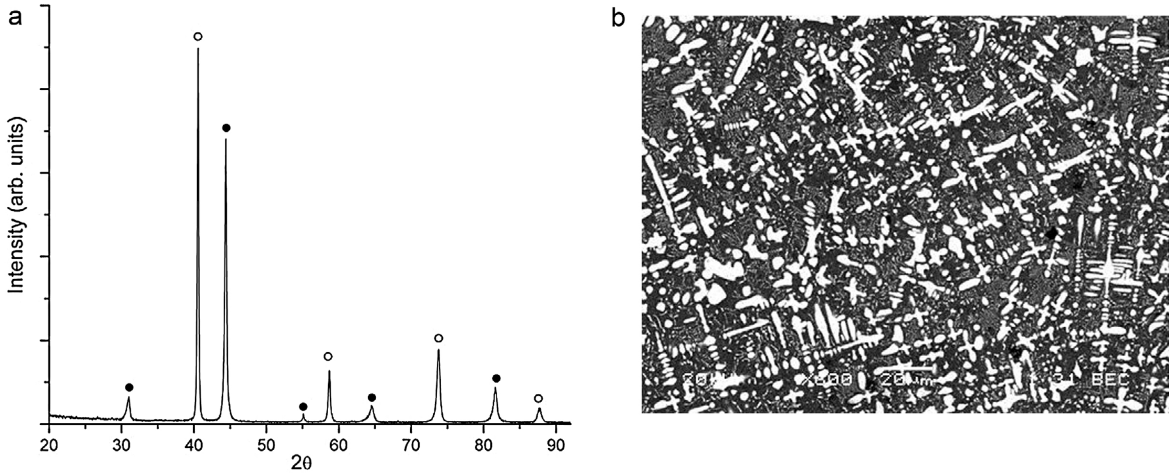

Fig. 1. (a) X-ray diffraction pattern of the NiAl–Mo alloy; (b) microstructure of the NiAl–Mo alloy.

of NiAl–Mo alloys showed that the mass loss rates in these alloys bear comparison with Mo–Si–B alloys at 1100 °C [15]. While the mass loss during the isothermal testing is relatively low, the oxide scale spallation when the oxidized coupons cool needs to be better understood, and this is the prime motivation for this study on the oxide scale development and oxidation behavior of such a NiAl–Mo alloy in the two phase (Mo + NiAl) region and thermal stability of the $NiMoO_4$ formed during this oxidation process.

2. Experimental

The alloys in the present study were prepared by arc melting of powder compacts. Pure elemental powders of Mo (Alfa Aesar, 99.5%), Ni (Materials Preparation Center, Ames Laboratory, 99.6%) and Al (Alfa Aesar, 99.8%) having a nominal composition $Ni_{40}Al_{40}Mo_{20}$ were mixed in appropriate ratios in a high energy SPEX 8000 mixer/shaker mill for 15 min and pelletized using a hydraulic press (Carver Inc.). The pellets were arc-melted in an ultra-high purity argon atmosphere (99.99% pure) on a water-cooled copper hearth using a Zr getter. The arc-melted buttons were then drop-cast into 10 mm diameter rods in a water-cooled cylindrical copper mold in an ultra-high purity argon atmosphere (99.95% pure). In order to better understand the oxidation behavior of this alloy, it was essential to know the thermal stability of the constituent phases in the oxide scale.

While the stabilities of most of the oxides observed are well studied, there is a relative paucity of data pertaining to the decomposition of $NiMoO_4$. Hence, we prepared $NiMoO_4$ by heating a pelletized mixture of Ni and Mo powders in equiatomic ratio at 900 °C for 24 h. X-ray diffraction of the oxidized product showed the formation of the α-$NiMoO_4$ compound. These powders were then heat treated for 2 h at different temperatures in ambient air, and the resulting products were studied using XRD to assess the phase changes that occurred in this process.

Alloy coupons for oxidation tests were cut from the drop-cast rods using a high speed saw equipped with an alumina blade. The isothermal oxidation tests were carried out at 1200 °C in ambient atmosphere for different time intervals. All the mass measurements were carried out *ex situ*. The coupons showed a tendency of significant spallation while cooling down to room temperature. The oxidized coupons were characterized using scanning electron microscopy. A JEOL 5910LV scanning electron microscope (SEM) was used to characterize the microstructures of the alloys. Semi-quantitative chemical analysis was done to identify the different phases in the microstructure using energy dispersive spectroscopy (EDS) (Noran-Vantage). Oxidized samples for scanning electron microscopy were prepared by first coating a thin layer of gold on the oxidized coupon. The coupon was then copper-plated electrolytically and cut to obtain cross-sections and polished for the SEM studies. X-ray diffraction (XRD) was carried out using an X-ray diffractometer (PANalytical, Philips) with a Bragg–Brentano geometry using a monochromatic Cu Kα radiation (wavelength = 1.54059 Å), with the data being collected over the range $2\theta = 20$–80°.

3. Results

Fig. 1(a) shows the X-ray diffraction pattern of the NiAl–Mo alloy. It can be seen that the alloy consists of two phases–NiAl and Mo. The lattice parameters of NiAl and Mo were found to be 2.89 and 3.15 Å respectively. These values are very close to the reported values of the pure phases in these materials, indicating that there is fairly low dissolution of Mo in NiAl or Ni and Al in a Mo based solid solution. Fig. 1(b) shows the microstructure of the NiAl–Mo alloy. It can be seen that this alloy exhibits a two phase microstructure consisting primarily of Mo dendrites in a NiAl matrix with a significant amount of a lamellar NiAl–Mo eutectic in the inter-dendritic regions. This is in accordance with the reported NiAl–Mo pseudo binary phase diagram as well as our prior work on this system [16,17].

Fig. 2(a) shows the oxidation kinetics of this alloy at 1200 °C. It can be seen that there is a rapid initial mass loss, which gradually slows over time. The initial mass loss can be attributed to the formation of MoO_3 during the oxidation of the Mo phase. MoO_3 volatilizes above 700 °C [14] and deposits in the cooler sections of the furnace. As MoO_3 volatilizes, fresh surface of either Mo or NiAl is exposed to the oxidizing atmosphere, resulting in the formation of a number of other oxide phases. The presence of these oxide phases were detected using both XRD and SEM. As the oxidation coupons are taken out from the furnace, they rapidly cool and outer scale spalls off after cooling, while the inner layers of the oxide scale adhere to the surface. Fig. 2(b) shows the X-ray diffraction pattern from the spalled oxide scale while Fig. 2(c) shows the X-ray diffraction pattern of the oxidized surface. It can be seen that the spalled scale comprises primarily of NiO and $NiAl_2O_4$ and some amount of $NiMoO_4$. On the other hand, apart from the Mo and NiAl phases of the base alloy, $NiAl_2O_4$ and Al_2O_3 can be observed as the major phases in the diffraction pattern from the oxidized coupon surface.