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E. Huape-Padilla

Centro de Investigación en Materiales Avanzados (CIMAV), Miguel de Cervantes No. 120, C.P. 31109, Chihuahua, Chih., México.

Universidad Michoacana de San Nicolás de Hidalgo, Edif. "W", C.U., C.P. 58000, Morelia, Mich., México.

E-mail: engelbert.huape@cimav.edu.mx

L. Bejar-Gómez

Universidad Michoacana de San Nicolás de Hidalgo, Edif. "W", C.U., C.P. 58000, Morelia, Mich., México.

A. Borunda-Terrazas

Centro de Investigación en Materiales Avanzados (CIMAV), Miguel de Cervantes No. 120, C.P. 31109, Chihuahua, Chih., México.

J.G. Chacón-Nava

Centro de Investigación en Materiales Avanzados (CIMAV), Miguel de Cervantes No. 120, C.P. 31109, Chihuahua, Chih., México.

A. Martínez-Villafañe

Centro de Investigación en Materiales Avanzados (CIMAV), Miguel de Cervantes No. 120, C.P. 31109, Chihuahua, Chih., México.

“HIGH TEMPERATURE OXIDATION BEHAVIOR OF Ni₃Al AND Ni₃AlNDPR INTERMETALLIC ALLOYS”

ABSTRACT

The influence of rare earth elements (REE's) i.e. Neodymium (Nd) and Praseodymium (Pr) on the oxidation behavior of a Ni₃Al intermetallic alloy with and without rare earths has been evaluated, and its role on the oxidation rate and oxide morphology and formation has been discussed. Specimens were isothermally oxidized in air at 800, 900, 1000, and 1100°C during 48 h. It was found that a simultaneous addition (≤ 0.03 wt. %) of both Nd and Pr, reduced the oxidation rate of the Ni₃Al intermetallic alloy. Analysis by scanning electronic microscope (SEM) revealed that the morphology of oxides formed on Ni₃Al intermetallic alloy specimens with and without REE's was very different. For these alloys mainly, aluminum enrichment at the metal/scale interface was observed.

INTRODUCTION

Intermetallic compounds such as nickel aluminides (Ni_3Al and NiAl), iron aluminides (FeAl , and Fe_3Al) and titanium aluminides (TiAl and Ti_3Al) are a class of advanced materials with considerable potential for low and high-temperature application [1–4]. Processing approaches for aluminides include casting, thermomechanical and powder processing of pre-alloyed powder [5]. Because of the potential use of nickel aluminides at high temperatures, it is imperative to understand and study of their oxidation behavior. It was reported that the types of scale (oxide or mixture of oxides) and scale morphology formed on the surface of the alloy during high-temperature oxidation were influenced by both the compositions of the gas and the alloy as well as the reaction temperature [6]. Both thermodynamic and kinetic factors should be considered to understand this complex oxidation process. Thermodynamics governs and predicts the type of oxide that can form under the operating conditions, and for nickel aluminides, the formation of alumina (Al_2O_3), nickel oxide (NiO), and nickel aluminate (NiAl_2O_4) have been reported to compete with one another, depending on which one is more thermodynamically stable to form at the operating temperature [7–10].

For many years, nickel-aluminum intermetallic has received special interest because of their potentially high oxidation resistance at high temperature. They offer a good alternative for use in automotive parts, chemical processing, and gas turbine technologies since they possess a high melting point, high thermal conductivity, excellent oxidation resistance, low density, and low cost. Other work has suggested that oxidation of nickel aluminides without these oxygen-active elements is worse in air than oxygen, particularly at 1000 and 1100°C, due to internal nitridation below a defective scale. The Ni_3Al alloys produced by ingot-metallurgy processes tended to have worse oxidation behavior, since they had greater spallation than oxide-dispersion-strengthened nickel aluminides of similar composition. [11] Rare-earth elements were originally added to alloys as deoxidizers or, in the form of oxides, as high-temperature strengtheners. For more than 60 years, it has been known that the presence of rare-earth oxides (e.g. CeO_2) dispersed in alloys could also improve oxidation resistance and improve scale adherence. Similar beneficial effects on oxidation behavior have been observed for the addition of small amounts of rare-earth elements in Cr_2O_3 and Al_2O_3 forming alloys. Later, it was found that the addition of oxygen-active elements such as Y, Hf, Th, Zr, Nb and Ti or their stable oxides to metals and high-temperature alloys also improves oxidation resistance and scale adherence. [12] In this work, a study of the oxidation behavior of ingot-metallurgy processes of nickel aluminides with and without Nd plus Pr, in air has been carried out.

EXPERIMENTAL PROCEDURE

Ni-13wt.%Al (Ni_3Al) and Ni-13wt.%Al-0.01wt.%Nd-0.01wt.%Pr (Ni_3AlNdPr), intermetallic ingots were produced by a standard electrical arc furnace with a purified argon atmosphere using high pure Ni, Al, Nd and Pr metals (99.99%). Coupons with the dimensions of 1.0 x 0.5 x 0.1 cm size were sectioned from the cast ingot. The samples were cleaned and degreased. Afterwards, the surfaces were ground to 1200 grit paper, rinsed with distilled water and degreased with acetone. Each specimen was set on a platinum plate for weight-gain measurements in an electronic microbalance (sensitivity 10^{-6} g). Experiments were conducted in an atmosphere of air, a fixed temperature of 800, 900, 1000 and 1100°C ($\pm 2^\circ\text{C}$) and an exposure time of 48 h. The oxidized samples were analyzed using a scanning electron microscope (SEM-Jeol JSM-5800LV microscope) coupled with energy dispersive x-ray spectroscopy (EDS). These techniques are useful in understanding the oxidation phenomena in terms of scale morphology and distribution products.

RESULTS AND DISCUSSION

Structure and Microstructure

In the Ni-Al alloy system, as the Al content is varied, other phases in addition to the γ , γ' , and β appear. A map of all of these phases formed as a function of composition and temperature is called the (equilibrium) phase diagram, shown in Fig. 1. ^[13] Equilibrium here refers to the fact that the phases in the map remain stable over time when held at appropriate temperatures. Because the diagram shown here describes an alloy of two components only, Ni and Al, it is called a binary phase diagram. The two phases bounding the diagram (in this case face center cubic (fcc) Al and Ni) are called the terminal phases.

Ni crystallizes in a fcc structure. If we alloy Ni by adding Al, several significant changes occur. For up to about 4wt%Al, there is no change in the atomic arrangement of Ni except an occasional Al atom replacing a Ni atom randomly, as in Fig. 2(a). The structure remains essentially like fcc Ni, called the γ phase. As the Al content is increased, it starts selectively replacing the corner atoms (Fig. 2(b)), while the atoms on the cube faces remain Ni. The share of atoms for each cell is 1 Al and 3 Ni, giving the composition Ni_3Al , which is known as the γ' phase. If the alloying addition is continued, eventually at about 25 wt%Al, the crystal structure changes so that the corner atoms remain Ni, while Al enters the center of the cube. The central Al atom belongs to this cell, while the corner atoms are each shared

with eight cells. The overall share is therefore 1 Al and 1 Ni, providing the composition of NiAl, known as the β phase, Fig. 2(c).

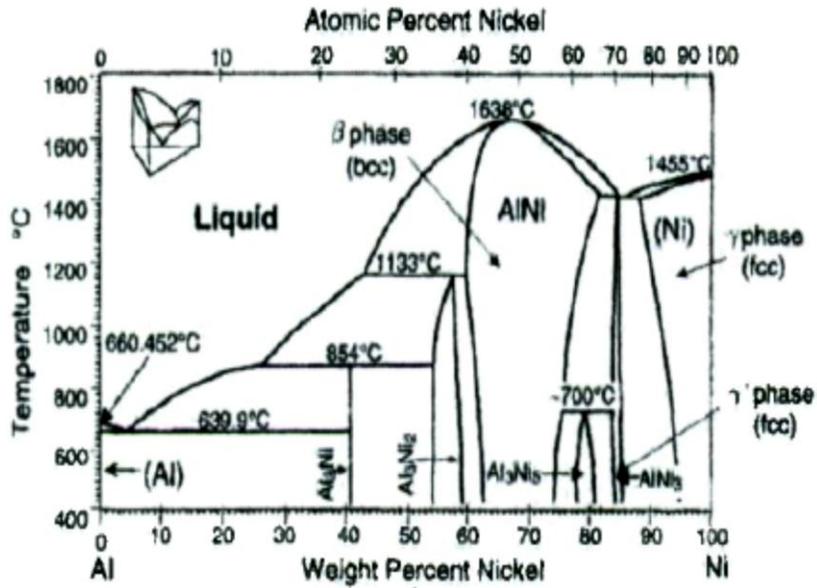


Figure 1. Ni-Al phase diagram. 2nd ed. ASM International; 1996

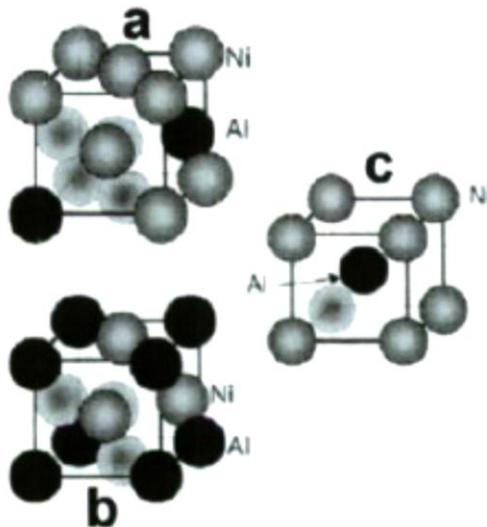


Figure 2. Effect of alloying on crystal structure

Microstructural examination of the compact in the as-cast condition revealed a no homogeneous grain size distribution, Fig. 3, with an average size of about 200 and 100 μm for as cast Ni_3Al and Ni_3AlNdPr respectively.

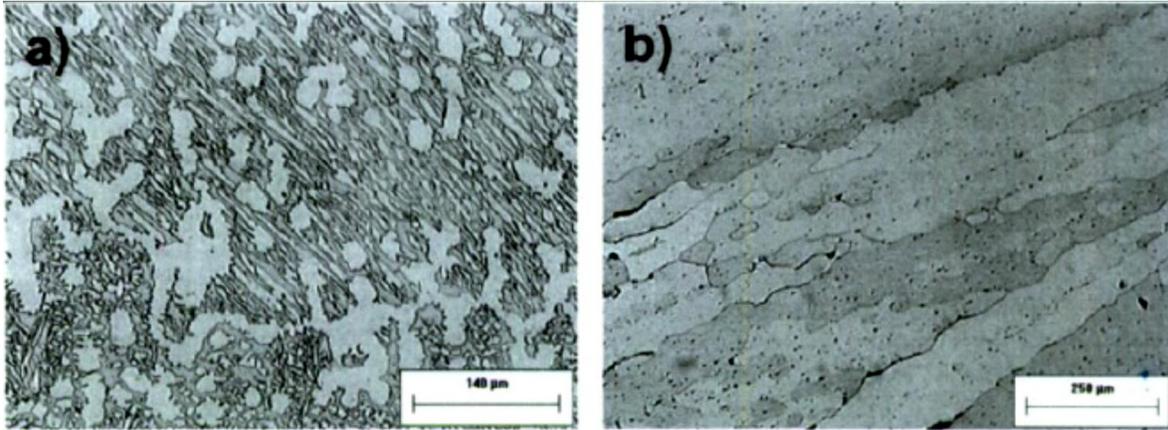


Figure 3. Some aspects of the a) as cast Ni_3Al microstructure and b) as cast Ni_3AlNdPr microstructure

Kinetics

Figures 4 and 5 shows the weight gain per unit area against time for Ni_3Al and Ni_3AlNdPr respectively; in samples oxidized in air at 800, 900, 1000 and 1100 $^{\circ}\text{C}$ for a period of 48 hours. In all cases, a parabolic behavior was found and the rate constants derived for all temperatures are shown in table 1.

The kinetic results confirmed the beneficial effect of Nd-Pr addition on the oxidation behavior of the Ni_3Al intermetallic alloys. Thus, the weight change observed for Ni_3AlNdPr at 800, 900, 1000 and 1100 $^{\circ}\text{C}$ was negligible (about 0.25, 0.33, 0.41 and 0.48 mg/cm^2 , respectively) as compared to that for Ni_3Al at 800, 900, 1000 and 1100 $^{\circ}\text{C}$ (2.15, 4.59, 8.90 and 11.83 mg/cm^2 , respectively). Ni_3Al specimens showed cracking on the scale surface under exposition during 48 h.

Regardless the temperatures, the kinetic constants in this work were about thirty times lower for the alloys without the addition of Nd and Pr, on the oxidation behavior of Ni_3Al intermetallic alloys. Thus, according with the present results, the addition of Nd-Pr helped to decrease the oxidation kinetics, probably by avoiding massive diffusion of Al towards the intermetallic/environment interface. Values of k_p were calculated from plots of square weight-change data versus time. Activation energy for were determined from the plot of parabolic rate law constants (k_p) in an Arrhenius diagram. The weight gain per unit area as a function of time, i.e. ($\Delta W/A$) versus t , constituted the primary data and curves

are shown in fig.4 and 5 for Ni_3Al and $Ni_3AlNdPr$ respectively. The parabolic rate law was first considered as the basis of data processing and interpretation of results in this research work.

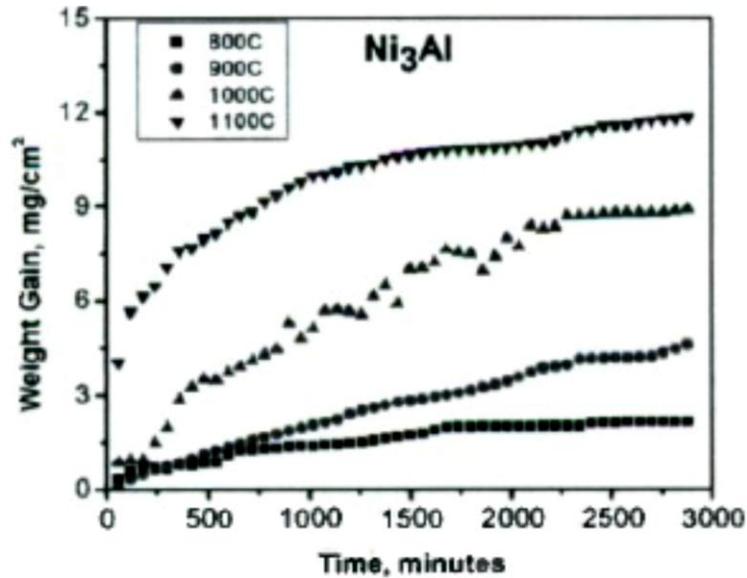


Fig.4. Kinetic data for the isothermal oxidation of Ni_3Al intermetallic alloy during oxidation in air at 800, 900, 1000 and 1100°C during 48h

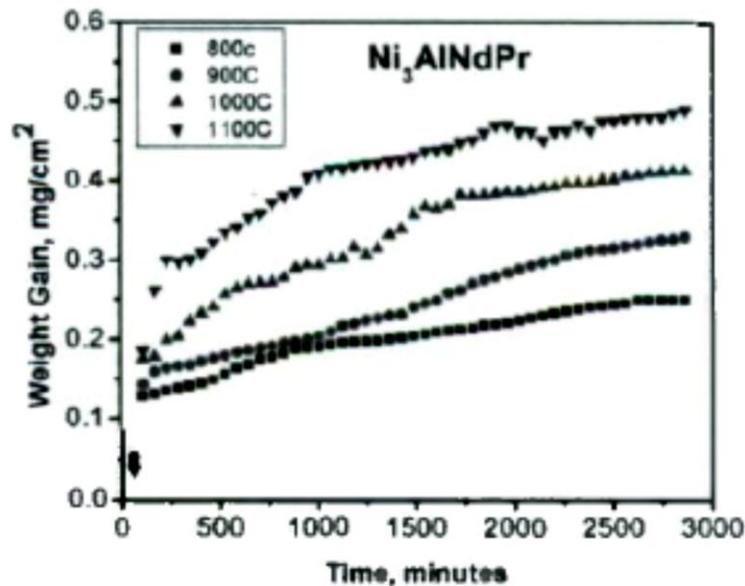


Fig.5. Kinetic data for the isothermal oxidation of $Ni_3AlNdPr$ intermetallic alloy during oxidation in air at 800, 900, 1000 and 1100°C during 48h

The parabolic rate constant (K_p) is related to the weight gain ($\Delta W/A$) and exposure time (t) by the following relation:

$$(\Delta W/A)^2 = K_p t + c \dots\dots\dots (1)$$

Where c is a constant. The rate constant K_p was obtained from the slope of the linear regression-fitted line of $(\Delta W/A)^2$ vs t plot. The rate constants are provided in table 1 for the experiments performed in this study.

Table 1. Oxidation rate constant k_p of Ni_3Al and $Ni_3AlNdPr$ intermetallic alloy at different temperatures

Intermetallic Alloys	$K_p, g^2cm^{-4}s^{-1}$	$K_p, g^2cm^{-4}s^{-1}$	$K_p, g^2cm^{-4}s^{-1}$	$K_p, g^2cm^{-4}s^{-1}$
	800°C	900°C	1000°C	1100°C
Ni_3Al	2.90×10^{-11}	1.29×10^{-10}	5.28×10^{-10}	6.28×10^{-10}
$Ni_3AlNdPr$	4.47×10^{-13}	5.62×10^{-13}	6.45×10^{-13}	9.22×10^{-13}

Fig. 6 shows the change in the experimentally determined values of K_p with the temperature for Ni_3Al and $Ni_3AlNdPr$ intermetallic alloys respectively. It is a normal practice to correlate the overall parabolic rate constant (K_p) and temperature through an Arrhenius-type equation:

$$K_p = K_0 \exp(-Q/RT) \dots\dots\dots (2)$$

Where R is the universal gas constant, K_0 the pre-exponential factor. T is the absolute temperature and Q is the activation energy.

The activation energies for this system were $Q_{Ni_3Al}=132$ and $Q_{Ni_3AlNdPr}=28$ KJ/mol. Babu et al. found an activation energy of 92 kJ/mol for oxidation kinetics of $Fe_{25}Al$ [14]. The activation energy values collected from the present kinetics data are in agreement with Babu's values.

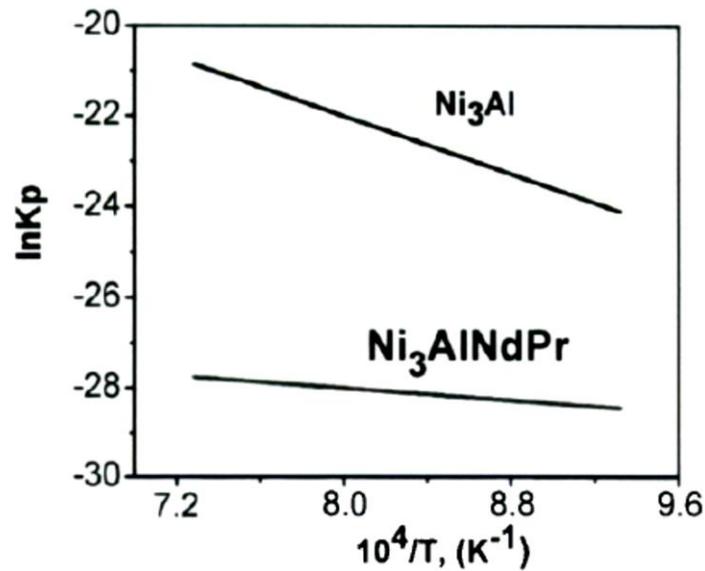


Figure 6. Activation energy for Ni_3Al and $Ni_3AlNdPr$ intermetallic alloys

Morphology

In the present study, it was clearly observed that the nature of the formed scale on the binary intermetallic changed with temperature. This was also evident from morphological observations in the SEM after the Ni_3Al specimens had been oxidized during 48h (fig. 7), Spalling of scale was more pronounced at the lower oxidation temperatures. After oxidation at 800C, the surface oxide morphology consisted mainly of granular oxides (fig. 7a) while, after 900°C oxidation crystal chains-like scales (extrinsic ridges structure) were observed. (fig.7b), at 1000°C oxidation spalling of scales was observed and some plate-like aluminum oxide were founded on the top surface (fig.7c) and convoluted morphology during oxidation at 1100°C for 48 h (fig. 7d). Morphological observations of the oxide layers indicated that the poor oxidation resistance was mainly evidenced by scale failure, especially cracking and severe spallation.

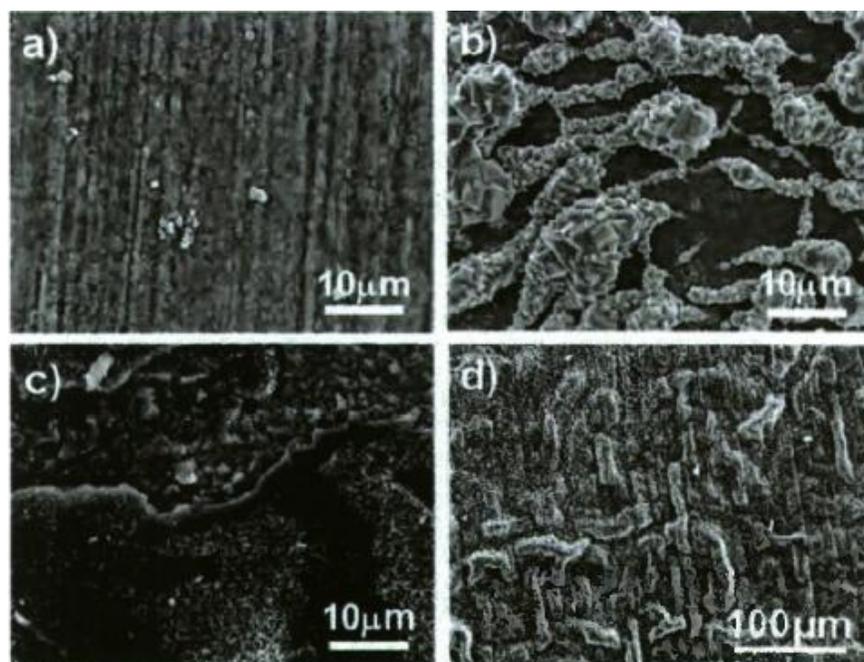


Figure 7. Surface morphologies of Ni₃Al intermetallic alloy oxidized in air at a) 800, b) 900, c) 1000 and d) 1100°C

Microalloying of REE's can significantly improve the oxidation resistance of Ni₃Al based alloy. Compared with REE's-free alloys, the oxidation rate of REE's-containing alloys was sharply reduced and slight spallation signs existed on the surfaces of oxide scales, Scales were sometimes granular, ridges-like (fig. 8a, b and c) and convoluted during oxidation at 1100°C for 48 h (fig. 8d). To understand the function of microalloying constituents during the growth of oxide scales, extensive studies have been conducted by many researchers. Graboski and Rehin^[15] summarized oxidation behavior of metals and alloys implanted with various elements.

They have found that only implanted yttrium has significant beneficial effects on oxidation resistance. Some beneficial effects of additions of Y, Ce, Hf, Y₂O₃, HfO₂, and CeO₂ on the development of protective oxide scales were founded by using surface salt-deposit techniques^[16] and conventional alloying techniques.^[17-22] Some other reactive elements, such as Th, Zr and La, also showed some influence on oxidation behavior; however, only a few studies were conducted on those elements.

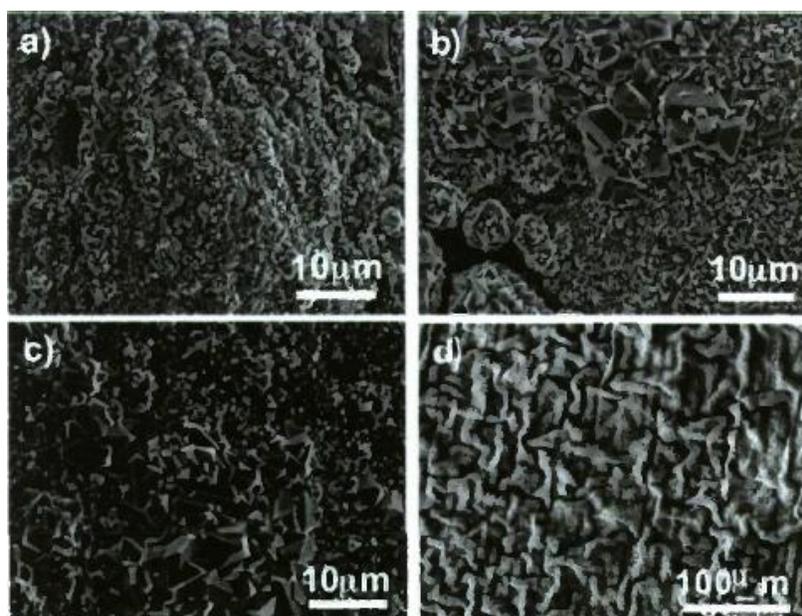


Figure 8. Surface morphologies of Ni₃AlNdPr intermetallic alloy oxidized in air at a) 800, b) 900, c) 1000 and d) 1100°C

In fig. 9 is also shown the backscattered image of the cross-section of Ni₃Al intermetallic alloy oxidized in air at 1100°C during 48h with X-ray maps of Al, Ni and O.

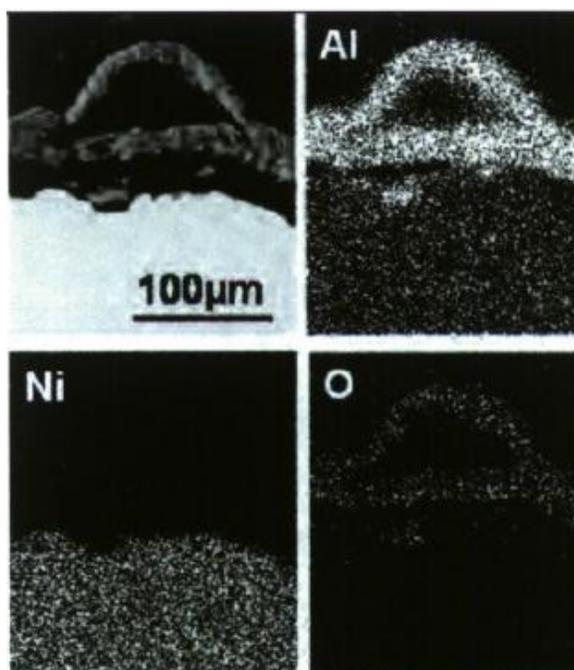
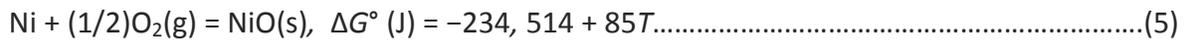
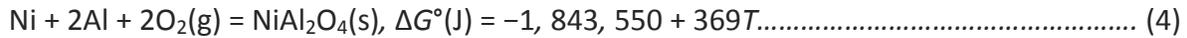
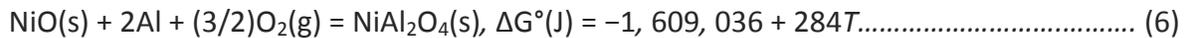


Figure 9. Cross-section general view of Ni₃Al alloy oxidized in air at 1100°C during 48h with X-ray maps of Al, Ni and O

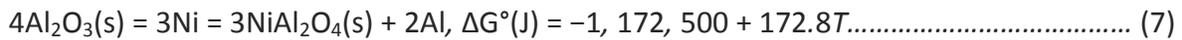
There are several potential oxidation reactions, when Ni–Al alloys are kept in oxygen-containing environments at elevated temperatures. The formations of these oxides (Al_2O_3 , NiO, and NiAl_2O_4) are governed by their free energies of formation ' ΔG° '; the following reactions are possible [21]:



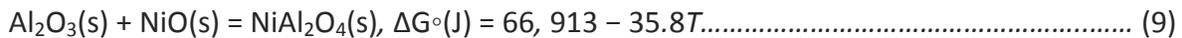
Eqs. (3) and (4) may combine to:



As the oxidation process continues, equilibrium between the alloy surface and the oxide phase is approached and the stability of the oxide nuclei determined by the composition of the alloy at the alloy/oxide interface is based on the following reactions [7]:



Combining Eqs. (7) and (8), we have:



The more negative the free energy of a given oxidation reaction the more spontaneous the reaction will be and the oxide phase resulting from this reaction is said to be more thermodynamically stable. Al_2O_3 and NiAl_2O_4 are considered the most stable oxide phases from the thermodynamic point of view. The alumina may form as a result of an oxidation reaction between Al atoms already present at the surface or diffuses across an existing oxide layer to react with O_2 gas at the oxide–gas interface. The NiAl_2O_4 may result from either the oxidation reaction between Ni and Al or Al and NiO already formed at the surface with the O_2 gas, respectively. Also, the positive ΔG° of NiAl_2O_4 resulting from the chemical reaction between NiO and Al_2O_3 suggest that NiAl_2O_4 would decompose to NiO and Al_2O_3 spontaneously [7].

The morphological observations and microanalyses suggest that Nd plus Pr have an effect on prevention of outward diffusion of cations through the short-circuit paths during oxidation, which prevents cavities forming near substrate–oxide interface, so that the

alloy shows a dramatic improvement in scale adhesion. Nd and Pr addition can refine the oxide grains and reduce the formation of nickel or spinel oxides in the alumina scale.

CONCLUSIONS

The present work provided a detailed comparison of the oxidation performance of Ni₃Al with and without Nd and Pr in air in the temperature range of 800–1100°C. The results based on specimen weight gain and microstructural characterizations indicated that Nd and Pr additions significantly improved the oxidation resistance of these alloys.

The oxidation behavior of a Ni₃Al and Ni₃AlNdPr intermetallic alloys in static air at 800, 900, 1000 and 1100°C followed a parabolic kinetic behavior.

The kinetic constants for Ni₃Al intermetallic alloys without the addition of Nd and Pr were about thirty times higher than those with these elements regardless the temperature.

The activation energies for this system were $Q_{\text{Ni}_3\text{Al}}=132$ and $Q_{\text{Ni}_3\text{AlNdPr}}=28$ KJ/mol

Nd and Pr additions improved the adherence of the α -Al₂O₃ scale.

The morphology of the oxides formed on specimens with and without REEs varies significantly from fine-grained, plate-like and ridges-like to convoluted oxide.

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