

Effect of Cr on oxidation of Ni-xAl alloy

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Abstract: The oxidation of the Ni-10Cr-xAl($x=7\%$, 10%, molar fraction) alloys was studied at 1 100 °C under 0.1 MPa O₂ and compared with that of the binary Ni-7Al and Ni-10Al alloys. The results show that the binary alloys form NiO external scales associated with an internal oxidation of Al. On the contrary, the ternary Ni-10Cr-7Al and Ni-10Cr-10Al form external alumina scale in contact with the alloy substrate. An addition of 10%Cr(molar fraction) into Ni-7Al and Ni-10Al inhibits the internal oxidation of aluminum and considerably reduces the critical content of Al needed to form exclusive alumina scales with respect to binary Ni-Al alloy, providing an example of third-element effect.

Key words: Ni-10Cr-xAl alloy; oxidation; third-element effect

1 Introduction

For applications in oxygen-rich environments at very high temperatures, alloys and coatings are often designed to develop surface layers of Al₂O₃. Ni-based alloys are often used as model to investigate the processes occurring in the oxidation of complex and multi-component alloys. The minimum aluminum concentration needed to form protective Al₂O₃ scales on Ni- based binary alloys has been estimated in the range from 8% and 17%(mole fraction)[1-4]. Unfortunately, these aluminum levels in binary alloys often result in unacceptable mechanical properties. The Ni-Cr-Al system forms a γ - γ' structure that exhibits improved mechanical properties and better oxidation resistance than the corresponding binary alloys. Therefore, this system becomes a basis for the development of more oxidation-resistant materials by the addition of further alloying elements. In practice, adding chromium to Ni-Al alloys decreases the concentration of aluminum required to establish Al₂O₃ scale, providing a case of the third-element effect (TEE), which is of considerable interest for optimizing the composition of commercial

alloys. The classical interpretation, initially proposed by WAGNER[5], assumes that the third element can reduce the flux of oxygen into the alloy, favoring the formation of external scales of the most reactive component. However, the precise role of the third element has not been yet very clear. One of other possible mechanisms advanced later[6], originally proposed by GIGGINS and PETTIT[7], is based on the idea that the simultaneous internal precipitation of the oxides of the two reactive components produces an overall volume fraction of internal oxide sufficient for the transition to an external scale according to a criterion defined by WAGNER[8] for binary alloys under reduced contents of the most reactive component than in binary alloys. In the present study, the effect of 10% Cr on the oxidation of Ni-7Al and Ni-10Al alloys at 1 100 °C was studied.

2 Experimental

The nominal compositions of the four alloys were Ni-7Al, Ni-10Cr-7Al, Ni-10Al, and Ni-10Cr-10Al. The corresponding actual composition of each alloy is listed in Table 1. The alloy ingots were prepared from high-purity metals by arc-melting under a Ti-gettered

argon atmosphere using non-consumable tungsten electrodes from appropriate amounts of pure nickel (99.99%), aluminum (99.999%) and Cr (99.99%). The alloy ingots were subsequently annealed in argon atmosphere at 1 200 °C for 24 h to remove the residual mechanical stresses to achieve a better equilibration of the alloy phases.

Flat specimens with a surface area of about 2 cm² were cut from the ingots by a diamond wheel saw, ground down to 1 200 emery paper, washed in water, alcohol and acetone and then dried immediately before use. Oxidation tests were carried out in 0.1 MPa of pure oxygen at 1 100 °C for 24 h with continuous mass gain measurement using a microbalance. The microstructures of the alloys and the oxide scales were characterized with scanning electron microscopy (SEM) and an energy-dispersive X-ray spectrometer (EDAX) attached to the SEM to establish the nature, composition, and spatial distribution of the compounds formed by oxidation.

Table 1 Actual compositions of four alloys(molar fraction, %)

Alloy designation	Al	Cr	Ni
Ni-7Al	6.80	—	Balance
Ni-10Cr-7Al	7.10	10.0	Balance
Ni-10Al	10.61	—	Balance
Ni-10Cr-10Al	10.11	10.23	Balance

3 Results and discussion

3.1 Scaling kinetics

The kinetics curves of Ni-7Al and Ni-10Cr-7Al oxidized at 1 100 °C are shown in Fig.1(a) and (b) as normal plots and parabolic plots, respectively. The oxidation kinetics of Ni-7Al obeys the parabolic rate law for the whole duration of the test with rate constant of $2.01 \times 10^{-9} \text{ g}^2/(\text{cm}^4 \cdot \text{s})$. On the contrary, the mass change curves of Ni-10Cr-7Al are composed of an initial parabolic stage with rate constant equal to $2.17 \times 10^{-10} \text{ g}^2/(\text{cm}^4 \cdot \text{s})$ for the first 0.6 h. After the first stage the slope of the parabolic plot decreases continuously with time down to a final value of about $1.18 \times 10^{-12} \text{ g}^2/(\text{cm}^4 \cdot \text{s})$.

The normal plots and parabolic plots of Ni-10Al and Ni-10Cr-10Al oxidized at 1 100 °C under 0.1 MPa O₂ are shown in Figs.2(a) and (b), respectively. The corrosion rate of Ni-10Al from the beginning of oxidation to 12 h obeys the parabolic rate law with a parabolic rate constant equal to $2.14 \times 10^{-9} \text{ g}^2/(\text{cm}^4 \cdot \text{s})$, which is followed by a second stage whose instantaneous parabolic rate constant (IPRC, i.e. the slope of the parabolic plot) decreases with time down to $1.64 \times 10^{-10} \text{ g}^2/(\text{cm}^4 \cdot \text{s})$. On the contrary, the oxidation kinetics of Ni-10Cr-10Al is composed of different stages with parabolic rate constants equal to $1.97 \times 10^{-12} \text{ g}^2/(\text{cm}^4 \cdot \text{s})$

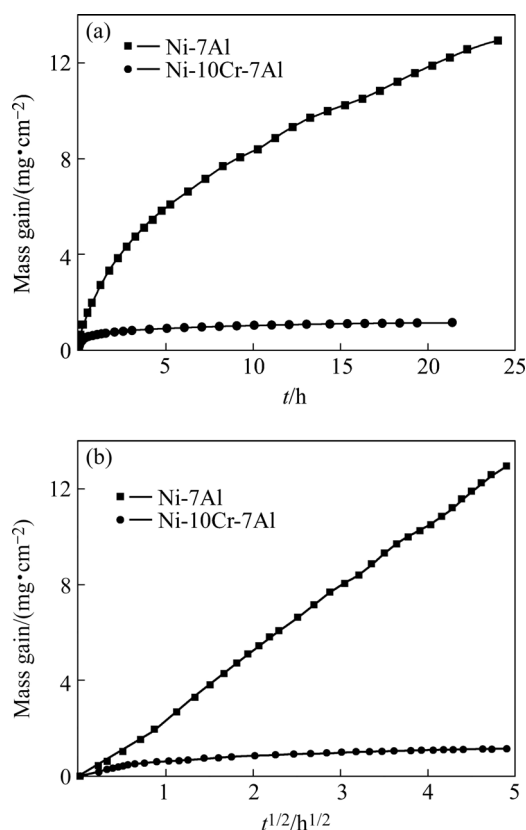


Fig.1 Scaling kinetics of Ni-7Al and Ni-10Cr-7Al alloys oxidized at 1 100 °C under 0.1 MPa O₂: (a) Normal plots; (b) Parabolic plots

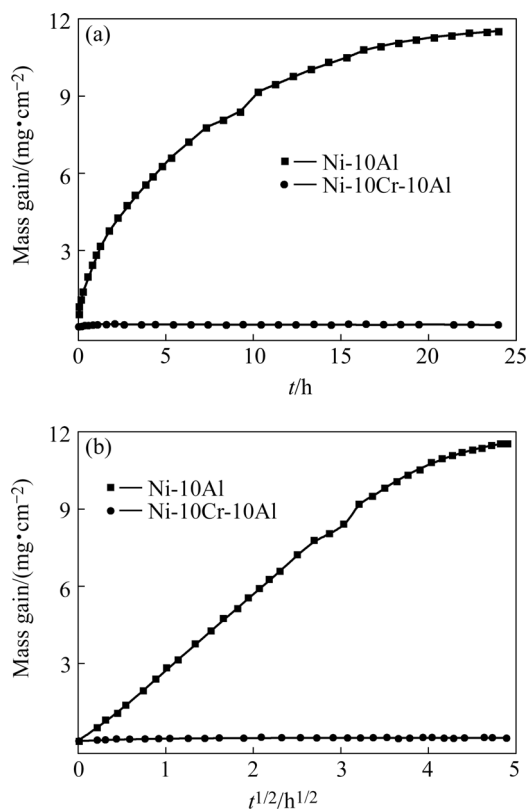


Fig.2 Scaling kinetics of Ni-10Al and Ni-10Cr-10Al alloys oxidized at 1 100 °C under 0.1 MPa O₂: (a) Normal plots; (b) Parabolic plots

from initial to 1 h and then followed by a very slow oxidation stage. However, the specimen shows a very slight mass gain loss after 10 h oxidation possibly due to the volatilization of Cr_2O_3 produced by the reaction of Cr_2O_3 with O_2 .

In general, the oxidation rate of the ternary alloy containing Cr is much slower than that of the corresponding binary alloy. In particular, the average parabolic rate constants of Ni-10Cr-7Al and Ni-10Cr-10Al are about three orders of magnitude smaller than that for the corresponding binary alloys.

3.2 Scale microstructure and composition

The microstructure of the scales formed on the four alloys after oxidized at 1 100 °C under 0.1 MPa O_2 for 24 h are shown in Fig.3. Ni-7Al forms a dense external layer of NiO containing some Ni-Al spinel particles in an inner region corresponding to the alloy consumption zone, which is followed by a zone of internal oxidation of aluminum. Intergranular oxidation and a discontinuous alumina scale in the front of the internal oxidation are also observed, as shown in Fig.3(a). On the contrary, after 24 h oxidation of Ni-10Cr-7Al at 1 100 °C, an outermost lighter layer of NiO, a subscale is composed of a mixture of oxides of all the alloy components and also their double oxides, and a very thin but continuous layer of alumina formed at the interface of oxide scale and the substrate, as shown in Fig.3(b). The scale formed on Ni-10Al after 24 h oxidation at 1 100 °C (Fig.3(c)) contains the outermost lighter layer of NiO, the intermediate layer made up of the mixture of

NiO, Al_2O_3 , and Ni-Al spinel, and the innermost layer of precipitates of alumina. A continuous alumina scale formed at the front of the subscale is observed. An exclusive external scale of alumina formed on Ni-10Cr-10Al (Fig.3(d)).

3.3 Discussion

A systematic study of the oxidation of ternary Ni-Cr-Al alloys at 1 000–1 200 °C carried out by GIGGINS and PETTIT[7] has identified three groups of alloys. Alloys of group I formed external NiO scales associated with an internal oxidation of chromium plus aluminium; alloys of group II formed external chromia scales coupled to an internal oxidation of aluminium; and alloys of group III formed exclusive external alumina scales. In addition, it has been found that the addition of chromium reduces the critical aluminum content needed to form alumina scales with respect to binary Ni-Al alloys[7].

The exclusive growth of external Al_2O_3 scales in the oxidation of ternary Ni-Cr-Al alloys requires to avoid two different kinds of internal oxidation: 1) the coupled internal oxidation of Al and Cr beneath external NiO scales and 2) the internal oxidation of Al beneath external chromia scales. The critical Al contents needed for the transitions from these forms of internal oxidation to the external oxidation of Al have been calculated by ZHANG et al[9–11]. It was concluded that the critical Al content needed to avoid the coupled internal oxidation of Cr + Al beneath external NiO scales, $N_{\text{Al}}^{0*}(\text{t}, \text{NiO})$, decreases almost linearly with an increase of the Cr

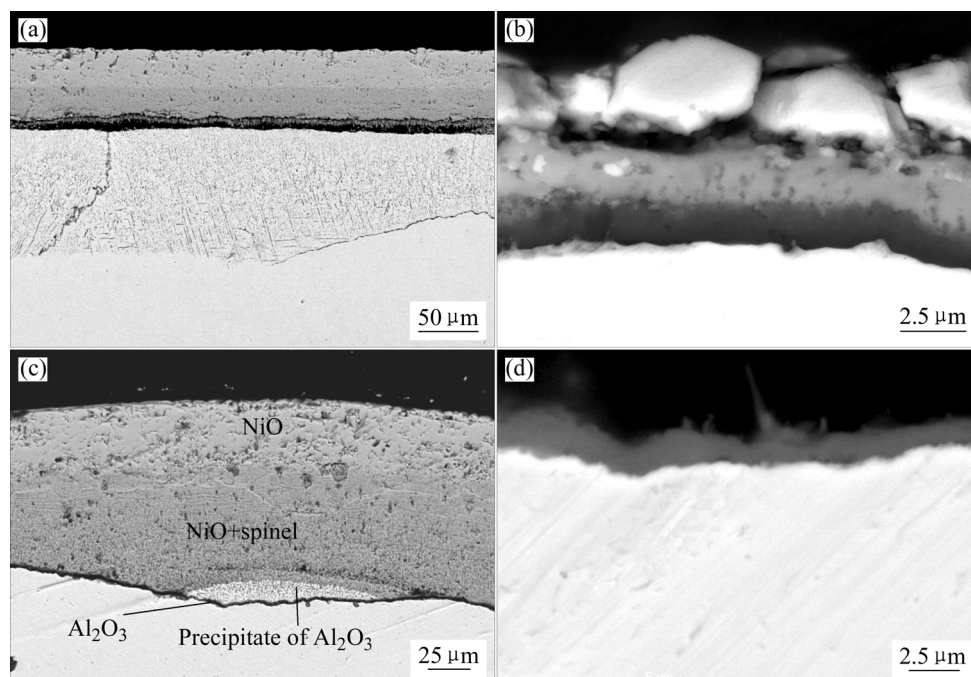


Fig.3 Cross sections (SEM/BEI) of Ni-7Al (a), Ni-10Cr-7Al (b), Ni-10Al (c) and Ni-10Cr-10Al (d) oxidized at 1 100 °C under 0.1 MPa O_2 for 24 h

content of the alloy. A second critical Al content needed for the transition between the internal oxidation beneath Cr_2O_3 scale and the formation of external alumina scales, $N_{\text{Al}}^{0*}(t, \text{Cr}_2\text{O}_3)$, which is again a function of the chromium content in the bulk alloy, N_{Al}^0 . According to the theoretical oxidation map[10–11], Ni-10Cr-7Al and Ni-10Cr-10Al fall into the zone of forming alumina protective scale. The present experimental results agreed with the theoretical analysis[10–11] and with the oxidation map obtained by GIGGINS and PETTIT[7].

4 Conclusions

1) The oxidation rate of the ternary alloy containing 10% Cr(molar fraction) is much slower than that of the corresponding binary alloys.

2) Ni-7Al and Ni-10Al alloys form external NiO scales followed by a zone of internal oxidation of Al. Conversely, the scales formed on Ni-10Cr-7Al and Ni-10Cr-10Al alloys are protective.

3) An addition of 10%Cr to Ni-7Al and Ni-10Al alloys is sufficient to prevent the internal oxidation of Al and to induce the formation of external alumina scales, providing an example of third-element effect.

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