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Influence of structural parameters on oxidation of austenitic Fe–Ni–Cr–Al alloys

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The influence of structural parameters on the oxidation of a $FeNi_{45}Cr_{20}Al_5Y_{0.02}$ alloy (composition by weight) is pointed out. The substrate grain size has no influence on the oxidation kinetics when β-phase (NiAl) has precipitated in the matrix. This second phase promotes Al_2O_3 formation and, consequently, increases the oxidation resistance. The thinner the samples, the greater the aluminium depletion in the substrate and the worse the cyclic oxidation resistance.

1. Introduction

The oxidation behaviour of Fe–Ni–Cr–Al–Y alloys, that is, alloys protected by Al_2O_3 scale, has already been described elsewhere [1–4]. The influence of impurities or trace additions was pointed out, especially the influence of yttrium on both isothermal kinetics [1, 5] and on scale adherence [2–6]. While aluminium and yttrium contents are of prime importance, nevertheless structural parameters such as grain size, second-phase precipitation, sample geometry, etc., have an influence on the hot corrosion of these alloys. The role of these parameters is described here with respect to the austenitic alloy $FeNi_{45}Cr_{20}Al_5Y_{0.02}$.

2. Material and experimental procedure

The composition (in wt%) of the hot-rolled alloy studied (provided by Imphy S.A.), is given in Table I. This alloy has an austenitic structure and develops, by oxidation, an inner Al_2O_3 protective layer at the surface. When the temperature is lower than 1200° C, β-phase (NiAl) precipitates (Fig. 1).

The experimental procedure was described in earlier papers [1–3] and will only be briefly recalled here. Oxidation tests were carried out on samples of 20 mm × 10 mm × 3 mm size, either under pure oxygen in a Cahn microthermobalance of high sensitivity (100 μg full scale) under isothermal conditions, or in air for cyclic oxidation treatments. Samples were previously homogenized under argon at varying temperatures in order to promote different grain sizes. Observation and analysis of the oxide scales were performed by use of combined scanning electron microscopy and X-ray diffraction, by X-ray and ionic microanalysis and by glow discharge spectroscopy. Substrate microstructure was observed on samples electrolytically etched in a 20% H_3PO_4 bath at 2 V.

Results

The oxide of austenitic Fe–Ni–Cr–Al alloys is made up of two layers: an inner Al_2O_3 film and an outer Cr_2O_3 + spinel layer (Fig. 2); it must be noted that the alumina scale develops faster on hot-rolled alloys than on as-cast, but the oxide scale composition is not modified. This difference must be related to the influence of grain boundaries either on alumina nucleation or on aluminium diffusion in the matrix. Thus, grain-size influence was studied.

After heat treatment for 48 h at 1000° C, the grain size of $FeNi_{45}Cr_{20}Al_5Y_{0.02}$ was about 10 μm, when heat-treatment at 1200° C produces a grain size of about 500 μm. Oxidation tests carried out in pure oxygen, at 900 or 1000° C (low enough to avoid grain growth) on both types of samples, showed that the oxidation kinetics depended on the previous treatment (Fig. 3): it appears that decreas-

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TABLE I

C	Si	S	P	Mn	Ni	Cr	Al	Y	Fe
0.043	0.14	0.003	0.003	0.14	44.9	19.9	5.00	0.0195	bal.

ing the grain size induces a decrease of the initial weight gain. However, in order to interpret these observed phenomena, it is necessary to take into account the possibility of β-phase precipitation. Indeed, when samples are previously heat-treated at 1200° C, β-phase does not precipitate, whereas it is present when samples are heat-treated at 1000° C (see Fig. 1).

Thus, the influence of grain size on oxidation behaviour was examined on samples previously heat-treated under conditions that provoked complete precipitation of β-phase, that is:

(1) heat-treatment at either 1000 or 1200° C, in order to promote different grain sizes;

(2) heat-treatment for 48 h at 900° C, in order to induce β-phase precipitation;

(3) oxidation at 900° C in pure oxygen.

Some results are reported in Fig. 4. It appears that the grain size has no influence on the oxidation kinetics when β-phase (NiAl) has entirely precipitated, contrary to samples of Fig. 3.

Actually, it is impossible to study grain-size influence alone, entirely independent of β-phase: indeed, in Fig. 3, during oxidation at 900° C, β-phase precipitates in a sample previously heat-treated at 1200° C (grain diameter ~ 500 μm), whereas β-phase is already present at the beginning of the oxidation treatment in a sample previously heat-treated at 1000° C (grain diameter ~ 10 μm); thus the differences observed in Fig. 3 can be related either to grain size or to the amount of β-phase. It is also impossible to study grain-size influence on oxidation at 1200° C, since grain growth will occur during oxidation.

The influence of β-phase was studied on $FeNi_{45}Cr_{20}Al_5Y_{0.02}$ with large grains (500 μm). Precipitation and oxidation treatments were carried out at 900° C. A brief study of the NiAl precipitation kinetics (Fig. 5) shows that the β-phase precipitation rate is much slower than Al_2O_3 growth rate: after 15 min oxidation at 900° C, Al_2O_3 forms a continuous scale [1–3] while after 20 min heating, not much β-phase has been precipitated (see Fig. 5b). Different samples were prepared by heating under argon:

(1) as-quenched after heating at 1200° C: no β precipitation (Fig. 5a);

(2) 1 h heating at 900° C: slight precipitation (Fig. 5c);

(3) 24 h heating at 900° C: complete precipitation (Fig. 5d).

The samples thus prepared were oxidized (Fig. 6): the presence of β-phase decreases the oxidation weight gain, especially in the second

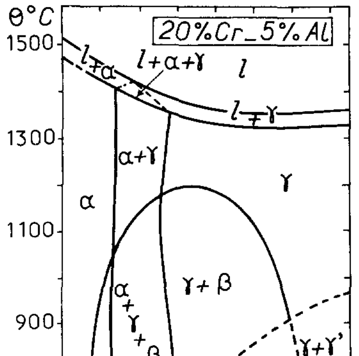

Figure 1 Equilibrium phase diagram of Fe–Ni–Cr–Al alloys (20 wt% Cr and 5 wt% Al) [3].

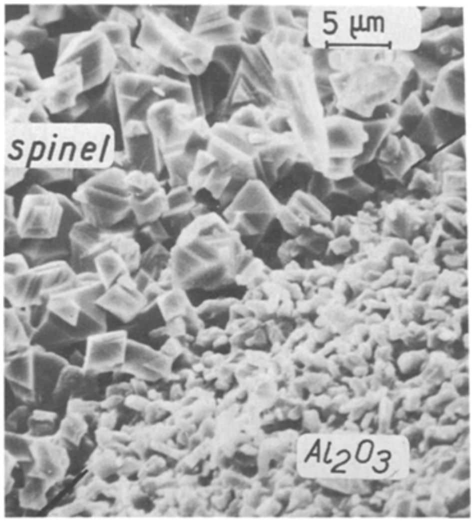

Figure 2 Microstructure of the oxide scale developed after 100 h oxidation at 1300° C, $FeNi_{45}Cr_{20}Al_5Y_{0.02}$ (by wt) alloy. Outer layer of spinel and Cr_2O_3; inner layer of alumina.

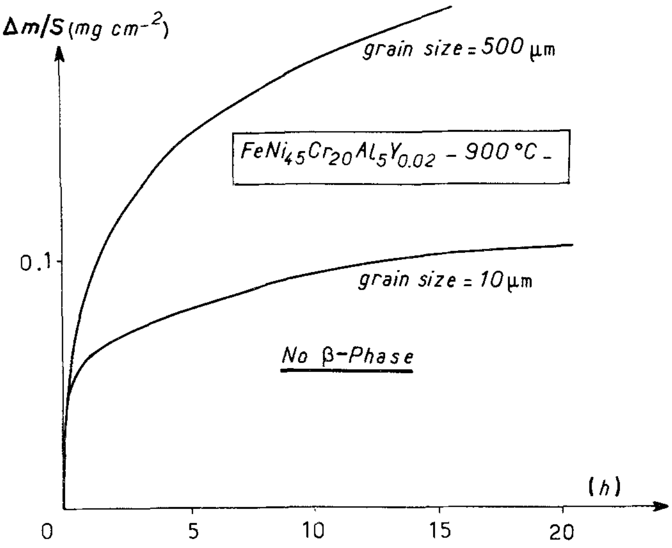

Figure 3 Oxidation kinetic curves of $FeNi_{45}Cr_{20}Al_5Y_{0.02}$ samples previously recrystallized either at 1200° C (grain size ~ 500 µm diameter) or at 1000° C (grain size ~ 10 µm diameter).

oxidation period. Curve 3 in Fig. 6 suggests that β-phase promotes the nucleation of Al_2O_3, since the second oxidation period, related to alumina growth (with a very low weight gain) begins sooner than for the other samples. This assumption is corroborated by X-ray analyses which show that the oxide scale grown on sample 3 is enriched in aluminium and depleted in chromium when compared to scale of samples 1 or 2. The results are related to the respective thickness of the inner Al_2O_3 layer and the outer Cr_2O_3 + spinel layer, observed by scanning electron microscopy.

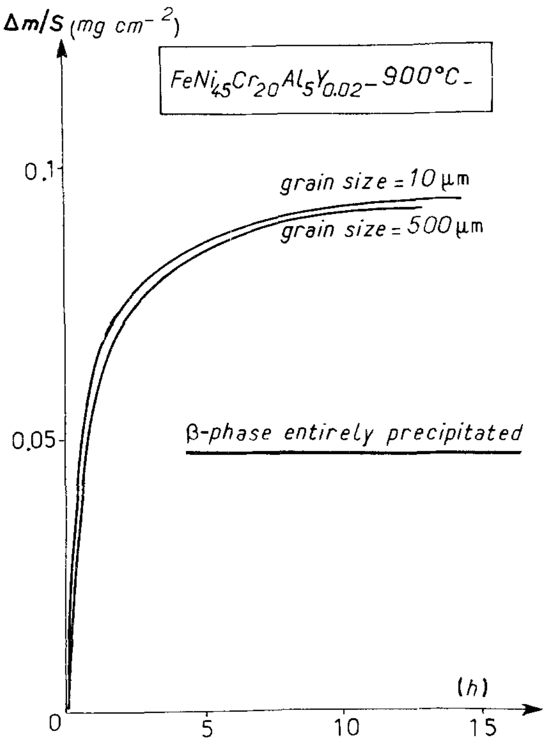

Figure 4 Oxidation kinetics curves of $FeNi_{45}Cr_{20}Al_5Y_{0.02}$ samples with varying grain sizes and with β-phase entirely precipitated by previous heat-treatment at 900° C.

Thus, it can be concluded that β-phase increases the formation rate of Al_2O_3 scale. NiAl precipitates, enriched in aluminium, act as preferential nucleation sites for alumina. It appears that the influence of β-phase is more important than the role of grain size on oxidation. A previous β precipitation treatment improves the oxidation resistance of Fe–Ni–Cr–Al alloys.

The influence of the sample geometry on oxidation behaviour has frequently been observed [7–10]. Most authors use plane samples for evident reasons: (i) theoretical analysis of mechanisms is simpler with planar interfaces; (ii) sample preparation and analysis are easier. Nevertheless, even with parallelepipeds, geometry (that is, thickness of sample, role of edges, etc.) can influence oxidation behaviour and oxide adherence.

The influence of sample thickness* was studied on samples of varying thickness (between 0.5 and 3 mm in steps of 0.5 mm) in cyclic oxidation conditions; cycles consisted of exposure for 15 h at 1300° C, followed by air-cooling to room temperature, weighing being carried out at intervals. It appears that the thinner the sample, the greater the eventual weight gain after some initial cycles (Fig.

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*Tests done in collaboration with J. H. Davidson.

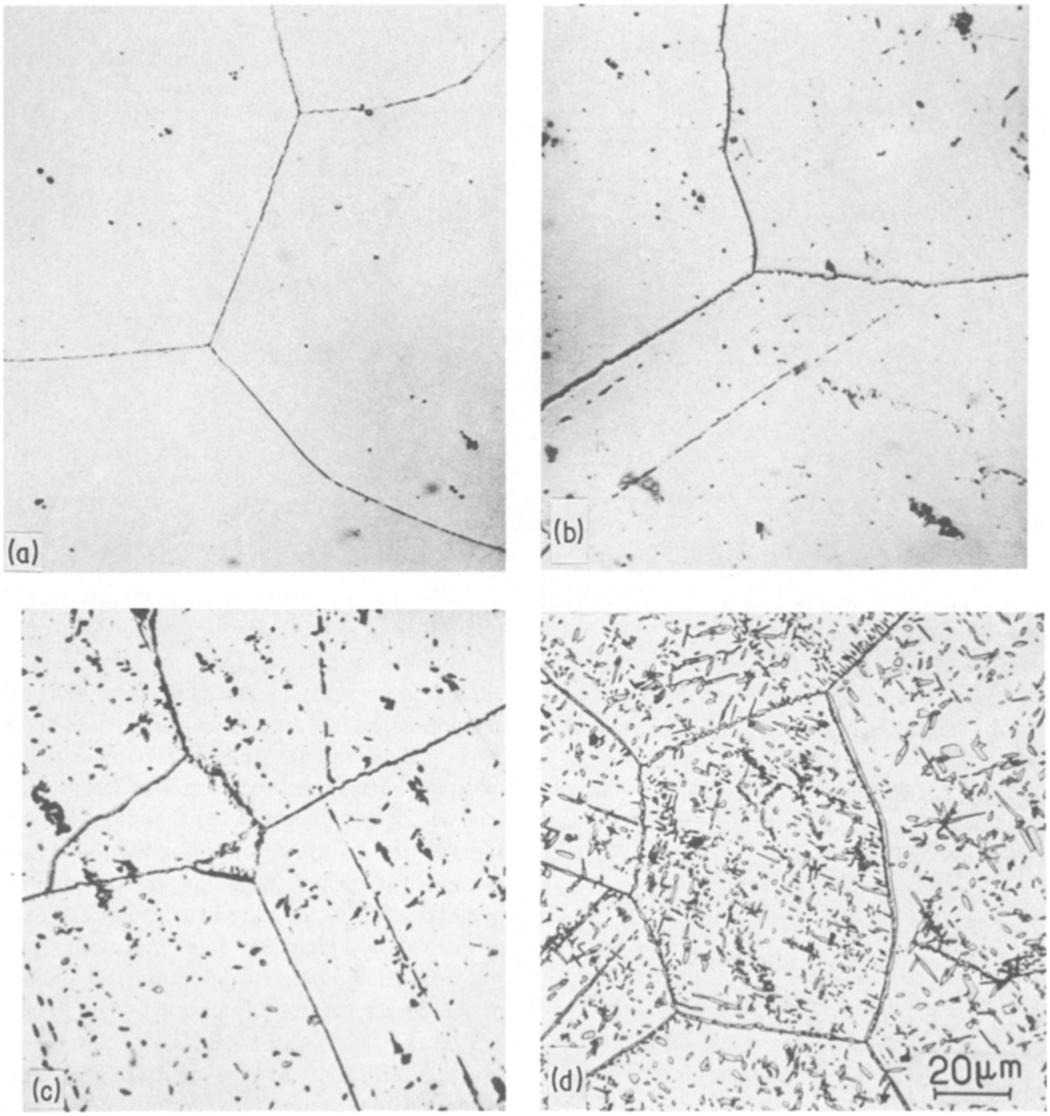

Figure 5 Optical micrographs showing the β-phase precipitation rate at 900° C in $FeNi_{45}Cr_{20}Al_5Y_{0.02}$. Electrolytic etching: H_3PO_4 20%, 2 V. (a) Hot-rolled; (b) heat-treated for 20 min; (c) heat-treated for 1 h; (d) heat-treated for 48 h.

7): the oxide breakdown is strongly dependent on thickness. The kinetic acceleration observed, after about 10 cycles, on samples of 0.5 or 1 mm thickness, suggests that, as cyclic oxidation proceeds, alumina growth is supplanted by the growth of other, less protective oxides. The thinner the sample, the sooner this damage is initiated.

In this case, the metallic substrate must be depleted in aluminium. So, on cross-sections, aluminium content was determined at the edges, at the corners and in the centre of the metallic substrate of such oxidized samples, by electron microprobe analysis. Fig. 8 shows results obtained after (a) five cycles on a 2.5 mm thick sample, and (b) 22 cycles on a 2 mm thick sample. Values of aluminium content are given in Table II. Even when thickness is not too small, aluminium depletion extends a long distance from the oxide alloy interface, and, after many cycles, the subtrate corners are entirely depleted in aluminium. Simultaneously, in the centre of the metallic substrate, internal oxidation of aluminium appears and the oxide scale is characterized by a progressive increase in the chromium, nickel and iron contents of the alumina layer. At the same time, oxide scale of corners and edges is only made up of

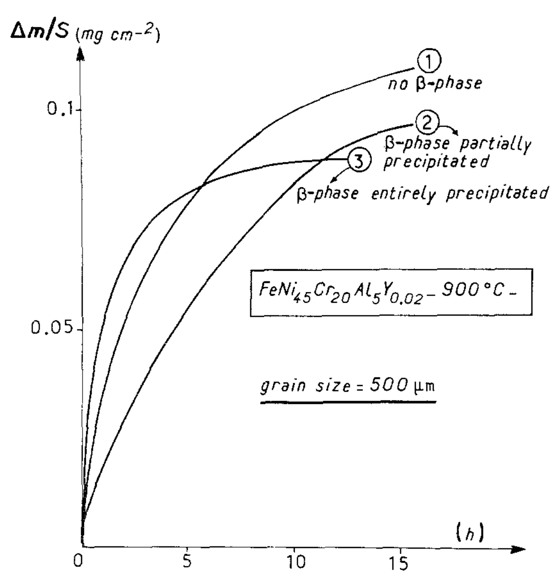

Figure 6 Influence of the presence of β-phase on the oxidation kinetics at 900° C of $FeNi_{45}Cr_{20}Al_5Y_{0.02}$ with large grains.

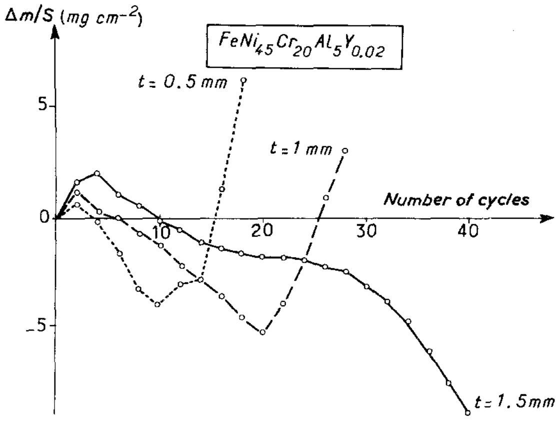

Figure 7 Influence of the sample thickness (t) on the cyclic oxidation resistance of $FeNi_{45}Cr_{20}Al_5Y_{0.02}$ alloy (room air, cycles of 15 h at 1300° C followed by an air cooling).

zones of coarse grained, iron-rich spinel. These patches then grow laterally and spinel gradually invades the whole surface.

Thus, the damage of thin samples during cyclic oxidation treatments is really due to an aluminium-depletion of the substrate; when this goes far enough, alumina cannot grow anymore and it is chromium, nickel and iron which are oxidized: growth of Cr_2O_3, NiO and spinel oxides is much faster than alumina growth and the protective character of the oxide scale disappears.

These results suggest that, in case of products of small cross-section – wires or strips – 5 wt% aluminium is insufficient to maintain a good high-temperature oxidation resistance by Fe–Ni–Cr–Al alloys.

4. Conclusions

The protective nature of the oxide scale developed on Fe–Ni–Cr–Al depends on structural parameters.

(1) When the alloy is heat-treated at high temperature, that is, when β-phase precipitation is not promoted, then the smaller the grain size, the slower the oxidation kinetics, especially at relatively low temperatures.

(2) When β-phase (NiAl) is previously precipitated in the metallic matrix, then the grain size has no influence on subsequent oxidation kinetics. Indeed, NiAl β-phase acts as a nucleation site for Al_2O_3, thus increasing the formation rate of alumina scale and notably decreasing in time the first period of the oxidation kinetics. Consequently, β-phase improves the oxidation resistance of Fe–Ni–Cr–Al alloys.

(3) The thinner the samples, the worse the cyclic oxidation resistance; this is associated with enhanced growth of oxides less protective than Al_2O_3. This damage is related to aluminium depletion in the metallic substrate and, consequently, to modification of the oxide scale composition.

Acknowledgement

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TABLE II

Number of cycles: 15 h at 1300° C and air-cooling	Initial Al content (wt%)	Al content after oxidation (wt%)			Initial thickness of the sample (mm)
		Centre	Edges	Corners	
5	5.00	~ 5	4.6	3.3	2.5
22	5.00	2.6	1.0	~ 0	2.0

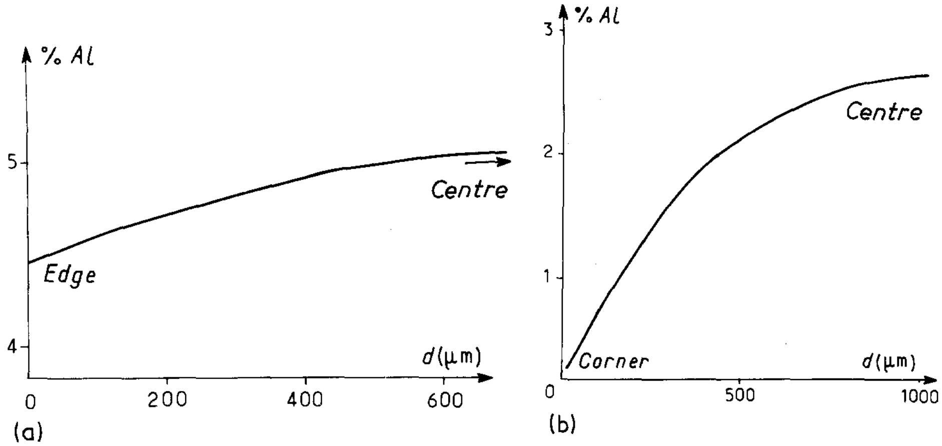

Figure 8 Aluminium content determined by electron microprobe analysis on cross-section of the metallic substrate of a $FeNi_{45}Cr_{20}Al_5Y_{0.02}$ oxidized at 1300° C. (a) 5 cycles, initial thickness 2.5 mm. (b) 22 cycles, initial thickness 2 mm.

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