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The effect of implanted yttrium on the oxidation behaviour of Fe-20Cr-5Al alloy at 1373 K in air

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Abstract. — The influence of implanted yttrium on the oxidation behaviour of an Fe-20Cr-5Al alloy was studied at 1373 K in air under isothermal and thermal cycling conditions in order to verify previous results obtained at 1473 K which indicated no beneficial effect of this addition. The implanted yttrium substantially improved the scale resistance to spalling, only slightly affected the scale growth rate, and altered the scale morphology. On unimplanted material developed ridged scales, while yttrium promoted the formation of buckled oxide layers, the higher the dose the more buckled the scale. After spalling of the scale from yttrium implanted material due to prolonged thermal cycling ridges were growing instead of buckles. These and previous results showed that the efficiency of the implanted yttrium depends on its amount in the substrate and on the reaction temperature as well and that there is no simple correlation between the scale thickness and its resistance to spalling.

1. Introduction.

The so-called reactive elements (Y, Sc, Ce) in most cases offer an improvement of the oxidation behaviour of the FeCrAl-type alumina forming alloys due to enhancing the scale resistance to spalling [1-10]. The efficiency depends upon the manner of their incorporation into the alloy. Ion implantation was found to bring about a rather weak effect as compared to conventional alloying of these elements and mechanical alloying of their dispersed oxides [4, 7, 9, 11, 12]. However, a beneficial effect of implanted reactive elements was clearly established [7, 13-15].

A negligible effect of implanted yttrium on the scale resistance to spalling was observed for Fe-20Cr-5Al alloy at 1473 K [12]. Moreover, yttrium increased the oxidation rate and favoured development of a buckled scale. Thus, it appeared to affect adversely the oxidation behaviour of this alloy.

This paper concerns the effect of implanted yttrium at lower temperature, 1373 K. It was approached by studying the oxidation rate under isothermal conditions, the scale resistance to spalling during thermal cycling, and the scale morphology by means of SEM.

2. Materials and experimental procedure.

The samples of wrought alloy of nominal composition Fe20Cr-5Al supplied as recrystallized, hot forged bar by Inco Alloys International, Hereford, UK, were prepared by means of stan-

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dard techniques in the form of 1 mm thick discs. Some of them were implanted with yttrium, two doses being applied 2×10^{15} and 2×10^{16} ions/cm². Further details concerning the composition and microstructure of the starting material and the implantation process are described elsewhere [12]. It is worthwhile to note that implantation led to an average content of yttrium of 8 at. % in a surface layer with a thickness of 300 Å.

The oxidation behaviour was studied at 1373 K, in air. The reaction kinetics under isothermal conditions was determined by thermogravimetry, using an automatic Sartorius thermobalance. The oxidation course in thermal cycling conditions was followed by discontinuous determination of the weight changes as a function of the number of 1-hour cycles. The scale morphology and composition of the scales were analyzed by means of scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS), respectively.

3. Results and discussion.

The results of the isothermal oxidation experiments are shown in figure 1A. It follows from this plot that the lower dose of yttrium exhibited a very small effect on the oxidation rate. Similar conclusions can be drawn for the higher dose of yttrium only for the short oxidation period, up to 15 hours. Subsequently, an accelerated oxidation was observed. It began with a typical and reproducible kink in the kinetic curve.

Since the oxidation kinetics in all cases obeyed the parabolic oxidation rate law the rate constants could be calculated. They are collected in table I. The differences are too small for any further interpretation.

Table I. — *The parabolic oxidation rate constants k_p'' (1373 K, air, 24 h).*

MATERIAL	K_p'' [g ² cm ⁻⁴ s ⁻¹]
Fe-20Cr-5Al - unimplanted	3.0×10^{-12}
Fe-20Cr-5Al + 2×10^{15} Y ⁺ /cm ²	2.5×10^{-12}
Fe-20Cr-5Al + 2×10^{16} Y ⁺ /cm ²	3.8×10^{-12} ($t < 16$ h)
	4.5×10^{-12} ($t > 16$ h)

The results obtained under thermal cycling conditions are shown in figure 1B. The implanted yttrium improved the scale resistance to spalling by retarding the beginning of this process. The best spalling resistance was observed for the scale on alloy implanted with the higher dose of yttrium (Fig. 1B). For both alloys less resistant to the scale spalling (unimplanted and implanted with the lower yttrium dose) gain of weight again occurred after prolonged thermal cycling (Fig. 1B) due to formation of fast growing non-protective oxides.

The surface of samples oxidized under isothermal conditions is shown in figure 2. Practically, the whole scale spalled away from the unimplanted alloy during cooling (Fig. 2A). However, the substrate was covered with a very thin oxide layer. No spalling indications were found for both implanted alloys (Figs. 2B and C). In both cases the scale was convoluted and exhibited typical buckles [4, 7, 9, 10, 13-15].

Fig. 1. — Oxidation course at 1373 K in air under: A) isothermal and B) thermal cycling (1 cycle = 1 hour) conditions (Notation: 1) unimplanted alloy; 2) implanted with $2 \times 10^{15} \text{ Y/cm}^2$ alloy; 3) implanted with $2 \times 10^{16} \text{ Y/cm}^2$ alloy).

Since the scale spalled from the unimplanted alloy was collected in the crucible a morphological study was possible. As shown in figure 3A, the ridges, typical features for the scales on alumina formers [16, 17], were formed at the outer surface of the scale. The inner surface morphology indicates only very local loss of contact between the scale and the substrate (Figs. 3B and C), presumably above some substrate grain boundaries. The oxide grains were rather small and only with high magnification one could observe that they were highly cracked (Fig. 3D).

All scales observed after 100 thermal cycles comprised oxide flakes, as shown in figure 4. However, for unimplanted material their surface was always covered with ridges, while two different regions were found on both yttrium implanted alloys: some thicker flakes were covered with buckles, while on the thinner flakes the ridges developed. It means that the effect of implanted yttrium which relies on favouring the buckled scales gradually disappeared, presumably due to the consumption of the whole implanted layer by the previously formed scale which spalled away.

Fig. 2. — Surface of the samples oxidized under isothermal conditions (1373 K, 24 h, air): A) unimplanted alloy; B) implanted with 2×10^{15} Y/cm² alloy and C) implanted with 2×10^{16} Y/cm² alloy.

Fig. 3. — Outer (A) and inner (B - D) surface of the spalled away scale formed on unimplanted alloy due to isothermal oxidation (1373 K, 24 h, air).

Fig. 4. — Surface of the samples oxidized under thermal cycling conditions (1373 K, 100 - 1 hour cycles, air): A) unimplanted alloy; B) implanted with 2×10^{15} Y/cm² alloy and C) implanted with 2×10^{16} Y/cm² alloy.

Summing-up the obtained results it should be noted that, in contrast to its effect at 1473 K, implanted yttrium improved the oxidation behaviour of the studied alloy at 1373 K. However, by virtue of its consumption by the growing scale, its efficiency was limited. In particular, the scale resistance to spalling was markedly improved, which was documented under both isothermal and thermal cycling conditions.

The scales on unimplanted material were covered with ridges which were found to grow in the through-scale cracks [16-18]. The oxide grains were highly cracked (Fig. 3D) which indicates low compactness of the scale. Formation of cracks can completely change the scale

growth mechanism and resistance to spalling. The cracks offer diffusion paths for oxygen and the additional surface area for the reaction. New oxide can, thus, be formed at the scale/substrate interface and at the walls of cracks, despite the earlier predominant matter transport mode and reaction mechanism. This should bring about additional stresses in the system which lead to scale spalling. The mechanism of scale spalling is not known, so far. Many hypotheses have been proposed to explain the beneficial effect of reactive elements, none of them being, however, generally accepted, as discussed elsewhere [19-21].

Yttrium implanted into the shallow surface layer of the substrate probably brought about different stress-relaxation modes to be active [17]. Instead of the cracking and spalling scale deformation occurred, resulting in a convoluted morphology (Figs. 2B, C). Should the convolutions further grow, the cracks would form due to the increased stresses. Growth of oxide in cracks could lead to the observed buckled scale surface. As yet, it is not clear why the higher dose of yttrium enhanced simultaneously both the scale propensity for buckling and its resistance to spalling. It should be noted, that ridges were never observed for yttrium implanted alloy having spalling resistant scales. They developed after the scale has spalled. Formation of cracks was probably responsible for the observed kink on the isothermal oxidation curves (Fig. 1A).

On the basis of the results obtained at 1473 K it was suggested that yttrium increased the scale growth rate and adversely affected its resistance to spalling [12]. Present results indicate, however, that the effect of implanted yttrium is more complex, and faster growing scale on yttrium implanted material can be much better resistant to spalling than more slowly growing scale on unimplanted alloy.

4. Conclusions.

- 1) Implanted yttrium improved the oxidation behaviour of Fe-20Cr-5Al alloy at 1373 K mainly by enhancing its resistance to spalling.
- 2) The efficiency of the higher dose of yttrium (2×10^{16} ions/cm²) was better than that of the lower dose (2×10^{15} ions/cm²), but in both cases it was limited to the relatively short reaction periods under thermal cycling conditions.
- 3) No simple correlation can be inferred between the scale growth rate and its resistance to spalling: the fastest growing scale formed on yttrium implanted alloy (2×10^{16} ions/cm²) was the best resistant to spalling.
- 4) Implanted yttrium retarded the scale cracking and facilitated formation of convoluted but more compact scale.

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References

- [1] TIEN J.K., PETTIT F.S., *Metall. Trans.* **3** (1972) 1587.
- [2] GOLIGHTLY F.A., STOTT F.H., *Oxid. Met* **10** (1976) 163.
- [3] SMEGGIL J.G., SHUSKUS A.J., *J. Vac. Sci. Technol.* **A4** (1986) 2577.

- [4] PANDEY J.L., PRAKASH S., MEHTA M.L., *J. Electrochem. Soc.* **135** (1988) 209.
- [5] RAMANARAYANAN T.A., AYER R., PETKOVIC-LUTON R., LETA D.P., *Oxid. Met.* **29** (1988) 445.
- [6] QUADAKKERS W.J., HOLZBRECHER H., BRIEFS K.G., BESKE H., *Oxid. Met.* **32** (1988) 67.
- [7] JEDLIŃSKI J., MROWEC S., DANIELEWSKI M., Proc. 9th European Congress on Corrosion, Royal Netherlands Industries Fair, Vol. I, FU-166 (Utrecht, October 1988).
- [8] TANIGUCHI S., SHIBATA T., *Oxid. Met.* **32** (1989) 391.
- [9] JEDLIŃSKI J., BORCHARDT G., MROWEC S., *Werkst. Korros.* **41** (1990) 701.
- [10] HOU P.Y., STRINGER J., Proc. Conf. "Microscopy of Oxidation" M.J. Bennett, G.W. Lorimer Eds. (March 1990) (The Institute of Metals, London, 1991) p. 362.
- [11] BENNETT M.J., HOULTON M.R., DEARNALEY G., *Corros. Sci.* **20** (1980) 69.
- [12] QUADAKKERS J.W., JEDLIŃSKI J., SCHMIDT K., KRASOVEC M., BORCHARDT G., NICKEL H., *Appl. Surf. Sci.* **47** (1991) 261.
- [13] BEN ABDERRAZIK G., MOULIN G., HUNTZ A.M., YOUNG E.W.A., DE WIT J.H.W., *Solid State Ionics* **22** (1987) 285.
- [14] HUNTZ A.M., BEN ABDERRAZIK G., MOULIN G., YOUNG E.W.A., DE WIT J.H.W., *Appl. Surf. Sci.* **28** (1987) 345.
- [15] JEDLIŃSKI J., BORCHARDT G., *Oxid. Met.* **36** (1991) 317.
- [16] DOYCHAK J., Ph.D. thesis, Case Western Reserve University (Cleveland, Ohio, 1986).
- [17] JEDLIŃSKI J., The role of active elements in the oxidation behaviour of high temperature metals and alloys, E. Lang Ed. (Elsevier Applied Science, London, 1989) p. 131.
- [18] JEDLIŃSKI J., *Oxid. Met.* **39** (1993) 61.
- [19] The role of active elements in the oxidation behaviour of high temperature metals and alloys, Proceedings of the European Colloquium, E. Lang Ed. (Elsevier Applied Science, London, 1989).
- [20] JEDLIŃSKI J., Proc. 11th Int. Corrosion Congress, Associazione Italiana di Metallurgia, vol. 4 (Florence, April 1990) p. 21.
- [21] JEDLIŃSKI J., *Solid State Phenomena* **21/22** (1992) 335.