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Effects of Al Addition and Minor Elements on Oxidation Behaviour of FeCr Alloys

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Abstract. It is shown that the addition of aluminium is very effective for the high temperature oxidation resistance of FeCr alloys. 1% aluminium produces a continuous protective Al₂O₃ oxide for FeCr alloy that contains more than 13% of chromium. However this aluminium content is not enough for the high temperature resistance of thin foils and a 5% aluminium content is needed since the substrate plays the role of an aluminium reserve susceptible to oxidation. Impurity elements such as sulphur are detrimental and give rise to scaling of the oxide layer. Active elements such as Y, Ce, La, Zr are therefore necessary to tie up sulphur and increase the life of the alloys.

1. INTRODUCTION

For temperatures up to 1000°C, chromium in alloys leads to the formation of a protective Cr₂O₃ layer. Fe-Cr grades without a high level of aggressive elements (Cl⁻, F⁻) are the best compromise for cheap, heat resistant alloys. At higher temperatures (T1000°C), degradation of oxidation resistance is observed until the formation of a CrO₃ volatile layer (1). For this reason, aluminium should be added cautiously. However high Cr and Al-content alloys are fairly brittle and make production difficult. These characteristics are rather incompatible with mass production. One of the objectives of the present study is to determine, on the basis of experimental and thermodynamic parameters, the critical aluminium and chromium contents to produce a protective alumina scale. In order to diminish Al and Cr contents, addition of different minor elements must be controlled. The effect of impurities on the basis of oxidation behaviour is also given. One of the applications concerns metal carriers for catalytic converters. The metal substrate must have very high oxidation resistance due to the high-temperature service conditions and its thickness (50 µm).

2. EXPERIMENTAL

2. 1 Laboratory casts :

The materials used were from 25 kg ingots cast in argon. The casts were then rolled into sheets of 1. 5 mm and foils of 50-60µm thick. Samples were annealed for a few minutes in an inert atmosphere at 1000°C. The chemical compositions of the alloys studied are given below.

	(a) Fe17Cr 0.03Al	(b) Fe17Cr 0.5Al	(c) Fe17Cr 1Al	(d) Fe17Cr 2Al	(e) Fe6Cr 2Al	(f) Fe13Cr 2Al	(g) Fe20Cr 2Al	(h) Fe18Cr 2Al	(i) Fe18Cr 2AlY	(j) Fe17Cr 2AlY	(k) Fe17Cr 2Al	(l) Fe18Cr 4AlZr	(m) Fe18Cr 4AlZr
C	0.019	0.017	0.023	0.014	0.024	0.019	0.021	0.004	0.010	0.020	0.017	0.015	0.022
Si	0.323	0.332	0.344	0.272	0.352	0.336	0.279	0.444	0.38	0.359	0.302	0.401	0.398
Mn	0.426	0.411	0.423	0.416	0.436	0.421	0.395	0.403	0.419	0.418	0.445	0.361	0.404
Cr	16.65	16.48	16.44	16.58	6.142	12.90	19.79	18.44	18.34	16.13	16.43	18.04	18.22
S	41 ppm	35 ppm	40 ppm	35 ppm	31 ppm	35 ppm	38 ppm	26 ppm	10 ppm	10 ppm	23 ppm	50 ppm	20 ppm
Al	0.027	0.5	1.04	1.9	2.09	2.04	1.93	1.97	2.0	1.89	2.10	5.20	4.70
Zr	0.267	0.303	0.305	0.333	0.368	0.279	0.307	<0.002	<0.002	0.301	0.295	0.276	0.314
Nb	0.465	0.482	0.462	0.483	0.487	0.467	0.469	<0.002	<0.003	0.466	0.480	0.002	<0.002
O	54 ppm	42 ppm	37 ppm	23 ppm	4 ppm	32 ppm	32 ppm	17 ppm	5 ppm	10 ppm	6 ppm	24 ppm	16 ppm
N	0.017	0.021	0.016	0.015	0.001	0.016	0.019	0.019	0.01	0.011	0.012	0.008	0.011
Y									0.012	0.013			

2. 2 Oxidation procedure

The coupons of 1.5 mm were polished to 1200 paper grade. Before oxidation tests, the samples were cleaned in an ultrasonic alcohol bath. Oxidation tests were carried out in air from 900°C to 1100°C. The weight of the samples was measured before and after the heat treatment in order to determine the weight gain corresponding to the oxidation behaviour. Each point of oxidation kinetics represents the average value of 3 different samples.

3. RESULTS

3. 1 Influence of aluminium content

3. 1. 1 Study of thick samples (1.5 mm)

Different Al contents : 0.03%; 0.5%; 1%; and 2% Al were investigated on 17% Cr stabilized stainless steels (0.3% Zr and 0.47% Nb). The oxidation kinetics are shown in Figure 1.

Figure 1 : Oxidation kinetics of 17%Cr alloys with various Al contents. Study on metal coupon (1.5 mm) at 1000°C.

The alloy containing 0.5% Al (b) exhibits intermediate behaviour close to that of the chromia-forming alloy. The microprobe X ray maps in Fig. 2 show strong internal oxidation with alumina flakes in the metal near the metal/oxide interface. Beyond this particular shape, the chromia continuous oxide can be seen. In this case, 0.5% Al is not enough to form a continuous, protective alumina scale.

From Fig. 1, we can see that Al additions exert a beneficial effect on oxidation behaviour. At this temperature, a continuous chromia scale is formed on alloy (a) without Al. The chemical composition is confirmed using EPMA (Electron Probe Micro-Analysis) pictures, shown in Figure 2. The oxidation resistance is poor compared to an alumina scale. Thus this chromia-forming alloy leads to a high weight gain.

The alloys containing 1% Al (c) or more (d) show very low oxidation rates. This result is related to the formation of a continuous alumina scale. This is confirmed looking at the EPMA pictures given in Fig. 2. A thin external layer of Cr_2O_3 was also observed.

Figure 2 : EPMA study of 17%Cr alloys (1.5 mm) with various Al Contents, after 25 hours at 1000°C.

3. 1. 2 Influence of thickness of the metal sheet :

Figure 3 : Influence of thickness on oxidation kinetics at 1000°C of 17%Cr 2%Al (d). Al consumption is given for the metal foil.

Lower oxidation kinetics observed on thin foils for shorter times can be explained by two hypotheses. The first one is related to a modification of oxide growth. The decrease of Al content which is effective for the thin foil induces a predominant inward anion diffusion and can slow down the oxidation kinetic. An other explanation can be attributed to a detrimental effect of grain growth during oxidation. As this phenomenon is more limited on the metal foil because the 50 µm thickness prevents the grain growth, we can expect better behaviour from the thin foil.

3. 1. 3 Influence of prior surface treatments :

The lifetime of thin foils depends largely on the Al reservoir. Thus, the oxidation rate must be as low as possible in order to limit the Al content. Therefore, and in order to achieve a protective alumina scale directly, without forming a less protective chromia layer first, the influence of prior surface treatments was studied. These treatments were carried out under low oxygen pressure in order to avoid Cr, Si and Mn oxidation. Experiments were carried out on alloy (d) under H_2 : 4 h - 900 °C with different P_{H_2O} : 3 and 15 ppm vol. Figure 4 shows Glow Discharge Optical Emission Spectroscopy of the samples preoxidized at different P_{H_2O} . A low P_{H_2O} treatment leads to a thin oxide film (<10 nm) which contains mainly Zr and Al. Zr, similarly to Al, has a strong affinity for oxygen. A higher P_{H_2O} treatment gives a thicker oxide film (> 50 nm) which contains aluminium as a major component. Zirconium contamination is less visible because of the dilution. These oxide films do not contain any chromium, silicon or manganese.

Figure 4 : GDOES of 17%Cr2%Al stabilized alloy (d) preoxidized in hydrogen with different P_{H_2O} .

The thermogravimetric study is shown in Figure 5. Oxidation experiments were performed at 1100°C and reveal a short lifetime for the foils due to low Al content.

Figure 5 : Oxidation kinetics at 1100°C on 17%Cr 2%Al stabilized alloy (d). Influence of preoxidation treatment with different P_{H_2O} .

3. 2 Influence of chromium content

The influence of Cr content was studied in 2%Al stabilized stainless steels (0. 3% Zr and 0. 47% Nb). Different chromium contents were added : 6%Cr (e); 13%Cr (f); 17% Cr (d); and 20% Cr (g).

3. 2. 1 Study of thick samples (1. 5 mm)

Oxidation kinetics are shown in Figure 6. Two types of behaviour can be distinguished according to the chromium content. Lower Cr alloy gives fast oxidation kinetics, showing that 6% Cr is not enough to help the formation of stable and continuous alumina scale. It was found that 13%Cr has to be added to favour alumina scale formation and provide high oxidation resistance. As Fig. 6 shows, the beneficial effect of Cr content above 13% is not clear for alumina-forming alloys.

3. 2. 2 Influence of grain growth :

Although the chemical composition acts as a major parameter favouring oxidation resistance, an elevated running temperature also modifies the metallurgical properties of the substrate, and this in turn induces changes in the external oxide layer.

At elevated temperatures grain growth occurs even on stabilized stainless steel due to Fe_2Nb dissolution. Thus, surface modifications can occur through grain growth. Figure 7 gives the weight gain, after an oxidation test at 1050°C 24 hours, of 2%Al stabilized stainless steels with 13 and 20% Cr :

- the beneficial effect of chromium content is not clearly demonstrated after standard annealing in inert atmosphere at 1000°C - for a few minutes. However, after a long annealing treatment at 1050°C for 24 hours in an inert atmosphere, a beneficial effect of large Cr additions on subsequent oxidation is observed.

However, the beneficial effect of the treatment is sensitive. Breakaway oxidation occurs after :

- 25 h. without pre-treatment
- 35 h. with pre-treatment at $P_{H_2O} = 3$ ppm vol.
- 45 h. with pre-treatment at $P_{H_2O} = 15$ ppm vol.

The most beneficial effect is recorded on the thicker alumina scale developed prior to oxidation. Thus, the low Al content of the alloy constitutes the main drawback with respect to oxidation resistance. So preoxidation treatment improves the lifetime of the alumina scale, but not sufficiently to enhance oxidation resistance very much.

Figure 6 : Influence of Cr content on oxidation kinetics for 2%Al stabilized alloys at 1000°C.

Figure 7 : Influence of prior grain growth treatment on weight gain (1050°C - 24 hours) of 2%Al alloys.

Figures 8 and 9, respectively, show the grain growth kinetics and the simultaneous weight gain at 1050°C of 1.5 mm thick 13%Cr 2%Al and 20%Cr 2%Al alloys after a standard annealing treatment. These figures help to explain the effect of grain growth on oxidation behaviour. Thus, faster grain growth is observed on the lower Cr alloy, as shown in Fig. 8, and the grain size reaches a steady state value after only 4 hours at 1050°C. On the other hand, for the higher Cr alloy, slow and continuous grain growth is observed up to 24 hours. The oxidation kinetics shown in Fig. 9 show parabolic laws. However, we can see that the parabolic constant is higher for the 20% Cr content alloy. This means a less protective oxide as compared to the lower chromium content alloy.

Figure 8 : Grain growth kinetics on thick metal coupons on 13%Cr 2%Al (f) and 20%Cr 2%Al (g) stabilized alloys at 1050°C.

Figure 9 : Oxidation kinetics on thick metal coupons on 13%Cr 2%Al (f) and 20%Cr 2%Al (g) stabilized alloys at 1050°C.

In fact, the oxide scale is destabilized by the grain motion inducing impurity segregation at the metal/oxide interface, modifying the manner of oxide growth and decreasing the oxide peps. Moreover, grain boundaries constitute short diffusion circuits. Therefore and according to these results, slow grain growth during oxidation does not seem to be beneficial for oxidation behaviour.

3. 3 Influence of active element additions :

3. 3. 1 Yttrium or Mischmetal (Ce, La)

Figure 10 : Influence of Y addition on 18%Cr 2%Al thick coupons at 1000°C.

Figure 11 : SEM micrographs on surface alumina scale formed on Fe 18%Cr 2%Al alloys (i) with and (h) without yttrium.

The influence of active elements such as yttrium was studied in Fe 18%Cr 2%Al alloys without stabilizers in order to determine separately the effects of conventional active elements (group IIIB) and the

effects of Zr used as a stabilizer (group IVB) on oxidation behaviour. Thus, as shown in Figure 10, yttrium addition has a clear beneficial effect on oxidation resistance. Study by SEM, in figure 11, reveals that the major effect is a drastic improvement in scale adhesion. The absence of active elements leads to scale spallation even without thermal cycling. The presence of yttrium on the outer surface of the oxide scale is also observed. Mischmetal addition, which is a combination of a few active elements (cerium, lanthanum, etc...), improved the oxidation resistance of FeCrAl alloys in a similar way to yttrium.

3. 3. 2 Zirconium and niobium stabilizers

Stabilizers are added to stainless steels for full stabilization of the ferritic structure and to improve hot workability. In fact, these elements have a strong chemical affinity for carbon and nitrogen, which are residual impurities in stainless steels. The stabilizers tie up carbon and nitrogen to form stable compounds : ZrC , ZrN and $Nb_xC_yN_z$. Moreover, Nb is added for creep resistance. This element combines with iron to form intermetallic compounds such as Fe_2Nb . They are localised at the grain boundaries, and limit grain growth. Nb has a low oxygen affinity compared to Al and does not participate at relatively low content (<0.6%) to oxide scale formation. It is very different for Zr, which has a strong affinity for oxygen. Free zirconium (not combined with carbon and nitrogen) can participate in oxide layer formation and can be compared to an active element.

Free zirconium (ΔZr) content is estimated by the following relation : $\Delta Zr = \%Zr - 7(\%C + \%N)$

Where $\%Zr$ is the total zirconium content, $\%C$ and $\%N$ are respectively carbon and nitrogen contents in the alloy.

Figure 12 shows oxidation kinetics on Fe 17-18%Cr 2%Al alloys :

- with no further addition (i)
- with Zr and Nb additions (d)
- with Zr, Nb and Y additions (g).

Regarding Fig. 12, the following remarks can be made :

- the addition of stabilizers markedly improved oxidation behaviour
- stabilizers and yttrium additions together give the lower weight gain.

Figure 12 : Influence of stabilizers (Zr and Nb) and yttrium additions on 17%Cr 2%Al thick coupons at 1000°C.

The different forms of zirconium in the oxide scale are shown in Figure 13. This element appears as nodules or in solution in the alumina scale. The nodules can emerge at the surface. The presence of zirconium generally promotes internal oxidation.

Figure 13 : different forms of Zr in the oxide (EPMA Study).

Two Fe 17%Cr 2%Al alloys (d and k) with different ΔZr are compared in Figure 14. It is clear that Zr addition has a beneficial effect on oxidation behaviour.

High levels of free zirconium induce a noticeable degradation of the properties. In fact, zirconium oxide nodules increase with Zr content. Thus zirconia is less protective than alumina and can, in large quantities, affect the oxidation resistance. Hence Zr additions must be controlled.

Figure 14 : Influence of temperature on oxidation behaviour after 24 hours. Influence of ΔZr .

3. 4 Influence of minor additions or impurities :

3. 4. 1 Influence of silicon

Silica formation occurs at the end of the life of metallic foils when the Al reservoir is not sufficient to provide oxide formation. Silica formation occurs at the inner part of the oxide (metal/oxide interface). A particular pyramidal morphology is attributed to silica as shown in Figure 15.

Figure 15 : SEM study of metal/oxide interface after pickling the metal substrate with a chemical reagent.

3. 4. 2 Influence of manganese

Manganese is present as an impurity in the metal and its content is below 1%. This element has a high chemical affinity for oxygen and participates in oxide scale formation. As can be seen in Figure 16, Mn is generally associated with Cr and is localised in the outer part of the alumina scale. Manganese oxides have a porous morphology. Manganese is also detected in defect zones, such as oxide cracks.

Figure 16 : EPMA study on Fe20%Cr 5%Al alloys oxidised at 1100°C.

3. 4. 3 Influence of sulphur

Stabilized zirconium Fe 18%Cr 4%Al alloys with different sulphur contents : 20 ppm (m) and 50 ppm (l) are oxidised at 1100°C. The results are shown in Figure 17.

Figure 17 : Influence of sulphur contents : S = 20 ppm (m) and 50 ppm (l) on oxidation kinetics of 18%Cr 4 %Al Zr thick metal coupons at 1100°C.

4. DISCUSSION

4. 1 Critical aluminium and chromium contents

The first steps of alumina scale formation are identified in the following way (1,2,3) :

Cr has high chemical activity in the metal. This allows formation of a chromia-rich layer which constitutes a transition scale. The formation of a rather protective layer induces a decrease in oxygen diffusion to the metal and a simultaneous decrease of oxygen pressure at the metal/oxide interface. The oxygen partial pressure at the metal/oxide interface is given by the dissociative pressure of the external chromium oxide. The slow-down of oxygen diffusion prevents internal aluminium oxidation and enhanced formation of a continuous alumina layer.

Thus, Al diffusion to the surface below the oxide is enhanced. In this way, an alumina healing layer can be formed immediately beneath the chromia rich transient scale. This highly protective oxide induces a strong decrease of the oxygen pressure at metal/oxide interface up to the oxygen dissociation pressure of alumina. The Gibbs energy formation of oxides is given at 1000°C :

- * -522 kJ/mol O₂ for Cr₂O₃
- * -585 kJ/mol O₂ for MnO
- * -677 kJ/mol O₂ for SiO₂
- * -844 kJ/mol O₂ for Al₂O₃.

Thus, among the most oxidizable elements in the alloy, only alumina can be formed and gives rise to oxide growth. In this process, Cr and Al levels play an important role in alumina scale formation. According to our results, an Al content of 1% is sufficient to provide a continuous Al₂O₃ formation. A lower content (0.5 %Al) gives large internal alumina flakes without forming a healing continuous scale. This phenomenon is due to the lack of Al at the surface when transient scale formation occurs.

A low Cr content alloy (6%) gives an insufficiently chromia-rich transient scale for a marked decrease in oxygen pressure at the oxide/metal interface. The fast oxygen diffusion through the scale does not allow Al enrichment at the interface and the continuous alumina scale layer cannot be formed. A value of 13% Cr is required to obtain protective alumina layers.

However, another parameter has to be taken into account in oxidizing thin metallic foils. The breakaway oxidation observed with low Al content (2%) at short oxidation times is caused by the lack of Al supply from the metal substrate to form an alumina scale. Al content in the foils must reach a value of 5% to provide acceptable oxidation resistance (3). Otherwise, different treatments prior to oxidation were studied and exert an influence on bulk properties like grain growth or on metal surfaces. The decrease in grain size generally favours diffusion in the metal and in this way the formation of a stable healing scale is enhanced (4). Grain growth of the substrate during oxidation is detrimental. In this case, the oxide layer is

Large weight gains were recorded in the alloy with higher sulphur content. This alloy is also very sensitive to spallation after cooling. On the other hand, low weight gains are obtained in the alloy with lower sulphur content. These results emphasise the detrimental effect of sulphur even at a level of 50 ppm.

Another similar alloy was tested which contains low sulphur (< 10 ppm), zirconium and rare earth (as mischmetal) added together. This alloy was compared with the previous one and similar behaviour was noticed. This result shows that at low sulphur levels (20 ppm) Zr is effective in tying up the residual sulphur in the substrate.

destabilized, both mechanically and chemically. When grain growth cannot be avoided, it is shown that fast growth is preferable. Thus, grain growth occurs in a thin layer which is better able to accommodate strains and chemical modifications at the metal/oxide interface.

Prior treatment in a reducing atmosphere and with low water vapour content drastically decreases oxygen pressure at the metal/oxide interface. Thus a protective alumina scale can be formed directly without the establishment of any chromia transient scale. This treatment tends to decrease the minimum Cr and Al contents for alumina layer formation. Oxidation resistance is enhanced, but it is not sufficient, and this does not allow Al and Cr contents to be drastically limited.

4. 2 Influence of active elements

Several theories have been proposed to explain the influence of active elements on oxide adhesion (5, 6) as :

- vacancy sinks in the oxide, which eliminate the formation of voids
- development of oxide pegs by internal oxidation from the scale to the substrate
- formation of an oxide compound, which accommodates differential dilatation strains between the oxide and the substrate generated by cyclic oxidation
- improvement of scale plasticity or chemical bonding
- decrease in growth stresses by modification of the scale growth mechanism
- tying up of sulphur at the metal/oxide interface and formation of a refractory compound.

Sulphur is known to decrease the surface energy of the substrate and thus segregates easily to the metal/oxide interface. Sulphur is detrimental to the adherence of the scale because it forms low melting compounds with metal, or reduces chemical bonding between oxide and metal (7).

The influence of active elements reaches maximum efficiency at low concentrations (a few tens of ppm). Catastrophic effects on hot workability (8, 9) and properties (9) are caused by high active element levels. Zr is not only used as a stabilizer but also as an active element. However Zr is less effective in tying up sulphur than group IIIB elements. It has a beneficial effect on oxide adherence. Similarly to common active elements (Y, Ce, and La), the free zirconium content must be lower than 1000 ppm to provide high oxidation properties. In fact, Zr (group IVB element) at higher levels acts as an oxygen getter and forms oxide nodules in the scale. These defects are less protective than alumina and conduce to a degradation of oxidation resistance.

4. 3 Influence of minor additions and impurities

Influence of niobium :

Nb is generally added as a stabilizer for its ability to form intermetallic compounds such as Fe_2Nb . Thus, the chemical oxygen affinity for Nb is lower than for Al. At levels of about 0. 5%, Nb has never been detected in alumina scale. However, we must mention that various oxide compounds can be formed, such as NbO , NbO_2 and Nb_2O_5 . These oxides are not protective or stable at high temperatures (10).

Influence of manganese :

This element is commonly present in industrial alloys. Mn is generally located in the outer part of the oxide scale and in oxide cracks which are fast diffusion pathways, as shown in Fig. 15. This phenomenon is linked to the fast diffusibility ($> \text{Cr}$ and Fe) of this element at high temperatures. Mn is associated with Cr to forms spinelle oxide MnCr_2O_4 in the alumina scale (11). This type of oxide is less protective than Cr_2O_3 and is also known to be detrimental in alumina-forming alloys (12).

Influence of silicon :

When Al is totally exhausted from the matrix, silicon is oxidised in silica (SiO_2) at the metal/oxide interface. This compound has a peculiar morphology and exhibits a pyramidal shape on FeCrAl alloys (see Fig. 14). Si is known to have a beneficial effect on FeCr alloys (13). Diffusion of detrimental species (Fe, Mn) is limited by a SiO_2 barrier in the inner part of the oxide. Thus Si is found to retard breakaway oxidation after complete Al depletion.

Influence of sulphur :

Sulphur has a detrimental effect, as mentioned above in the section on the influence of active elements.

5. CONCLUSIONS

It is shown that Al addition is very effective for high temperature oxidation resistance of FeCr alloys. 1% Al leads to a continuous protective Al_2O_3 oxide on FeCr alloy that contains more than 13% of Cr.

However, this aluminium content is not enough for high temperature resistance of thin foils and 5% Al is necessary, since the substrate plays the role of an aluminium reserve capable of being oxidised. Impurity elements such as sulphur are detrimental and give rise to spalling of the oxide layer. Therefore, active elements such as Y, Ce, La, Zr are necessary to tie up sulphur and increase the life of the alloys.

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