Effect of Trace Amounts of Carbon and Nitrogen on the High Temperature Oxidation Resistance of High Purity FeCrAl Alloys

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The growth rate and adhesion of the protective alumina scales on the heat resistant FeCrAl alloys are known to depend on minor metallurgical additions of the “reactive elements” such as Y, Ti, Zr, etc. The present study of high purity model FeCrAl alloys illustrates that the oxidation behaviour of these materials is strongly affected by trace amounts (up to 300 mass ppm) of carbon and/or nitrogen impurities. During long term high temperature oxidation testing of high purity model alloys it has been found that the carbon and nitrogen can interact with the reactive elements, such as Zr and Ti in the ferritic alloy matrix, resulting in a number of important effects on the scale growth and adherence. These effects can be beneficial as well as detrimental, depending on the exact amount and/or distribution of the mentioned minor alloying elements and C/N-impurities.

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1. Introduction

Due to their excellent oxidation resistance, FeCrAl alloys are used in a large number of high temperature applications. In most technically relevant atmospheres and temperatures as high as 1400°C, these materials with typical composition Fe + 20Cr + 5Al (mass%) form alumina scales that protect the metallic components from corrosive degradation.¹

In spite of the excellent stability of the alumina surface scales even at temperatures above 1100°C, the lifetime of the FeCrAl based alloy components can be significantly shortened by oxidation. This is because the scale-forming element (aluminium) exists only in a limited supply within the alloy matrix. Scale growth and frequently observed spallation of the protective alumina scales can, after long exposure times, lead to a substantial depletion of the alloy aluminium reservoir. When the aluminium is depleted below a certain critical level, the protective alumina scale can no longer be maintained. The oxidation products of the major alloying elements, i.e. Fe and Cr at high temperatures are not protective and a rapid “breakaway” corrosion process occurs, which eventually results in a failure of the component within some hours.²

In order to extend the oxidation limited life of the FeCrAl components or enable their operation at higher temperatures it is necessary to decrease the rate of consumption of the Al-reservoir. This can be achieved by reduction in the growth rate of the alumina scale as well as by improving the scale adherence to the metal substrate. In turn, both growth rate and adherence of the scale are determined to a large extent by minor additions (in the order of several hundred ppm’s) of the elements from Groups IIA–IV A, commonly referred to in oxidation literature as “reactive elements” – RE.³ The most typical additions are Y, La, Ce, Zr. Two main positive effects of the RE-additions on the oxidation resistance of alumina forming alloys are generally accepted today. The first one is suppressing the outward diffusion of Al-cations in the alumina scale, which has been experimentally proved elsewhere.⁴ This results in a decrease in the oxidation rate and changes in the scale structure and morphology. The second important RE-effect is attributed to prevention of the deleterious sulphur segregation to the scale/metal interface.⁵

Although plenty of scientific literature exists on the RE-effect, some of the data extremely important for industrial manufacturing of the FeCrAl alloys are still not available. In particular, little is known about the interaction of the RE with common alloy impurities other than sulphur. Hence, in the first part of this paper the interaction of Ti-addition and N-impurity in a commercial FeCrAl alloy is briefly described in an attempt to explain the observed batch to batch variations in the oxidation behaviour. In the second part studies of high purity Y-containing FeCrAl model alloys will be presented. The latter will show the importance of carbon interaction with alloy major element Cr as well as with minor Ti and/or Zr additions for the long term cyclic oxidation resistance.

2. Experimental

The studied materials were delivered as recrystallised sheets of different thickness. The commercial materials were two batches of the Oxide Dispersion Strengthened (ODS) alloy PM 2000 supplied by Plansee GmbH. The powder metallurgical production route of the ODS alloys including mechanical alloying, hot isostatic pressing followed by hot and cold rolling has been described in Ref. 6). The high purity model alloys were produced by induction melting in Ar-atmosphere with subsequent hot and cold rolling down to 1 mm thick sheets. The final heat treatment conditions were: 1 h anneal at 1473 K in Ar, slow cooling to 1073 K, then water quenching. All three model alloys had a basic composition of Fe–20Cr–5Al–0.05Y. In addition, model alloys M + Ti and

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The chemical compositions of the materials studied are summarised in Table 1. 20 mm × 10 mm specimens were cut from as-received sheets, ground to 1200 grit finish and degreased in a detergent before oxidation. The cyclic oxidation tests (up to 10000 h total exposure time) were performed in a resistance heated furnace at 1473 K in laboratory air. The cyclic parameters were 96 h at temperature followed by 4 h air cooling intervals at room temperature, during which the specimens were visually examined and weighed. The heating/cooling rate was approximately 100 K/min. The oxidised specimens were investigated by optical metallography, scanning electron (SEM) and transmission electron (TEM) microscopy.

3. Results and Discussion

3.1 Batch to batch variations in oxidation behaviour of commercial FeCrAl alloys

The results of cyclic oxidation testing of the two batches of PM2000 are presented in Fig. 1. It can be seen that after around 300 h exposure batch CKT exhibits clearly higher scale growth rate than batch CKS. Moreover, the fracture surfaces of the scales on the two batches in Fig. 2 show that the observed differences in oxidation kinetics can be related to the differences in scale microstructure. On batch CKS the oxide is dense and possesses a columnar structure (Fig. 2(a)). This scale structure has been typically observed on RE-doped FeCrAl alloys and attributed to the scale growth occurring mainly via oxygen grain boundary diffusion. In contrast on batch CKT the columnar structure cannot be distinguished and the scale contains pores and microcracks (Fig. 2(b)). The latter observation suggests that fast molecular oxygen transport through the above scale defects enhances the oxidation process for batch CKT. Extensive TEM studies were performed on the oxide scales as well as on the bulk alloys of batches CKS and CKT. The detailed results of these TEM studies as well as those of other analytical examinations of the CKS and CKT specimens are presented and discussed in a separate paper. The main outcome of the mentioned TEM studies was that in the bulk of batch CKT precipitates of titanium carbo-nitrides were present, which is in good agreement with the higher nitrogen content of this batch (Table 1). Furthermore, the TEM of the cross-sectioned oxidised CKT
specimens, showed that the Ti(C, N) precipitates became incorporated into the inwardly growing alumina scale. Oxidation of the carbo-nitride particles within the scale leads to a volume change and to the release of gaseous reaction products of CO and N₂. Both latter effects can be responsible for the formation of microcracks and pores observed in the scale on batch CKT.

3.2 Effect of carbide precipitates in FeCrAl alloys on the alumina scale integrity

In the previous section it was shown that carbo-nitride precipitates in the FeCrAl-alloy can have a detrimental effect on the oxide scale growth rate. The main difficulty in clarifying the oxidation mechanisms in commercial alloy systems is the complex chemistry of the latter. Hence, in order to unequivocally attribute an effect to a particular addition and/or contaminant it is necessary to use model alloy systems with precisely defined compositions. In the present work the interaction of carbon with two carbide-forming elements (Ti and Zr) and its effect on the oxidation was studied on the model system Fe–20Cr–5Al–0.05Y. This is a typical composition of the commercial wrought alloys, however, the levels of other impurities, such as S, are significantly lower than those in the commercial materials (normally less than 10 ppm; Table 1).

Two observations can be made when comparing cyclic oxidation kinetics at 1473 K of the high purity model FeCrAl alloys. First the Zr-doped alloy showed initially a high oxidation rate up to around 500 h, which then decreased and became similar to those of the reference model alloy (MRef) and M + Ti (Fig. 3). Second, after about 4000 h exposure alloy MRef started to exhibit an enhanced oxidation rate, which finally resulted in a breakaway failure of this material after 9300 h.

Visual examination of the MRef specimens during cooling intervals revealed that enhanced oxidation of this alloy after long exposure times (i.e. around 5000 hours) can be related to the formation and growth of “broccoli”-like nodules protruding through the alumina scale. It must be mentioned that in contrast to MRef, alloys M + Ti and M + Zr did not show any such protrusions. Optical metallography of the oxidised MRef specimens show that a “broccoli”-like nodule is in fact a kind of local scale disruption resulting from severe, local internal alumina formation and the associated volume increase (Fig. 4). The SEM studies on the MRef specimens after short term oxidation were performed in order to find the scale and/or alloy inhomogeneities, which could trigger the “broccoli” effect. After 96 h oxidation (i.e. after one cycle) large precipitates at the alloy grain boundaries in alloy MRef were observed, as shown in Fig. 5(a).
scale/metal interface the Y-rich pegs were found, which according to EDX data were attributed to Y/Al-mixed oxides, presumably Y$_2$Al$_5$O$_{12}$. A noteworthy point about the Y-rich pegs was that after medium cyclic oxidation of 2000 h, crack initiation in their vicinity was observed in our SEM studies. Another type of alloy grain boundary precipitate deeper in the matrix was chromium carbide, as indicated by the EDX line scan data in Fig. 5(b).

Taking into account all the above observations, the “broccoli” effect in alloy MRef is likely to be initiated by scale cracking in the vicinity of the Y/Al-oxide pegs, which apparently serve as stress concentrators during temperature cycling. The oxide crack allows oxygen ingress to the alloy grain boundary decorated with chromium carbides. At the high exposure temperature of 1473 K rapid oxidation of the carbides results in volume change and release of gaseous carbon oxides with pressure high enough to deform the mechanically weak alloy substrate. This substrate deformation leads to the typical sponge-like internal alumina morphology after longer exposure times (Fig. 4), with the consequence of an increased effective specimen area available for oxidation. The increased effective oxidizing area explains a higher oxidation rate (Fig. 3) and consequently a faster depletion of the Al-reservoir and shorter times to breakaway for alloy MRef.

The most important positive effect of Ti and Zr additions in the high purity model alloys was the suppression of the “broccoli” type local oxides. Based on the studies of the two batches of commercial alloy PM 2000 it is believed that Ti and Zr additions apparently serve as a getter of the carbon impurity by formation of thermodynamically stable Ti-carbides, thus preventing Cr carbide formation on alloy grain boundaries. An additional important finding for alloy M + Zr was that the formed alumina scale exhibited a porous structure (Fig. 6). This porosity can in fact explain the higher scale growth rate observed on M + Zr after short time oxidation at 1473 K. It can be that, similar to the high nitrogen PM 2000 batch CKT, the high initial oxidation rates in M + Zr are due to the incorporation and subsequent oxidation of Zr-carbides.

This assumption is confirmed by the presence of Zr-rich oxides in the vicinity of the pores in the scale formed on M + Zr (Fig. 6). However, in contrast to batch CKT, the enhanced oxide growth on M + Zr diminishes after ca 500 h exposure. At the moment, the reason for the decrease in the oxidation rate on M + Zr after longer exposure times is not clear to the authors. One of the possible explanations can be that in the high purity model alloys the amounts of the carbide forming elements are much lower than those in the commercial alloy PM 2000, so that the amount of carbide precipitates is expected to be lower as well.

It is important to note that the oxidation effects caused by formation of the carbo-nitrides within the FeCrAl alloy matrix cannot be considered as entirely negative. Indeed, the incorporation of the carbo-nitride particles into the alumina surface scale may result in enhanced oxidation kinetics. However, an interesting observation was made with batch CKT and model alloy M + Zr during long term cyclic oxidation. In spite of the presence of large-size defects in the oxide scales on these materials, the scales seem to possess excellent adherence to the substrate metal. The observed scale thickness on CKT and M + Zr exceeded 50 µm, i.e. much higher than the typical values for FeCrAl alloys for initiation scale spalling under thermocyclic conditions.²,8) It might be that due to the formation of pores and microcracks the scales on the above materials attain a certain “pseudo-plasticity”, as was proposed by other authors.⁹) Hence, in terms of the long-term cyclic oxidation behaviour, the improved adherence of the porous scales on CKT and M + Zr materials may have a positive effect on the lifetime. This is because the spallation of the protective scales consumes much more alloy Al for scale re-healing than is normally needed for the scale growth.²1)

4. Concluding Remarks

Impurities of carbon and nitrogen may have a significant although indirect effect on the oxidation behaviour of FeCrAl alloys. In an earlier work⁵) it has been found that carbon together with sulphur tend to segregate to the scale/metal interface, hence deteriorating the scale adhesion. In the present work the impurities of C and N were found to form carbo-nitride precipitates by reaction with the minor additions of Ti and Zr, or, in the absence of the latter, with the alloy Cr. Precipitation of Ti and Zr carbo-nitrides occurs homogeneously in the alloy matrix, whereas in the Ti/Zr-free alloy, the chromium carbides precipitate mainly to the alloy grain boundaries.

During long term oxidation of FeCrAl alloys incorporation of the Ti/Zr carbo-nitrides into the inwardly growing alumina scale occurs. Subsequent oxidation of these particles within the scale results in scale microcracking and pore formation. Faster molecular oxygen transport through the latter defects leads to a higher oxidation rate, i.e. to a faster depletion of the alloy Al-reservoir, which has negative consequences for the alloy oxidation limited life. However, during cyclic oxidation the porous scales were found to possess excellent adherence to the alloy substrate, which has a positive effect on the lifetime.

In the Ti/Zr-free alloys, chromium carbide precipitation to the alloy grain boundaries is likely to be responsible for
the severe internal oxidation attack, macroscopically apparent as the “broccoli effect”. This internal oxidation attack is apparently triggered by cracking of the oxide scale in the vicinity of the alloy grain boundary, followed by oxidation of the chromium carbides precipitates. As a result the effective surface area available for oxidation becomes significantly increased, which can shorten the alloy life by a large margin.

Generally, the results presented in this work reveal the complexity of the minor chemistry effects in the oxidation of FeCrAl-alloy based systems. The interaction between the minor alloying additions and C/N-impurities may lead to enhanced scale growth, however, simultaneously the scale adhesion seems to be improved. The prevailing net effect on the alloy lifetime is expected to depend on the exact amounts and distribution of the above elements. Hence, optimising the alloy composition with respect to the minor elements and C/N-impurities for particular FeCrAl applications should allow a significant extension of the alloy lifetime.

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