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The effect of gaseous atmosphere and pre-treatment on the oxidation–nitridation of Fe–31Mn–9Al–6Cr–0.86C alloy at 1000° C

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The Fe–Mn–Al-based alloys have attracted considerable interest for their potential application in stainless steel usage. In this study the oxidation and nitridation behaviour of Fe–31Mn–9Al–6Cr–0.86C (wt%) alloy is investigated. The effects of a gaseous atmosphere, a pre-existing oxide layer and the alloy phase distribution in the matrix are evaluated with respect to the morphological development and kinetics. The nitridation behaviour of the alloy in air is sensitive to the alloy surface condition, such as the alloy phases in the matrix and the oxides in the scale. For the aged multiphase alloy, oxidation occurs in the ferrite phase and nitridation takes place in the austenite phase due to the higher solubility of nitrogen. The existing interphase boundaries provide an easy path for nitrogen migration and thus promote the nitridation. However, the surface oxide layers act as a diffusion barrier for nitrogen. The effectiveness of the barrier in the retardation of nitridation depends on the amounts of $MnAl_2O_4$ and α-Al_2O_3 in the oxide layer.

1. Introduction

The Fe–Mn–Al alloy system has currently attracted considerable attention as a potential candidate to replace the conventional Ni–Cr stainless steel. One of the important tasks in the study of this alloy is to develop the oxidation resistance of the aluminium oxide layer which is characteristic of the Fe–Al alloys. Unfortunately, an α-Al_2O_3 layer was frequently not observed in alloys with ~30 wt % Mn [1, 2], or only discontinuous Al_2O_3 was found instead [1].

Recently some investigators reported that a continuous α-Al_2O_3 layer could be formed by the addition of some alloying elements, such as silicon [3] or chromium [4, 5]. As the chromium content increased to 6 wt %, the formation of AlN rather than α-Al_2O_3 was observed by Wang and Duh [6] during the high-temperature oxidation of Fe–31Mn–9Al–6Cr–0.86C (wt %) alloy in air. In chromium-free Fe–Mn–Al–C alloys, nitridation was also reported [7]. In the literature, Seybolt and Haman [8] indicated that the rate of nitridation was 30 times faster than for the oxidation of pure chromium, and the pre-existing oxide was not an effective barrier to nitride formation. It was also reported that chromium-based alloys exhibited almost 100 times greater solubility for nitrogen than for oxygen and the Cr_2N could be replaced by other more stable nitrides [9] such as AlN, VN and TiN. The purpose of this study is to investigate the oxidation and nitridation behaviour of an Fe–Mn–Al–Cr–C alloy, with emphasis on the effect of the gaseous atmosphere, pre-existing oxide layer and the alloy phase distribution in the matrix.

2. Experimental details

The alloy was prepared by vacuum induction-melting from high-purity elements. The chemical composition is shown in Table I as obtained by the wet chemical method. The metallic concentrations of iron, manganese, aluminium and chromium were further checked with electron microprobe quantitative analysis. The cast ingot was first hot-forged and homogenized at 1200° C for 10 h. Annealing was carried out at 1150° C for 50 h under an argon atmosphere and followed by hot-rolling. After annealing, austenite is the only phase present in the alloy. The specimens were polished with 0.05 μm alumina powder. Three types of specimen treatment were employed in this study: (a) annealed state, (b) pre-heat treatment at 800° C for 24 h after annealing, (c) pre-oxidation in oxygen at 1000° C for either 2 or 4 h.

The gaseous atmospheres introduced were oxygen, air and nitrogen. The oxidation and nitridation were carried out at 1000° C for 24 h. The gas–metal reaction product layers and alloy phases were identified by X-ray diffraction. Oxidation kinetics were recorded continuously with a computerized thermogravimetric analyser (TGD-1500, Ulvac/Sinku Riko, Japan). The morphologies of the oxide and alloy substrate were examined with the optical microscope. In addition,

TABLE I Chemical composition of the alloy employed

Element	Mn	Al	Cr	C	Fe
Content (wt %)	31.30	8.92	5.96	0.86	Balance

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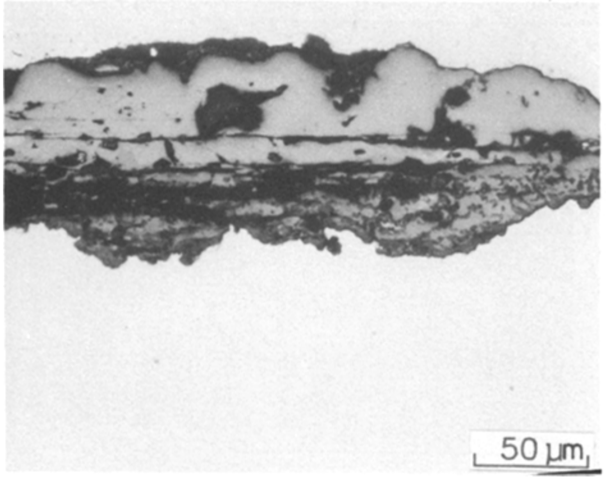

Figure 1 Metallographic picture of alloy oxidized in oxygen at 1000° C for 24 h.

quantitative analysis was performed with a computerized electron microprobe (Jeol JCXA-733) on the basis of a ZAF-corrected program.

3. Results and discussion

3.1. Morphology after reaction

The typical morphologies of the alloy after reaction at 1000° C in different atmospheres are shown in Figs 1 to 3. Two oxide layers are observed in Fig. 1 for the sample oxidized in pure oxygen. The oxides formed in pure oxygen are identified as $(Fe, Mn)_3O_4$ in the outer layer, and MnO, $MnAl_2O_4$, $Fe(Al, Cr)_2O_4$ and α-Al_2O_3 in the inner layer. Fig. 2 presents the morphology of the alloy after nitriding in nitrogen. A region with a width around 393 μm containing the nitrided product AlN is found beneath the free surface. The morphology of the alloy oxidized in air, as shown in Fig. 3, is in fact a mixed mode of Figs 1 and 2. Phases of the outer layer in Fig. 3 are identified as $(Fe, Mn)_3O_4$, while the needle-like AlN as well as fine oxides of MnO and $Fe(Al, Cr)_2O_4$ are observed in the middle darker region. A region containing AlN is found in the inner grey layer which is similar to Fig. 2. The aluminium content between the AlN particles is measured to be 0.08 wt %.

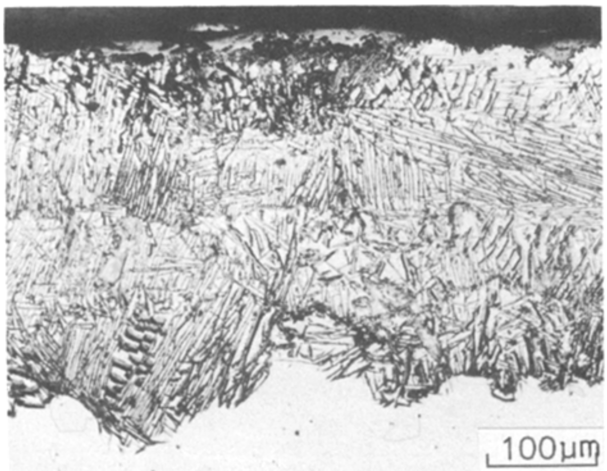

Figure 2 Metallographic picture of alloy nitridized in nitrogen at 1000° C for 24 h.

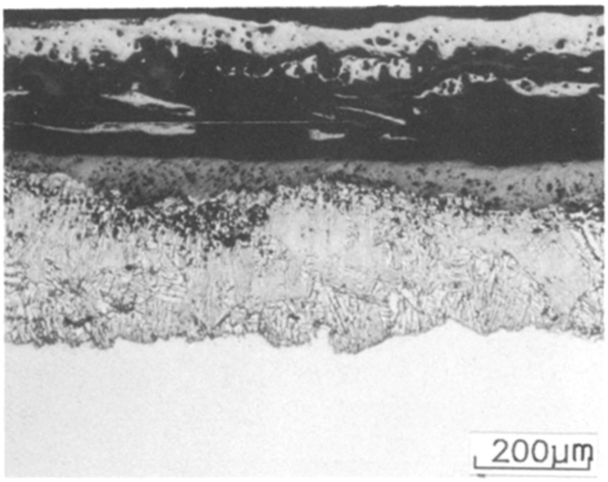

Figure 3 Metallographic picture of alloy oxidized in air at 1000° C for 24 h.

As seen in Fig. 3, it is apparent that the nitridation is ahead of the oxidation for the alloy oxidized in air. As the nitridation occurs prior to the oxidation and results in AlN, the content of aluminium is depleted in this nitrided region and oxidation is thus dominated by iron and manganese. Consequently, the weight gains of the alloy oxidized in air are higher than in oxygen, as shown in Fig. 4. It is worthwhile to point out that this is not a common phenomenon in the oxidation of the conventional Fe–Ni–Cr system, and it implies that oxidation-associated nitridation should be taken into consideration in the oxidation phenomenon of these new Fe–Mn–Al based alloys.

3.2. The effect of pre-treatment and gaseous atmosphere

The presence of the ferrite phase could retard the growth of AlN in this type of alloy [6]. In order to further investigate the effects of alloy composition and the existing phases on the growth of AlN, a pre-heat treatment was introduced. Fig. 5 shows the microstructure of alloy which was aged at 800° C for 24 h followed by furnace-cooling. Phases present in this condition are γ, α, Cr_7C_3 and β-Mn, and the concentrations of manganese, aluminium and chromium in the α-phase are measured as 25.74, 10.48 and 3.31 wt %, respectively.

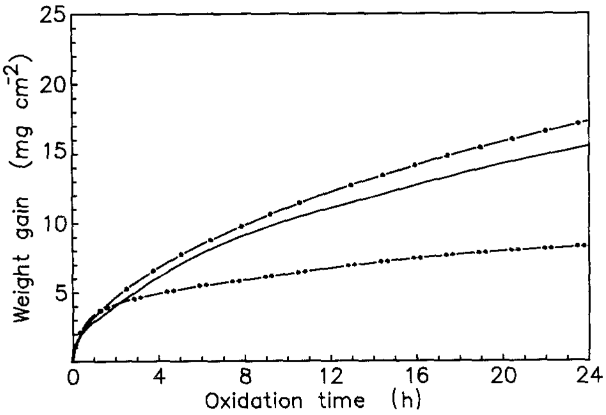

Figure 4 Oxidation kinetics of alloys oxidized at 1000° C in (——) air, (—··—) oxygen and (—·—) air, pre-heated at 800° C for 24 h.

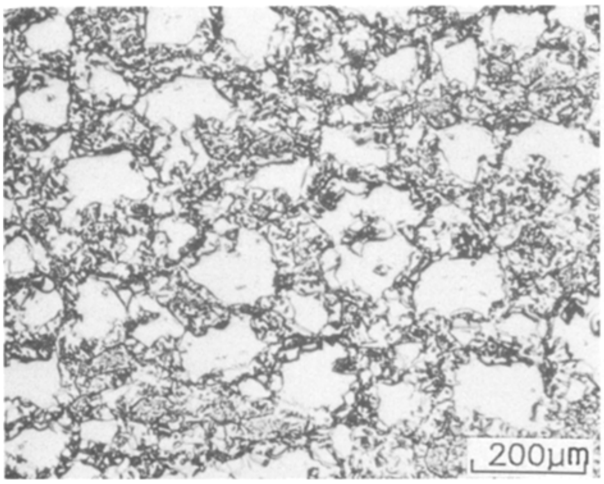

Figure 5 The furnace-cooled microstructure of alloy aged at 800° C for 24 h; the dark stringers within ferrite grains are chromic carbides.

For the aged specimen oxidized in air, localized oxide–nitride nodules and a nitrided region beneath the ferrite phase are observed as shown in Fig. 6. This is compatible with the conclusion of the preliminary study [6] that the growth of AlN is favoured within the austenitic phase. Since more aluminium is oxidized as Al_2O_3 rather than AlN, the oxidation kinetics in air for the aged specimen are faster than in the annealed state as seen in Fig. 4. When the aged specimen is nitrided in pure nitrogen, a uniform nitrided layer similar to Fig. 2 is observed. The depth of this layer is estimated to be 520 µm, which is wider than that of the annealed state. This indicates that in pure nitrogen, the nitridation is independent of the existing phase and composition in the multi-phase microstructure. It is argued that there exist more interphase boundaries in the aged specimen, which provide an easy path for the entrance of nitrogen into the matrix and thus the nitridation is enhanced.

To investigate the effect of a pre-existing oxide layer on the nitridation behaviour, the annealed alloy was pre-oxidized in pure oxygen and then nitrided in nitrogen or in air. For the specimen pre-oxidized for 2 h, the major oxides are $(Fe, Mn)_3O_4$ with a little $Fe(Cr, Al)_2O_4$. As indicated in Fig. 7 a nitrided layer with a width around 322 µm is formed when nitrided in nitrogen. However, no nitride is found for the nitridation in air. As the pre-oxidation time is increased to 4 h, large amounts of $MnAl_2O_4$ and α-Al_2O_3 are detected in the oxide layer, and no nitridation takes place in either nitrogen or air. This implies that the $MnAl_2O_4$ and α-Al_2O_3 act as effective barriers for the inward diffusion of nitrogen. This is different from the observation reported by Seybolt and Haman [8], in which the pre-existing oxide was not an effective barrier to nitride formation in the oxidation of pure chromium.

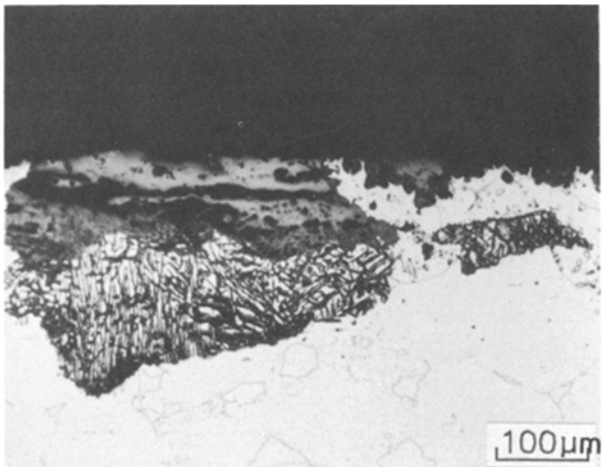

Figure 6 Cross-section of aged multi-phase alloy oxidized in air at 1000° C for 24 h.

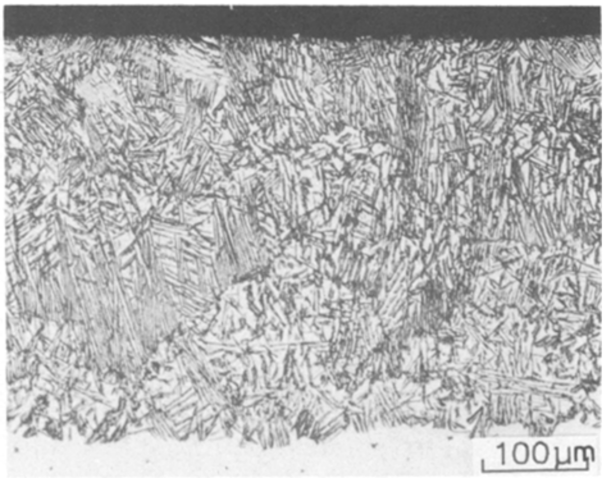

Figure 7 Cross-section of alloy pre-oxidized in oxygen for 2 h and then nitrided in nitrogen for 24 h.

It is argued that $(Fe, Mn)_3O_4$ may also be considered as a barrier since the nitrided depth for 2 h pre-oxidation treatment is shorter than that of the oxide-free specimen. In fact, the nitridation, i.e. the formation of AlN, could occur within 10 min for the alloy oxidized in air [6]. Nevertheless, the surface condition, i.e. the presence of the oxide film, would influence the nitridation phenomenon when oxidized in air. For the alloy oxidized in air with pre-existing oxide films, nitridation rather than oxidation would be retarded. As oxidation predominates over nitridation, the oxidation of aluminium prevails and hence it is favourable for the formation of a protective aluminium oxide layer. This feature may be of practical importance in the consideration of alloy development in this new Fe–Mn–Al-based system.

4. Conclusions

1. Oxidation and nitridation are carried out in Fe–31Mn–9Al–0.86C alloy at 1000° C.

2. The nitridation behaviour of the alloy in air is sensitive to the alloy surface condition, such as the alloy phases in the matrix and the oxides in the scale.

3. For the aged multiphase alloy, oxidation occurs in the ferrite phase and nitridation takes place in the austenite phase due to the higher solubility of nitrogen. The existing interphase boundaries provide an easy path for the nitrogen entrance into the matrix and thus promote the nitridation.

4. Surface oxide layers act as a diffusion barrier for nitrogen. The effectiveness of the barrier in the

retardation of nitridation depends on the amounts of $MnAl_2O_4$ and α-Al_2O_3 phases in the oxide layer.

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