

Corrosion behavior of ternary Fe-15Cu-5Al alloy in pure oxygen at 1 000 °C

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Abstract: The corrosion behavior of ternary Fe-15Cu-5Al (mole fraction, %) alloy was studied at 1 000 °C in 0.1 MPa pure oxygen. The Fe-rich alloy shows two parabolic oxidation stages, with a small increase of the parabolic rate constant from 1.9×10^{-9} to 4.1×10^{-9} g²/(cm⁴·s). The scale grown on the alloy is very complicated, with formation of overgrown nodules interspersed among bulky stratified scales. The nodules and the bulky stratified scales are always composed of an outer layer of CuFe₂O₄ and of an inner layer containing Fe₂O₃ and Fe₃O₄. Beneath the external scale of the nodules, there is an internal oxidation zone where iron oxide is mixed with copper metal. Furthermore, the base of the internal oxidation zone is characterized by a discontinuous aluminum-enriched layer of either Al₂O₃ or FeAl₂O₄. For the stratified scales, no internal oxidation zone is present beneath the innermost Al₂O₃ or FeAl₂O₄ layer. Aluminum depletion is present in advance of the internal oxidation front, while iron depletion is not observed. The corrosion feature of the ternary Fe-15Cu-5Al alloy is partly associated with that of the corresponding binary Fe-Cu and Fe-Al alloys. The peculiar scale microstructure observed is considered mainly as a consequence of the limited solubility of the iron and copper components in one another and of the monovariant system of the ternary Fe-15Cu-5Al alloy.

Key words: Fe-15Cu-5Al alloy; ternary alloy; corrosion behavior; nodules

1 Introduction

For practical applications, the presence of three or more alloy constituents is often required to offer adequate protection against corrosion at high temperatures without loss of good mechanical properties[1]. Fundamental and comprehensive knowledge is required on the relations between the oxidation mechanism and the resulting composition and microstructure of the developing oxide. However, only few mathematical models have been developed for the oxidation or nitridation of ternary alloys[2–5]. Recently, NIU et al[6–9] have made great efforts to collect experimental results and develop theoretical models about the third-element effect in multi-component

systems, since a non-classical type of third-element effect has been found in some multi-component systems[7]. Though great efforts have been made, the oxidation theory of complex alloys has not yet been established systematically, even for the relatively simple ternary systems.

The thermodynamic stabilities and the growth rates of the oxides of the three components involved in the present ternary Fe-Cu-Al systems are very different. Moreover, the components of the system do not form any intermetallic phase between each other in the composition range examined. Therefore, the Fe-15Cu-5Al alloy can be considered typical model systems useful for the investigation of the oxidation mechanisms of multi-component complex systems. In the present work, the corrosion features of the ternary

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Fe-Cu-Al alloy associated with that of the corresponding binary Fe-Cu, Fe-Al and Cu-Al alloys were investigated, and the oxidation mechanisms of multi-component alloys were clarified.

2 Experimental

The phase diagram of the ternary Fe-Cu-Al system is quite complex, showing the existence of many phases [10]. However, in the region of aluminum contents below 20% the stable phases are only a solid solution of Fe and Al in copper and a solid solution of Cu and Al in iron [10]. The phase diagram in the region of low aluminum contents remains similar even at 1 000 °C [10].

Fe-15Cu-5Al alloy was prepared by repeated melting appropriate amounts of the three pure components (99.8%) under a Ti-gettered inert atmosphere using non-consumable tungsten electrodes. The alloy ingot was subsequently annealed at 900 °C for 24 h in a pure argon atmosphere to remove residual mechanical stresses and to achieve a better equilibration of the alloy phases. In agreement with the phase diagram of ternary Fe-Cu-Al system at 25 °C, at room temperature Fe-15Cu-5Al (nominal composition) is composed of a mixture of two phases, including a Cu-rich solid solution (α -phase, light) and a Fe-rich solid solution (β -phase, dark) (Fig.1). The situation remains the same at 1 000 °C. The actual average compositions of α and β -phase are shown in Table 1. Thus, for the Fe-15Cu-5Al alloy the α -phase contains a little more aluminum than the β -phase. The dark β -phase forms the alloy matrix, while the light α -phase is present in the form of dispersed islands or particles (Fig.1).

Samples with a dimension of 12 mm $\times$ 6 mm $\times$ 1.2

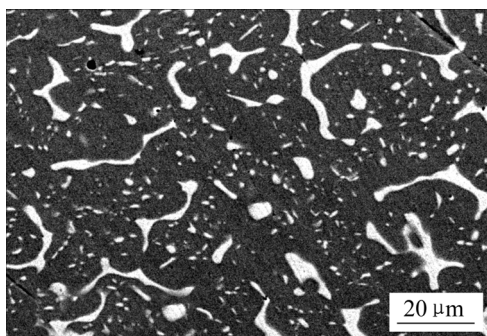


Fig.1 Microstructure (SEM/BEI) of ternary Fe-15Cu-5Al alloy at room temperature (Light phase: Cu-rich-phase; Dark phase: Fe-rich-phase)

Table 1 Actual average compositions of α and β phases of Fe-15Cu-5Al alloy (mole fraction, %)

Alloy	α phase			β phase		
	Fe	Cu	Al	Fe	Cu	Al
Fe-15Cu-5Al	13.4	79.3	7.3	92.0	3.2	4.8

mm were oxidized at 1 000 °C under 1×10^5 Pa flowing pure O₂. Continuous mass change measurements were carried out by a Cahn Versatherm TGA system for 24 h. The oxidized specimens were examined by X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy-dispersive X-ray microanalysis (EDX) to establish the nature, composition and spatial distribution of the oxidized products.

3 Results and discussion

3.1 Scaling kinetics

The kinetic curve and the corresponding parabolic plot for the oxidation of individual sample of Fe-15Cu-5Al alloy at 1000°C are shown in Figs.2(a) and (b), respectively. Fe-15Cu-5Al shows two quasi-parabolic stages, the first with an average rate constant $k_p = 1.9 \times 10^{-9}$ g²/(cm⁴·s) up to 300 min, and the second with $k_p = 4.1 \times 10^{-9}$ g²/(cm⁴·s) from 400 min up to the end of the test.

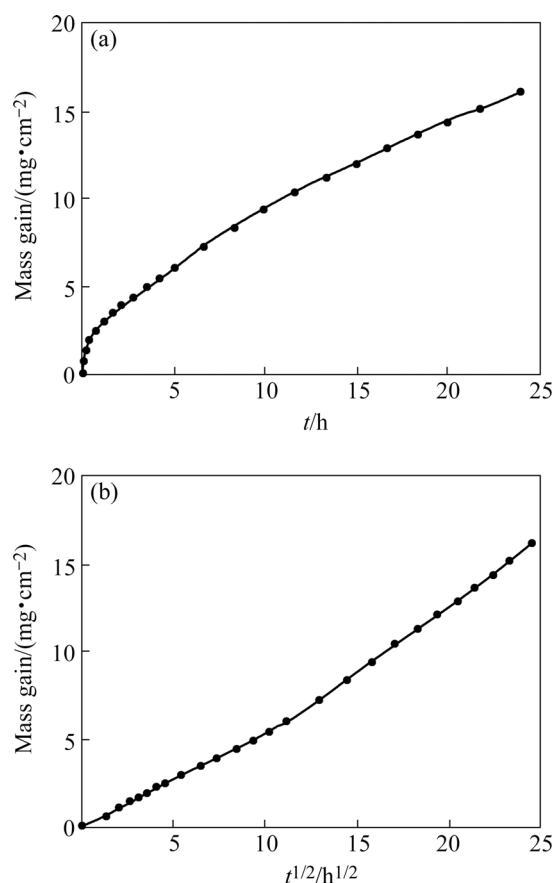


Fig.2 Oxidation kinetics of Fe-15Cu-5Al alloy in 0.1 MPa O₂ at 1 000 °C: (a) Normal plot; (b) Parabolic plot

3.2 Scale microstructure and composition

The scale grown on the alloy at 1 000 °C is very complicated, with formation of overgrown nodules composed mainly of iron-oxides (Figs.3(a)–(h)). Proceeding from the scale/gas interface towards the

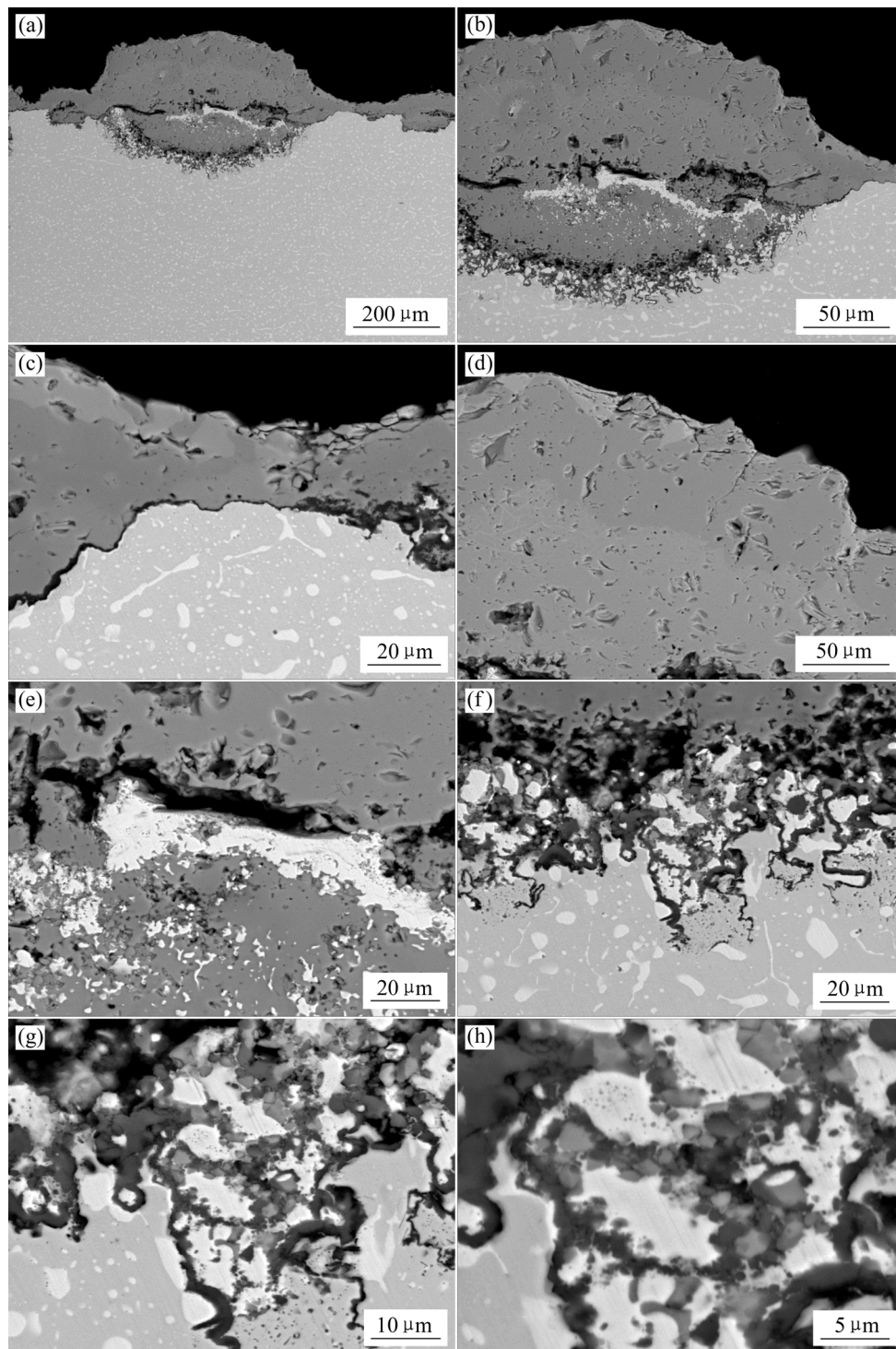


Fig.3 Micrographs (SEM/BEI) of cross sections of Fe-15Cu-5Al alloy oxidized at 1 000 °C: (a) General view; (b) Enlarged view of bulky nodules; (c) Enlarged view of stratified scales; (d) Enlarged view of outer region of nodules; (e) Enlarged view of copper islands; (f) General view of inner mixed region; (g)–(h) Enlarged view of inner mixed region

interior, the nodules are first composed of an outermost irregular gray layer of CuFe_2O_4 (Figs.3(b) and (d)). The following darker layer is composed of Fe_2O_3 (Figs.3(b) and (d)). In turn, this intermediate layer is in contact with a third lighter complex layer composed of a Fe_3O_4 matrix, which sometimes contains very large copper islands

(Figs.3(b) and (e)). In addition to the large copper islands, a significant number of small copper particles dispersed in the oxide matrix are also present (Figs.3(b) and (e)). A little aluminum is present in the external scale, possibly in solution. Moreover, the content of aluminum increases gradually from the outer region towards the inner region.

Beneath the external scale there is an inner zone, corresponding essentially to the alloy-consumption region, where iron oxide is mixed with copper metal following closely the spatial distribution of the original alloy (Figs.3(f)–(h)). Furthermore, the base of the alloy-consumption region is characterized by a discontinuous aluminum-enriched layer of either Al_2O_3 or FeAl_2O_4 (Figs.3(f)–(h)). Finally, aluminum depletion is observed in advance of the internal oxidation front, while iron depletion is not observed. Between the overgrown nodules, oxidation produces bulky stratified scales, with formation of an outermost layer of CuFe_2O_4 , followed by a thick iron oxide layer, which is very similar to the scale structure of the nodules (Fig.3(c)). However, at the base of the stratified scales there is a very thin layer of Al_2O_3 or FeAl_2O_4 and no internal oxidation zone is present underneath (Fig.3(c)).

The corrosion feature of the ternary Fe-15Cu-5Al alloy is partly associated with that of the corresponding binary Fe-Cu and Fe-Al alloys. However, this relationship is not obvious between Fe-15Cu-5Al and the corresponding binary Cu-Al alloy. The microstructure and composition of the scales formed on Fe-15Cu-5Al alloy are of the common characteristics of the corresponding binary Fe-Cu alloy to some extent. The air oxidation of three Fe-Cu alloys containing 25%, 50% and 75%Cu(mass fraction) has been examined previously[11]. The scales are always composed of an inner layer containing a mixture of copper metal and iron oxide and an outer oxide layer whose composition depends on the copper content of the alloy. For Fe-25% Cu(mass fraction) alloy, whose composition is very similar to that of the ternary Fe-15Cu-5Al alloy, the oxidation of the alloy produces external scales of iron oxides that may or may not contain particles of copper metal. At certain locations very large copper islands are also present in the external region of the scale. Moreover, in the outermost region where the local oxygen pressure is sufficiently high, the Cu-rich particles are oxidized to form a double Fe-Cu oxide. Beneath the external scale there is an internal oxidation zone where iron oxide is mixed with copper metal. The corrosion feature of Fe-25% Cu(mass fraction) mentioned above is also present in the scales of the ternary Fe-15Cu-5Al alloy. The main difference between them is that the ternary alloy forms overgrown nodules, which is correlated directly with its corresponding binary Fe-Al alloy.

As summarized by PRESCOTT and GRAHAM[12], the oxidation behavior of Fe-Al alloys is influenced by temperature, oxygen pressure and aluminum content. For a protective behavior, these alloys must contain enough aluminum to develop an Fe-Al spinel layer beneath the outer layers of Fe_2O_3 and Fe_3O_4 . As the aluminum concentration increases, Al_2O_3 becomes stable in

preference to spinel and the scales consist of layers of Fe_2O_3 and Al_2O_3 . A further increase of the aluminum content produces a transition from internal to external formation of Al_2O_3 . However, Al_2O_3 scales are not always fully protective because the formation of flaws may allow the growth of bulky Fe-rich nodules. If the Al_2O_3 scale fails to repair itself, these nodules may coalesce and cover the whole surface, giving rise to catastrophic oxidation. Thus, for satisfactory oxidation resistance, Fe-Al alloys should contain sufficient aluminum to resist nodule formation. It has been proposed that for a protective behavior at least 8%Al (mass fraction) is necessary at 800 °C, while 10%–12%Al(mass fraction) is required at 600 °C[13]. At 1 000 °C, 5%Al(mass fraction) was reported to be sufficient to form an external protective scale. At around 800 °C, alloys with about 2.5%Al(mass fraction) can form alumina scales that, however, are not fully protective since they may permit the development of nodular growths of bulky iron oxide, associated with a large increase in the oxidation rate[12]. Oxidation of the ternary Fe-15Cu-5Al alloy produces external scales of iron oxides. Furthermore, a build-up of aluminum, Al_2O_3 or FeAl_2O_4 , is always located at the base of the nodule and bulky stratified scale. This kind of corrosion feature is very similar to the corresponding binary Fe-5Al alloy.

On the whole, the peculiar scale microstructure observed on ternary Fe-15Cu-5Al alloy is of the characteristic of that of the corresponding binary Fe-Cu and Fe-Al alloys. Furthermore, this situation will not change for the Fe-Cu-Al alloy with a much wider composition scope if 5% Al(mass fraction) is not enough to form continuous protective Al_2O_3 layer. The two-phase structure of Fe-15Cu-5Al, which derives from the corresponding binary Fe-Cu alloy, demands that the distribution of the copper islands in the internal oxidation zone follows closely that of the Cu-rich α phase in the original alloy, mainly as a consequence of the limited mutual solubility of the two components. Moreover, no Fe-depleted layer, which should consist of a layer of single-phase α solid solution, develops behind the region of internal oxidation, in spite of the great tendency for the preferential oxidation of iron. The corrosion behavior of these alloys is not only a consequence of the difference between the stabilities and rates of growth of the oxides of the two or three metals, but mostly of the two-phase microstructure of these materials (Fe-Cu and Fe-Cu-Al alloys). However, the corrosion feature of the ternary Fe-15Cu-5Al alloy is not directly correlated with that of the corresponding binary Cu-Al alloy, probably due to the relatively small amount of Cu in the whole alloy composition. Finally, for the Fe-15Cu-5Al alloy, aluminum depletion is observed in advance of the internal oxidation front due to the monovariant system of

the ternary Fe-15Cu-5Al alloy and the large solubility of aluminum in both phases[14–15], which is quite different from the invariant system of the binary Fe-Cu alloy. Therefore, aluminum can diffuse rather easily through the alloy, resulting in aluminum depletion in advance of the internal oxidation front.

4 Conclusions

1) Oxidation of the ternary Fe-15Cu-5Al alloy at 1 000 °C results in development of complex scales, with formation of overgrown nodules mainly composed of iron oxides. Beneath the external scale, iron oxide is mixed with copper metal. Furthermore, the base of the alloy-consumption region is characterized by a discontinuous aluminum-enriched layer.

2) The corrosion feature of the ternary Fe-15Cu-5Al alloy is partly associated with that of the corresponding binary Fe-Cu and Fe-Al alloys, but does not seem to be correlated with that of the binary Cu-Al alloy. The two-phase structures of Fe-15Cu-5Al alloy and the corresponding binary Fe-Cu alloy, demand that the distribution of the copper islands in the internal oxidation zone follows closely that of the Cu-rich α -phase in the original alloy.

3) No iron-depleted layer develops behind the region of internal oxidation. However, aluminum depletion is observed due to the monovariant system of the ternary Fe-15Cu-5Al alloy and the large solubility of aluminum in both phases.

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