GD-OES Characterization of Copper Enrichment at the Interface between Oxide Layer and Matrix in Iron-Copper Alloys

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GD-OES has been used for characterizing the behavior of copper with oxidation in Fe-Cu alloys. GD-OES depth profiles show that copper is enriched at the interface between the oxide layer and matrix, and copper is almost depleted in the oxide layer. Based on these results, the oxidation mechanism is discussed.

1. Introduction

Copper is a typical tramp element in steel, and the residual amount of copper in steel tends to increase with increasing use of scrap. On the other hand, copper is known to demonstrate characteristic behaviors such as the surface segregation in an iron-base alloy [1]. Furthermore, copper seems to give a detrimental influence on mechanical properties; especially the workability of the surface region of steel. This may be because copper is enriched on the surface of steel during oxidation at high temperatures. However, systematic data on enrichment behaviors of copper on the steel surface have not been obtained, since oxidation is accompanied by complicated phenomena such as spalling.

GD-OES is one of the powerful techniques for characterizing depth profiles in steel covered with a relatively thick layer, which enable us to investigate the enrichment behavior of constituent elements in a layered structure [2]. This prompts us to study enrichment behaviors of copper at the interface between an oxide layer and matrix in different samples by GD-OES. The purpose of this work is to investigate enrichment of copper with oxidation in iron-copper alloys, and to discuss the oxidation mechanism based on these results.

2. Experimental

Sheet samples of Fe-0.9%Cu and 1.6%Cu alloys, in which copper is in solution at high temperatures, were produced from high-purity iron and copper by vacuum melting, and hot rolled to 0.5mm in thickness. They were cut to 20mm square, and polished mechanically. They were annealed at 773 K and 873 K for different periods in air, to form an oxide layer on the surface.

GD-OES measurements were carried out to evaluate the depth profiles of samples covered with an oxide layer; in which the oxide thickness and enrichment of copper were focused on. The experimental technique and quantification method were described in a previous report [3]. The concentration of oxygen, iron and copper in depth profiles was estimated based on the effective optical emission yields obtained by reference materials. The sputter depth was calculated from the concentration and density in each layer. From this analysis, a GD-OES quantitative depth profile was obtained.

3. Results and Discussion

Figures 1 (a) and (b) show the quantitative depth profiles for Fe-0.9%Cu and Fe-1.6%Cu alloys which were oxidized at 773 K for 1200 s, respectively. Two oxide layers are formed on the surface, as observed in other iron base alloy systems [2]; the major oxide layer was Fe_3O_4, while a thin oxide layer covering the major oxide layer was Fe_2O_3, of which the oxygen concentration may be overestimated due to oxygen adsorption. Enrichment of copper is clearly found at the interface between the oxide layer and matrix, whereas copper is almost depleted in the oxide layer.

Figures 2 (a) and (b) show changes in the thickness of oxide layers formed on the surface at 773 and 873 K as a function of time in Fe-0.9%Cu and Fe-1.6%Cu alloys, respectively. The thickness of oxide layers increases with increasing oxidation time at each temperature, and does not seem to be significantly changed by the bulk copper concentration. Therefore, the copper enriched layer between the oxide layer and matrix does not act as a protective layer for the iron oxidation, while the chromium enriched layer between the oxide layer and matrix prevents the oxidation [3].

In order to understand the enrichment behavior of copper at the interface with oxidation, the amount of copper enriched at the interface should be estimated in the depth profiles. Practically, a copper enriched layer at the interface is observed as an enriched zone in the depth profile, mainly due to reduction of the depth resolution in GD-OES profiles and roughness of the interface. Therefore, the copper enriched zone may include information on the thickness and amount of enriched copper, as illustrated in Fig.3. If copper contained in oxide layers is assumed to move to the interface between the oxide layer and matrix, the thickness of copper, t_{Cu}, may be given by

$$t_{Cu} = t_{Fe\text{-}O} (c_{Cu}^{Fe} / c_{Cu}^{Ox/Fe}) \cdot n_{Fe/Fe\text{-}O} (\rho_{Fe} / \rho_{Cu}) , \quad (1)$$

where $t_{Fe\text{-}O}$ is the oxide thickness, c_{Cu}^{Fe} the copper concentration in an alloy, $c_{Cu}^{Ox/Fe}$ the copper concentration at the interface between the oxide layer and matrix, $n_{Fe/Fe\text{-}O}$ the fraction of iron in the oxide layer. ρ_{Fe} and ρ_{Cu} the density of iron and copper, respectively. For simplicity, if copper is enriched at the interface as to form pure copper, $c_{Cu}^{Ox/Fe} = 1$, the effective thickness of the copper layer can be calculated from Eq.(1), which should be proportional to the oxide thickness. The effective thickness obtained experimentally is plotted against the oxide thickness, as circles and triangles shown in Fig.4. It was clearly recognized that the thickness of copper enriched at the interface, t_{Cu}, increases with increasing thickness of the oxide layers, $t_{Fe\text{-}O}$, and bulk composition of copper, c_{Cu}^{Fe}. The linearity in these plots may prove that this model is satisfactory. On the other hand, the constants given in Eq.(1), which correspond to the slope shown in Fig.4, are in good agreement with the experimental results within a factor 1.1, suggesting the validity of this model.

The above results indicate that copper in an oxide layer formed on the surface of the iron-copper alloys is swept out to the interface between the oxide layer and matrix, and the copper enrichment at the interface does not significantly affect the oxide growth in steel under the present conditions. On the other hand, it has been shown that the surface segregation of copper takes place in iron-copper alloys at high temperatures over 700 K, and the copper segregation is not effective in preventing the initial oxidation at room temperature [1]. This fact may be consistent with the present results on high temperature oxidation, in spite of different conditions.

Also, it may be interesting to note that a considerable amount of copper is enriched at the interface, of which the effective thickness of enriched copper is nanometer order of magnitude in the present conditions. This thickness may be enough to influence the interfacial properties, such as the cohesion between the oxide layer and substrate or oxide spalling, although they have not been investigated yet. Thus, the copper layer enriched at the interface between oxide layers and substrate is considered to play an important role in controlling the surface properties of steel.

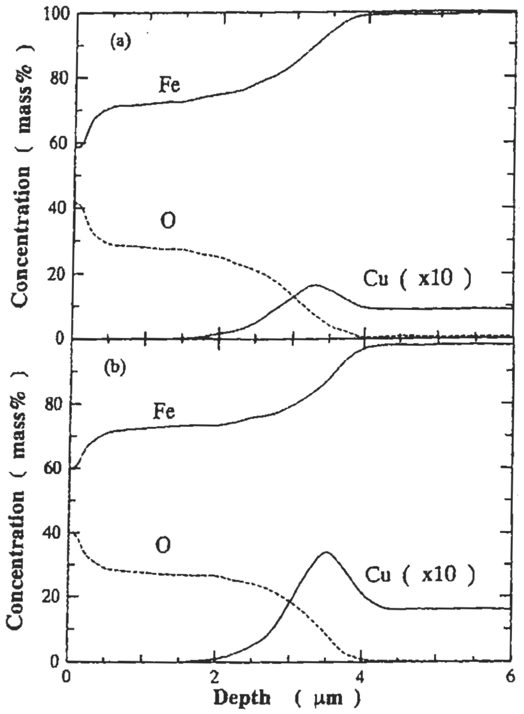

Figure 1. Quantitative depth profiles for (a) Fe-0.9%Cu and (b) Fe-1.6%Cu alloys which are oxidized at 773 K for 1200 s.

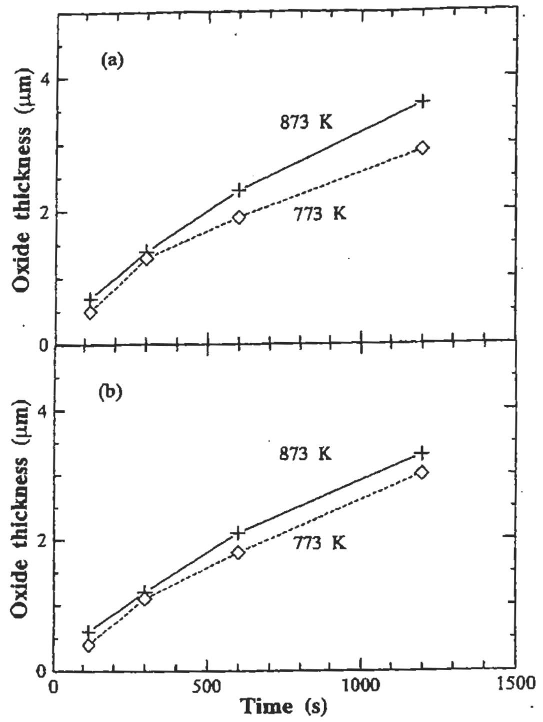

Figure 2. Thickness of oxide layers in (a) Fe-0.9%Cu and (b) Fe-1.6%Cu alloys at two temperatures against oxidation time.

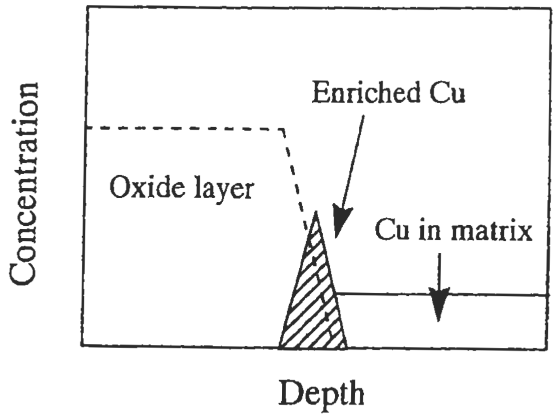

Figure 3. Illustration demonstrating the amount of copper enriched at the interface in depth profile.

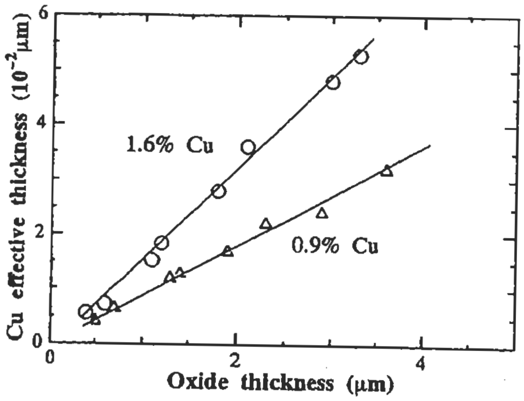

Figure 4. Effective thickness of copper at the interface versus oxide thickness of iron-copper alloys.

There are several surface analytical methods for characterizing surface layers; XPS, AES and SIMS. However, the present results clearly demonstrate that GD-OES is a convenient technique to characterize surface layers of micrometer order of magnitude thickness, as relatively thick oxide layers.

4. Concluding remarks

GD-OES was used for characterizing the behavior of copper with oxidation in Fe-Cu alloys. The main results are as follows:

(1) Copper is enriched at the interface between the oxide layer and matrix, and copper is almost depleted in the oxide layer.

(2) There are linear relationships between the effective thickness of copper enriched at the interface and the oxide thickness in these samples. This indicates that copper in the oxidized iron layer is swept out to the interface between the oxide layer and matrix.

5. References

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