Nickel Enrichment at the Interface between Oxide Layer and Matrix in Iron-Nickel Alloys

Shigeru Suzuki* and Katsuyuki Yanagihara

Advanced Technology Research Laboratories, Nippon Steel Corporation,
Futtsu, Chiba 292-8511, Japan

(Received November 19, 2001; accepted February 14, 2002)

GD-OES has been used for characterizing the behavior of nickel during oxidation in Fe-Ni alloys. GD-OES depth profiles show that nickel is enriched at the interface between the oxide layer and matrix, and nickel is almost depleted in the oxide layer. Based on the relationship between the amount of nickel and the oxide thickness, characteristic features of nickel in the oxidation of Fe-Ni alloys is discussed.

1. Introduction

Nickel is a typical alloying element in steel, and influences surface and interface phenomena in steel more or less. In particular, nickel seems to be enriched at the interface between an oxide layer and steel substrate during oxidation at high temperature, which influences mechanical properties [1,2]. However, systematic data on the enrichment behavior of nickel on the steel surface have not been obtained, since oxidation is accompanied by complicated phenomena such as spalling.

GD-OES is one of the very effective 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 [3,4]. Thus, we were prompted to study enrichment behaviors of nickel at the interface between an oxide layer and matrix in different samples by using GD-OES. The purpose of this paper is to investigate enrichment of nickel during oxidation in iron-nickel alloys, and to discuss the oxidation mechanism based on these results.

2. Experimental

Sheet samples of Fe-4.9%Ni and 9.8%Ni alloys, in which nickel is dissolved, were produced from high-purity iron and nickel by vacuum melting, and hot rolled to 0.5mm in thickness. These sample were cut to 20mm square, and polished mechanically. They were then 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 nickel were focused on. The experimental technique and quantification method were described in a report [3]. The concentration of oxygen, iron and nickel 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 X-ray diffraction patterns for Fe-4.9%Ni and Fe-9.8%Ni alloys which were oxidized at 773 K for 1200 s, respectively. X-ray diffraction measurements were carried out using Cu Kα radiation. These results show that the substrate of these two samples is ferritic iron, and it is similarly covered with an iron oxide, mainly Fe_3O_4.

Figures 2 (a) and (b) show the quantitative depth profiles for Fe-4.9%Ni and Fe-9.8%Ni 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 [3]; 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 nickel is clearly found at the interface between the oxide layer and matrix, whereas nickel is almost depleted in the oxide layer.

Figures 3 (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-4.9%Ni and 9.8%Ni alloys, respectively. The thickness of oxide layers increases upon oxidation time at each temperature being increased, and does not seem to be significantly changed by the bulk nickel concentration. Therefore, the nickel enriched layer between the oxide layer and matrix does not act as a protective layer for the iron oxidation, while it is known that some alloying elements such as chromium and silicon enriched between the oxide layer and matrix prevent the oxidation [2].

In order to evaluate the enrichment of nickel at the interface between the oxide layer and matrix, the amount of nickel enriched at the interface should be estimated in the depth profiles. Practically, a nickel-enriched layer at the interface is observed as a broad zone in the depth profile due to the low depth resolution in GD-OES profiles and the roughness of the interface. Nevertheless, the nickel-enriched zone may include information on the amount of enriched nickel, as illustrated in Fig.4 [5]. If nickel contained in oxide layers is assumed to move to the interface between the oxide layer and matrix by oxidation, the thickness of nickel, t_{Ni}, may be expressed by

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

where $t_{Fe\text{-}O}$ is the oxide thickness, c_{Ni}^{Fe} the nickel concentration in an alloy, $c_{Ni}^{Ox/Fe}$ the nickel concentration at the interface between the oxide layer and matrix, and $n_{Fe/Fe\text{-}O}$ the fraction of iron in the oxide layer. ρ_{Fe} and ρ_{Ni} are the density of iron and nickel, respectively. For simplicity, nickel may be assumed to be enriched at the interface so as to form pure nickel, $c_{Ni}^{Ox/Fe} = 1$, although nickel is practically dissolved in iron. Then, the effective thickness of the nickel layer can be calculated from Eq.(1), which should be proportional to the oxide thickness. The effective thickness estimated from depth profiles is plotted against the oxide thickness, as marks shown in Fig.5. These plots clearly indicate that the effective thickness of nickel enriched at the interface, t_{Ni}, increases upon the thickness of the oxide layers, $t_{Fe\text{-}O}$, increasing, and the bulk composition of nickel, c_{Ni}^{Fe}, increasing. The linearity in these plots proves that this model is satisfactory. In addition, the constants given in Eq.(1), which correspond to the slope shown in Fig.5, are in good agreement with the experimental results within a factor 1.1, suggesting the validity of this model.

The above results suggest that nickel in an oxide layer formed on the surface of the iron-nickel alloys is swept out to the interface between the oxide layer and matrix, and the nickel 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 alloying elements may take place in iron-based alloys at high temperatures over 700 K, and the segregation is not always effective in preventing the initial oxidation at room temperature [6]. 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 nickel is enriched at the interface, of which the effective thickness of enriched nickel is a sub-micrometer 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 the substrate, and the interaction with the other elements.

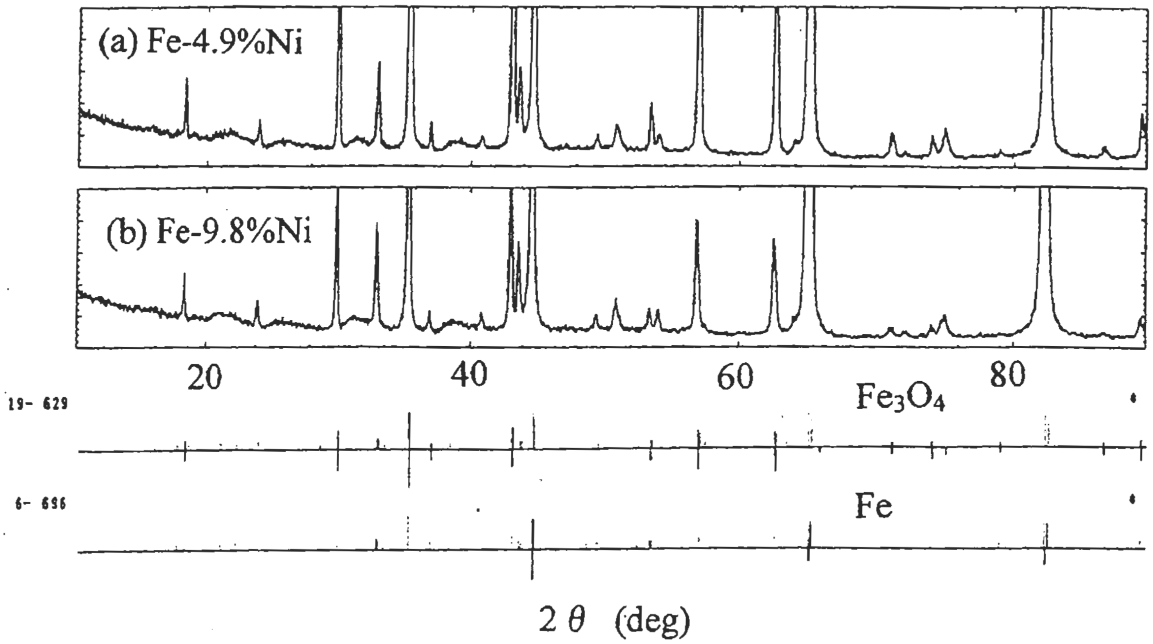

Fig.1 X-ray diffraction patterns from oxidized (a) Fe-4.9%Ni and (b) Fe-9.8%Ni alloys.

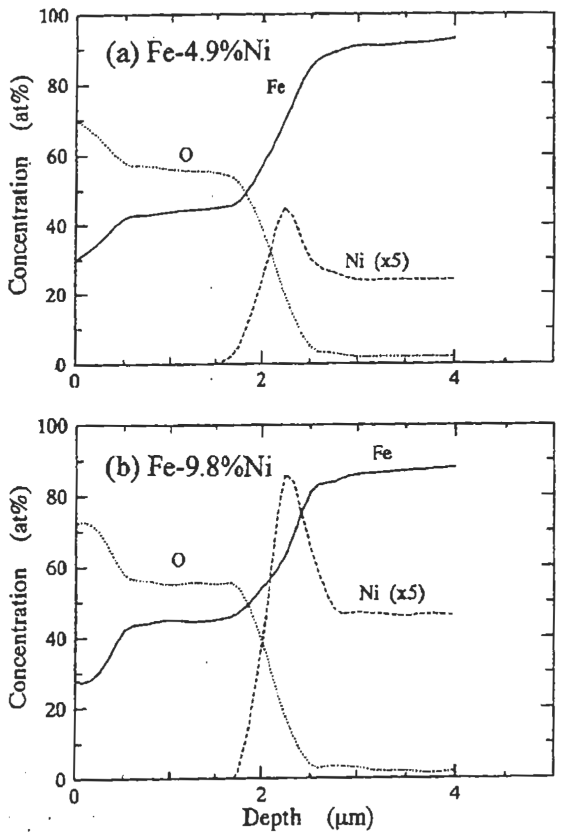

Figure 2. Quantitative depth profiles for (a) Fe-4.9%Ni and (b) Fe-9.8%Ni alloys which are oxidized at 773 K for 1200 s.

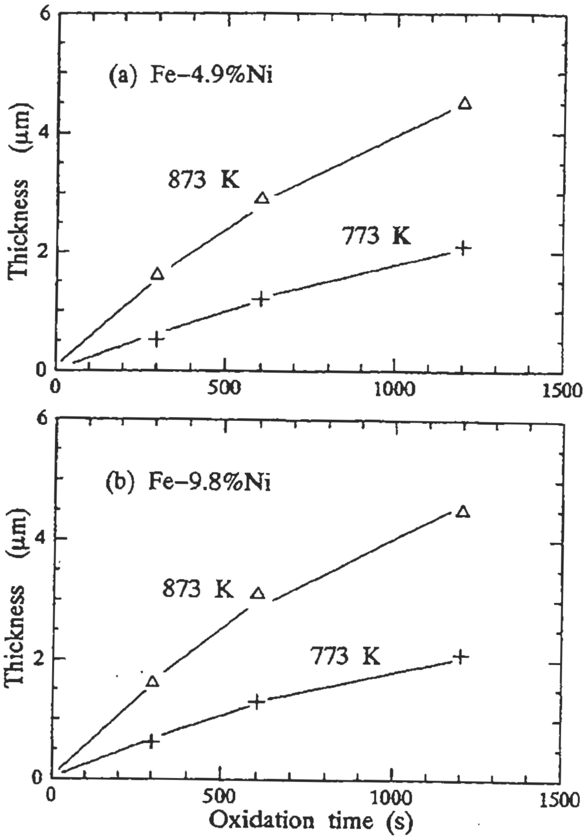

Figure 3. Thickness of oxide layers in (a) Fe-4.9%Ni and (b) Fe-9.8%Ni alloys formed at 773K and 873K versus oxidation time.

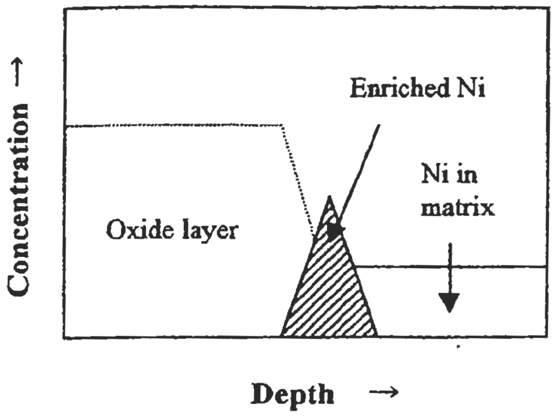

Figure 4. Illustration demonstrating the amount of nickel enriched at the interface in depth profile.

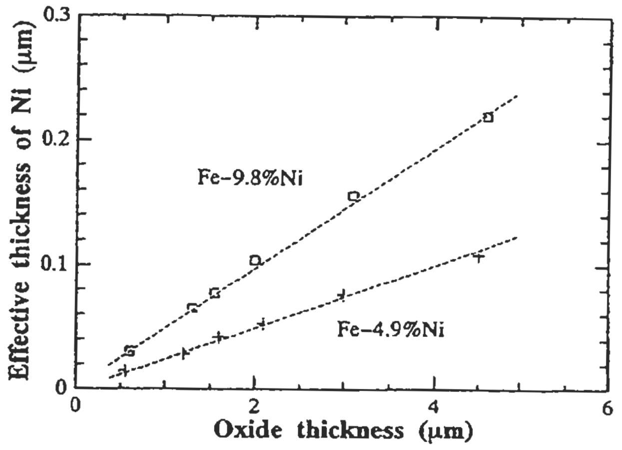

Figure 5. Effective thickness of nickel at the interface versus oxide thickness of iron-nickel alloys.

Thus, the nickel layer enriched at the interface between oxide layers and substrate is considered to play an important role in controlling the oxidation behavior of iron and steel. In addition, the present results clearly demonstrate that GD-OES is a convenient technique to quantitatively characterize surface layers of micrometer order of magnitude thickness, such as oxide layers.

4. Concluding remarks

GD-OES was used for characterizing the behavior of nickel during oxidation in Fe-Ni alloys. The main results are as follows:

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

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

5. References

[1] S. Akamatsu, K. Koyama, and O. Akisue, CAMP.ISIJ, **7**, 1712(1994).

[2] S. Suzuki, M. Wake, M. Abe and Y. Waseda, ISIJ International **36**, 700 (1996).

[3] Edited by R. Payling, D. G. Jones, and A. Bengtson, "Glow Discharge Optical Emission Spectrometry", John Wiley & Sons, p.575 (1997).

[4] S. Suzuki, K. Mizuno and K. Suzuki, Surf. Interface Anal., **22**, 134 (1992).

[5] S. Suzuki and Y. Takagi, J. Surf. Anal. **36**, 915 (1997).

[6] S. Suzuki and Y. Waseda, Scripta Mater., **36**, 915 (1997).

*present address
Institute of Multidisciplinary Research for Advanced Materials, Tohoku University
2-1-1 Katahira, Aoba-ku, Sendai, Miyagi 980-8577, Japan
ssuzuki@tagen.tohoku,ac.jp