High Temperature Oxidation and Sulfidation of Ni-15at.%W Coatings

Chanwou Kim[a], Teayoul You[a], Yuriy Shapovalov[a], Jaehwang Ko[a], Dongbok Lee[a*],
Kyuhwan Lee[b], Doyon Chang[b], Dongsoo Kim[b], Sikchol Kwon[b]

[a]Center for Advanced Plasma Surface Technology, Sungkyunkwan University,
Suwon 440-746, Korea
[b]Surface Engineering Department, Korea Institute of Machinery and Materials(KIMM),
Changwon 641-010, Korea

Abstract

Ni-15at.%W coatings with film thicknesses of 20-40 μm were electroplated on a steel substrate, and their oxidation behavior was investigated at 700 and 800°C in air. For comparison, a pure Ni coating and a bulk Ni were also oxidized. The Ni-15at.%W coating displayed the worst oxidation resistance, due to the formation of less-protective NiO, Fe_2O_3, $NiFe_2O_4$ and $NiWO_4$. The corrosion behavior Ni-15at.%W coatings electroplated on a steel substrate was similarly investigated at 700 and 800°C in the Ar-1%SO_2 atmosphere. For comparison, the uncoated steel substrate was also corrosion-tested in the Ar-1%SO_2 atmosphere. Severe scale spallation and the internal corrosion of the steel that occurred in the uncoated substrate were not observed in the coated specimen. However, it seemed that the Ni-15at.%W coating cannot be a potential candidate as a sulfidation-resistant coating, due to the formation of less-protective NiO, NiS, WO_3 and $NiWO_4$.

Keywords : Nickel, Tungsten, Coating, Corrosion, Sulfidation, Oxidation, Sulfur dioxide

1. Introduction

Electrodeposited hard Cr is widely used as wear- and corrosion-resistant coatings due to its high hardness, corrosion resistance and decorative color. However, the solution for Cr electrodeposition is based on environmentally hazardous Cr^{+6} ions, so that the Ni-W electrodeposits were developed as alternatives[1-5]. They have high hardness, good wear resistance, smooth surface, good corrosion resistance and thermal stability.

In a number of modern technologies such as high-temperature gas turbines, petrochemical units, and coal gasification and liquefaction systems, structural components are exposed to oxygen- and sulfur-containing atmospheres. Hence, it is important to protect the components from oxidation and sulfidation. For this, the oxidation/sulfidation behavior of Ni-W coatings was studied in this study. Ni-W coatings may be oxidation- and sulfidation-resistant, because Ni can form NiO in the oxygen atmosphere and W can form W-sulfides

(WS$_2$) in the sulfur atmosphere. Among the metallic elements, only W, Mo and Nb have sulfidation-resistance because of their very low deviations from stoichiometry[6,7]. Conventional oxidation-resistant elements such as Cr, Al and Si suffer from catastrophic corrosion in the S-containing atmosphere, because of the rapid diffusion of ions through their highly nonstoichiometric sulfide scales. Until now, no satisfactory alloy- or coating-systems that are resistant to both oxidation and sulfidation were developed.

In spite of numerous studies on Ni-W coatings[1-5], the air-oxidation behavior of Ni-W coatings was not adequately studied before. Also, no attention has been paid to the sulfidation behavior of Ni-W coatings. The aim of this study is to characterize the high-temperature corrosion behavior of Ni-W coatings in both air and the SO_2 atmosphere in an attempt to utilize them as protective coatings.

2. Experimental

Ni-15at.%W coatings were electrodeposited from

*Corresponding author. E-mail : dlee@yurim.skku.ac.kr

$NiSO_4 \cdot 6H_2O$ (Ni source) and $Na_2WO_4 \cdot 2H_2O$ (W source) solution on both sides of the steel plate (STD 61; $2 \times 0.5 \times 0.3$ cm^3 in size) to about (20~40) μm-thickness. The electrodepositing procedure is described elsewhere in detail[8]. The composition of the coating was determined by electron probe microanalyzer (EPMA).

The oxidation and sulfidation tests on Ni-15at.%W coated steel specimens were done in air and in the Ar-1%SO$_2$ atmosphere, respectively, at 700 and 800°C.
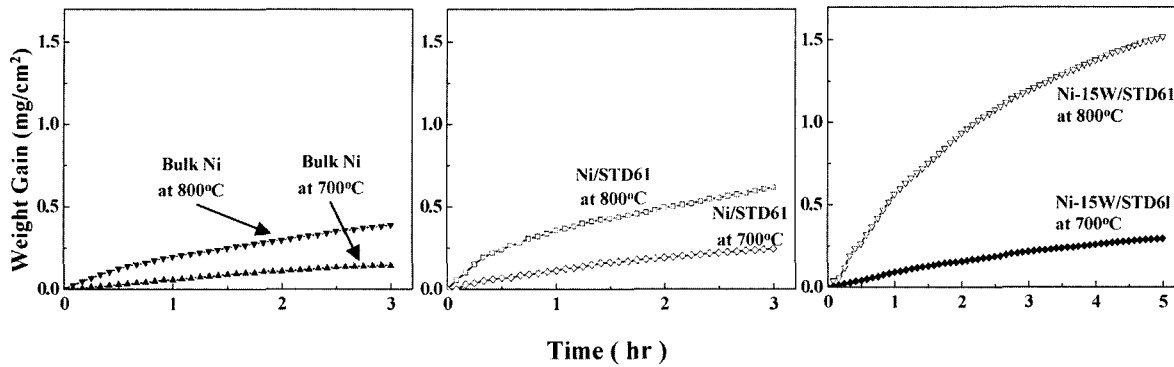

Fig. 1. Weight gain vs. oxidation time curves for the Ni-15at.%W coating electroplated on steel, the Ni coating electroplated on steel and the bulk Ni plate at 700 and 800°C in air.
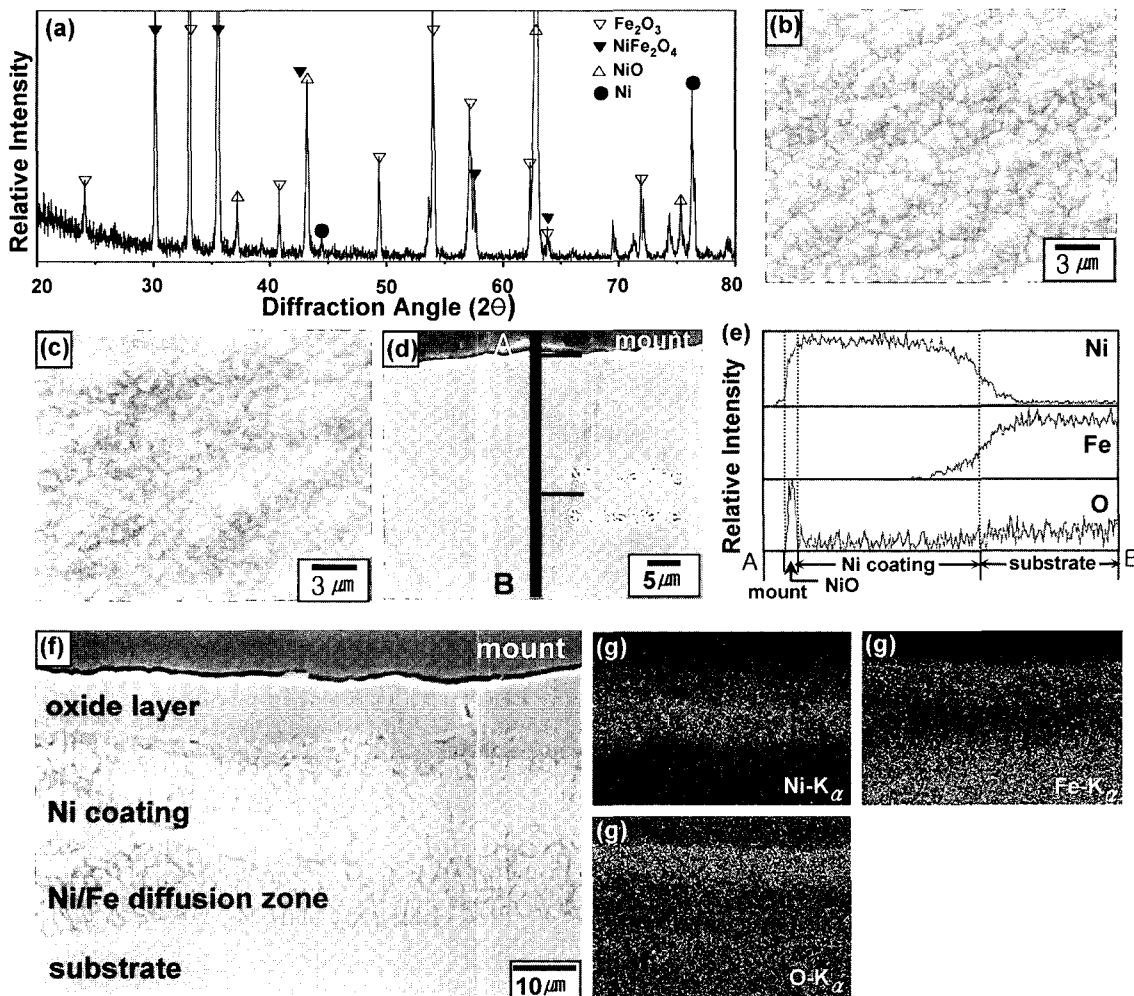

Fig. 2. Pure Ni coating electroplated on steel. (a) XRD pattern after oxidation at 800°C for 30 hr, (b) SEM top view after oxidation at 700°C for 5 hr, (c) SEM top view before oxidation, (d) cross-sectional SEM image after oxidation at 700°C for 2 hr, (e) EDS line profile of (d), (f) cross-sectional SEM image after oxidation at 800°C for 5 hr, (g) EDS elemental mappings of (f).

Weight gains during oxidation were measured continuously using a thermogravimetric analyzer (TGA). To investigate the oxidized- and sulfidized-samples, a scanning electron microscope (SEM) equipped with an energy dispersive spectroscope (EDS), an X-ray diffractometer (XRD with Cu-K_α radiation) and a glancing-angle X-ray diffractometer (GAXRD with Cu-K_α radiation) with 4° incident angle were utilized.

3. Results and Discussion

Fig. 1 shows the oxidation kinetic curves of the Ni-15W coated steel specimen. They were obtained from the TGA tests performed at 700 and 800°C in air. For comparison, both the bulk Ni plates (99.995% pure) and the pure Ni coating were also tested. The latter coating was obtained by electroplating using the Watts nickel solution (NiSO$_4$·6H$_2$O, NiCl$_2$·6H$_2$O, H$_3$BO$_3$)[9] on both sides of the steel plate (STD 61; 2 × 0.5 × 0.3 cm^3 in size). All the specimens were oxidized nearly parabolically. All the weight gains are small at 700°C. Particularly for the Ni-15W coated steel specimen, the sharp increment in the oxidation rate at 800°C is noticeable. Interestingly, the oxidation resistance decreased in the order of bulk Ni, the Ni coating and Ni-15W coating. The worst oxidation resistance of the Ni-15W coating should be attributed to the presence of W, whereas the decreased oxidation resistance of the Ni coating when compared to the bulk Ni to the effect of the substrate. On the other hand, on the bulk Ni, a pure NiO scale should form, whose growth is mainly controlled by the outward diffusion of Ni^{2+} ions via cation vacancies[10]. To find the reasons for the observed oxidation rates of the tested specimens, their oxide scales were analyzed in detail as follows.

Fig. 2(a) shows the XRD pattern of the pure Ni coating after oxidation at 800°C for 30 hr. Since most of the Ni coating was oxidized, only a weak Ni diffraction peak is seen. Also, rather strong diffraction patterns of NiO, Fe$_2$O$_3$ and NiFe$_2$O$_4$ are seen. The formation of the Fe-containing oxides indicates that the outward diffusion of Fe^{+3} ions through the Ni coating occurred. Since the oxidation resistance of Fe is poorer than Ni, the pure Ni coating displayed the worse oxidation resistance than the bulk Ni (Fig. 1). The outwardly transported Fe^{+3} ions flattened the surface of the oxidized Ni coating, as shown in Fig. 2(b). For comparison, the surface of the unoxidized Ni coating is shown in Fig. 2(c), which displays numerous, fine electrodeposits. Because of the outward

diffusion of Fe^{+3} ions into the coating, the interface between the coating and the substrate became ambiguous after oxidation at 700°C for 2 hr, as shown in Fig. 2(d). The corresponding EDS line profiles are shown in Fig. 2(e). Here, a thin NiO layer is seen. Oxidation at 800°C for 5 hr resulted in the formation of a thick oxide layer, a partially oxidized Ni coating and a Ni/ Fe interdiffusion zone above the substrate (Fig. 2(f) and (g)). The upper part of the oxide layer is rich in Fe, while the lower part of the oxide layer is rich in Ni. Clearly, Fe has diffused up to the outermost surface of the coating, resulting in the formation of Fe$_2$O$_3$ and NiFe$_2$O$_4$ over the retained Ni coating. According to the concentration gradient, Ni as well as Fe counter-diffused to make the Ni/Fe interdiffusion or reaction zone.

Fig. 3(a) shows the XRD pattern of the Ni-15W coating after oxidation at 700°C for 6 hr. The oxides formed are NiO and NiWO$_4$. Tungsten, which has an extremely poor oxidation resistance at high temperatures, was readily oxidized to WO$_3$ to combine with NiO, resulting in the formation of NiWO$_4$. As a diffraction pattern of the coating, a Ni peak is seen, because Ni-15W exists as the W-supersaturated Ni phase[2]. The matrix peaks, (Fe-Cr), are also seen. Fig. 3(b) and (c) show the XRD patterns of the Ni-15W coating after oxidation at 700°C for 50 hr. The conventional XRD pattern shown in Fig. 3(b) indicates that the oxidation products are NiO, NiWO$_4$, Fe$_2$O$_3$ and NiFe$_2$O$_4$. The NiWO$_4$ and NiFe$_2$O$_4$ spinels, along with NiO and Fe$_2$O$_3$, are not oxidation resistant. The formation of Fe$_2$O$_3$ and NiFe$_2$O$_4$ again indicates that Fe^{+3} ions diffuse outward through the Ni-W coating, as they do in the pure Ni coating. The GAXRD pattern shown in Fig. 3(c) indicates that the oxidation products formed on the surface are NiO, Fe$_2$O$_3$ and NiFe$_2$O$_4$. Hence, it can be seen that NiWO$_4$ forms underneath those three oxides. The cross-sectional SEM image shown in Fig. 3(d) indicates a densely-looking outer oxide layer (layer I), an array of voids at the top, scattered voids at the upper part and the zigzag cracks at the bottom of the original coating (layer II), and the steel substrate. The corresponding EDS line profiles shown in Fig. 3(e) indicates that the layer I is rich in Ni, Fe and O. This is the reason for the detection of NiO, Fe$_2$O$_3$ and NiFe$_2$O$_4$ in Fig. 3(c). After oxidation at 700°C for 50 hr, the original coating was completely oxidized. W was segregated in the layer II, which is the reason for the absence of NiWO$_4$ in Fig. 3(c). Between Ni and W, Ni diffused outward more easily than W, due to the different diffusion rate.
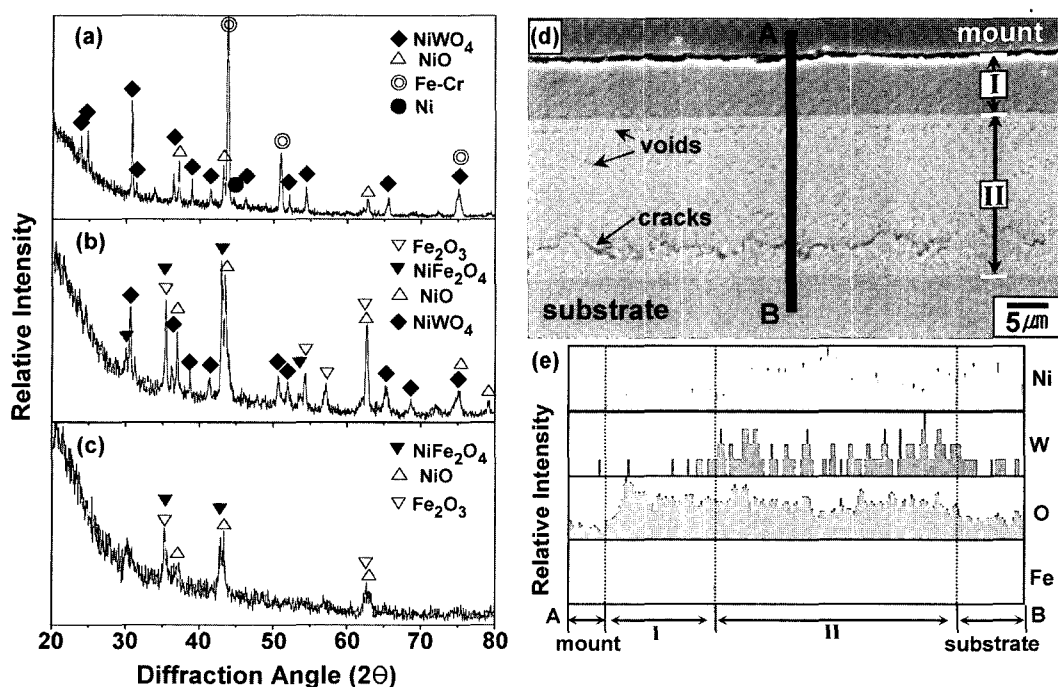
Fig. 3. Ni-15at.%W coating electroplated on steel oxidation at 700°C in air. (a) conventional XRD pattern (for 6 hr), (b) conventional XRD pattern (for 50 hr), (c) GAXRD pattern with a 4° incident angle (for 50 hr), (d) cross-sectional SEM image (for 50 hr), (e) EDS line profile of (d).
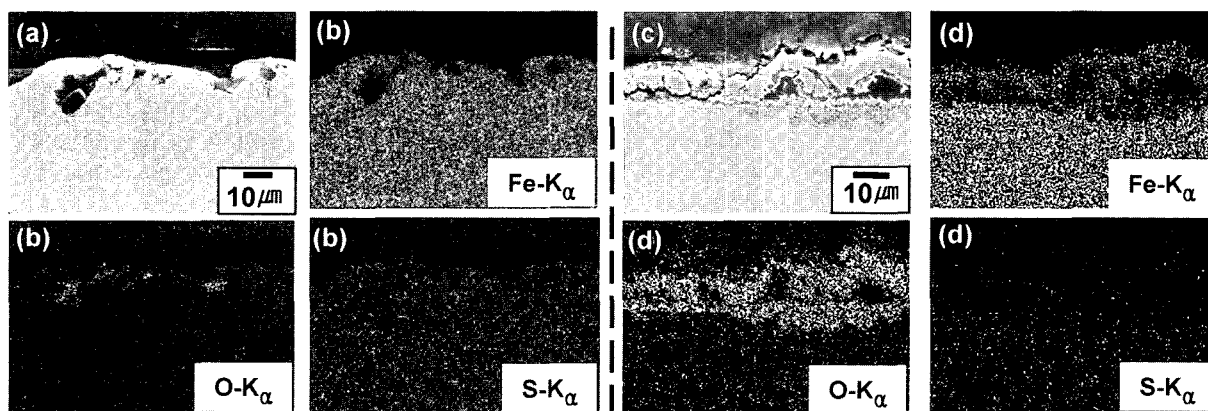

Fig. 4. STD 61 steel plate after corrosion in Ar-1% SO_2 atmosphere for 5 hr. (a) cross-sectional SEM image at 700°C, (b) EDS mappings of Fe, O and S shown in (a), (c) cross-sectional SEM image at 800°C, (d) EDS mappings of Fe, O and S shown in (c).

Unlike in the case of the Ni coating, the interface between the coating and the substrate is rather distinct, due to the presence of W in the Ni-W coating. In Fig. 1, it was shown that the oxidation resistance of the Ni-15W coating was worse than that of the pure Ni coating. This should be mainly attributed to W, which oxidizes to WO_3.

Fig. 4(a) and (b) show the cross-sectional SEM image and the corresponding EDS mappings of the STD61 steel, respectively, which was corroded in the Ar-1%SO_2 atmosphere at 700°C for 5 hr. $SO_2(g)$ dissociates into $S_2(g)$ and $O_2(g)$, making the sample

be exposed to both the oxidation and sulfidation atmosphere. The scale formed was completely lost due to serious spallation. Internal oxides were embedded in the matrix. Fig. 4(c) and (d) show the cross-sectional SEM image and the corresponding EDS mappings of the STD61 steel, respectively, after corrosion at 800°C for 5 hr. Only the scale formed next to the matrix was retained. It consists primarily of highly fragile iron oxides. There was also an indication of the internal oxidation in the matrix in Fig. 4(c) and (d). Although there was little indication of sulfidation, serious corrosion occurred
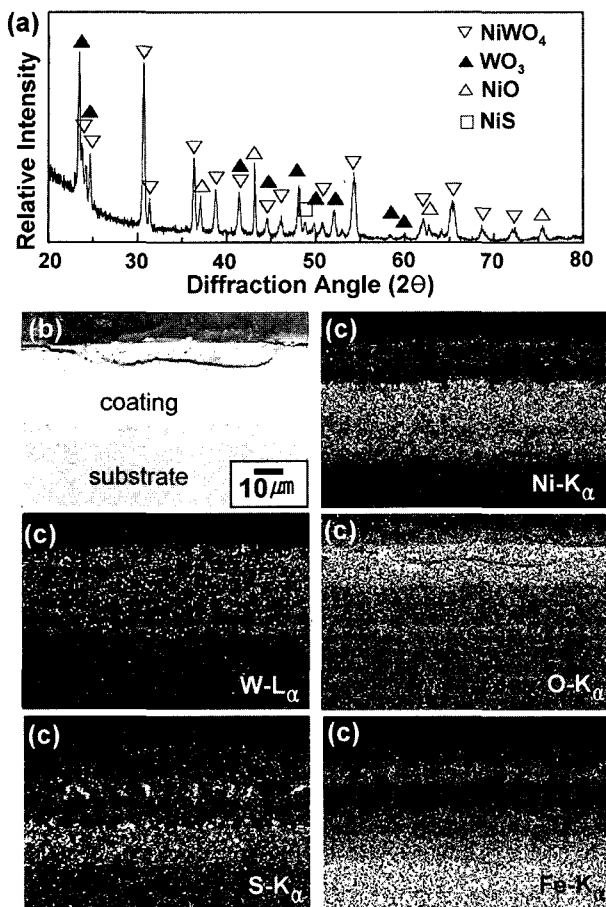
Fig. 5. Ni-15at.%W coating electroplated on steel after corrosion at 700°C in Ar-1% SO₂ atmosphere for 5 hr. (a) XRD pattern, (b) cross-sectional SEM image, (c) EDS mappings of Ni, W, Fe, O and S shown in (b).
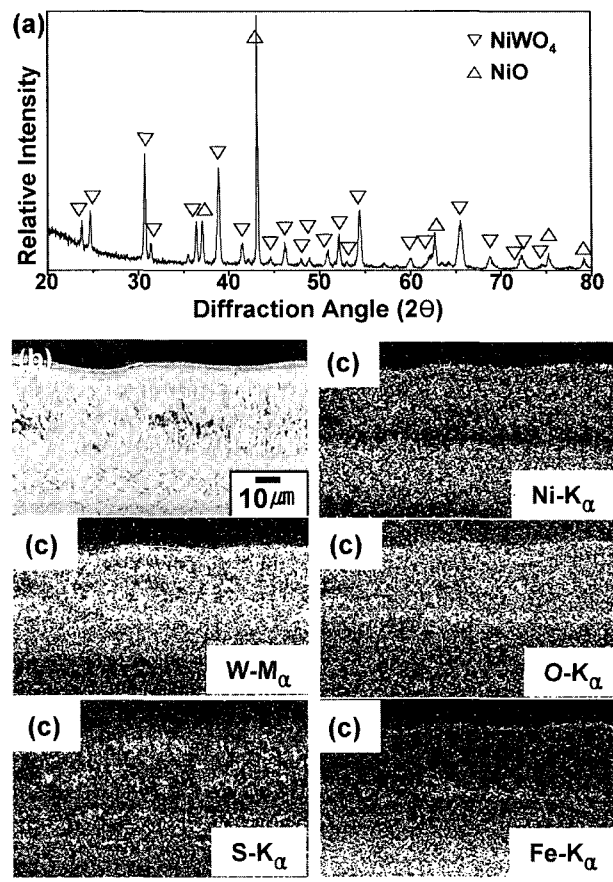

Fig. 6. Ni-15at.%W coating electroplated on steel after corrosion at 800°C in Ar-1% SO₂ atmosphere for 5 hr. (a) XRD pattern, (b) cross-sectional SEM image, (c) EDS mappings of Ni, W, Fe, O and S shown in (b).

in the steel matrix indicates that the S-atmosphere affects corrosion significantly.

Fig. 5(a) shows the XRD pattern of the Ni-15W coating after corrosion in the Ar-1%SO₂ atmosphere at 700°C for 5 hr. The corrosion products are mainly WO_3 and $NiWO_4$, together with some NiO and NiS. No W-sulfides were however detected, owing to their small amount. This indicates that the oxidation potential was largely higher than the sulfidation potential. The stress that was developed mainly by oxidation caused the coating to be cracked. From Fig. 5(b) and (c), it is seen that the upper part of the scale is rich in W, Fe and O, whereas the lower part of the scale is rich in Ni, being consistent with Fig. 5(a). Sulfur diffused inward through the oxide scale, and Fe diffused outward toward the coating, according to the concentration gradient. Especially, a noticeable amount of Fe diffused up to the outermost surface, as Fe did in the oxidation tests. However, no iron-oxides were detected in Fig.

5(a) owing to their small amount.

Fig. 6(a) shows the XRD pattern of the Ni-15W coating after corrosion in the Ar-1%SO₂ atmosphere at 800°C for 5 hr. Only $NiWO_4$ and NiO were detected. Most of WO_3 formed was reacted with NiO to become $NiWO_4$. NiS, which were detected in Fig. 5(a), was not seen, because the amount of NiS was small. Fig. 6(b) and (c) show the corresponding SEM/EDS analytical results. The W map denotes the original coating. When compared to Fig. 5(b) and (c), the following phenomena can be seen. Due to the progressed corrosion; (1) more Ni diffused inward into the substrate, and outward toward the surface, (2) oxygen penetrated deeply into the coating, (3) there is more S, and (4) more Fe diffused up to the outermost surface.

4. Conclusion

The Ni-15W coating oxidized faster than the bulk Ni and the Ni coating, because W formed nonprotective

WO_3 and the coating was electroplated on the Fe substrate whose oxidation rate was faster than Ni. The non-protective oxide scale formed had some voids and cracks. The major oxidation products were NiO, $NiWO_4$, Fe_2O_3 and $NiFe_2O_4$. The $NiWO_4$ and $NiFe_2O_4$ spinels, along with NiO and Fe_2O_3, were not oxidation resistant. A noticeable amount of Fe ions diffused outward in both the Ni-W and pure Ni coatings, according to the concentration gradients.

In the SO_2 atmosphere, the Ni-15W coating corroded seriously due to S. Although the coating protected the steel substrate under the given corrosion condition, it can not be a protective coating because of the formation of less protective WO_3 and $NiWO_4$, together with some NiO and NiS. Most of the scale consisted mainly of not sulfides but oxides. A noticeable amount of Fe ions again diffused outward in the Ni-15W coatings.

The initial scheme of this study was to form the semi-protective NiO in the O-atmosphere and to form the protective W-sulfides in the S-atmosphere on the Ni-W coating. However, this was not achieved. One possible attempt to overcome this failure may be adding oxidation-protective elements such as Si, Al or Cr and increasing the amount of W in the coating.

Acknowledgments

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