Wear 368-369 (2016) 344–349

Contents lists available at ScienceDirect

Wear

journal homepage: www.elsevier.com/locate/wear

Effect of oxidation film on the fretting wear behavior of Alloy 690 steam generator tube mated with SUS 409

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ARTICLE INFO

Article history:
Received 1 July 2016
Received in revised form
11 October 2016
Accepted 13 October 2016
Available online 15 October 2016

Keywords:
Alloy 690
Oxidization
Fretting wear

ABSTRACT

Effect of formation of oxidation film on the wear behavior of Alloy 690 steam generator (SG) tubes for nuclear power plants was investigated. Alloy 690 SG tubes are normally oxidized during operation due to the high temperature of the pressurized water. Based on the previous tribology research for metallic materials, we reasoned that the oxidation film can have an important effect on the wear behavior of the Alloy 690 SG tubes. Therefore, in this study, Alloy 690, oxidized in an autoclave under secondary water conditions, was used for wear test. The result of the wear test showed that as the oxidation treatment time increased, the thickness of oxidation film increased and the wear resistance of Alloy 690 increased.

1. Introduction

Alloy 690 is widely used for steam generator (SG) tubes in nuclear power plants. Because of the high temperature (270–330 °C) and pressure (2–3 ksi) of the secondary water in SGs, oxidation films form on the surface of Alloy 690. During the initial stage of oxidation, Cr oxidizes preferentially by reacting with dissolved oxygen to form Cr_2O_3 on the inner layer. Additionally, Fe and Ni can selectively dissolve into the surface and combine with anions to form oxides or hydroxides. Then, $NiFe_2O_4$ spinel forms on the outer layer during the later stage by reactions between the oxides, hydroxides, and anions [1].

According to previous studies [2–5], in some cases, oxidation films can enhance the wear resistance. Oxidation films prevent metal-to-metal contact and hinder material transfer which causes the weight loss of materials [3]. In other works [2,4,5], oxidation films have been shown to increase the resistance to surface deformation due to their high hardness. Alternatively, oxide films can also decrease the wear resistance because they can accelerate the delamination wear [6]. Therefore, oxidation films can have both positive and negative effects on the wear behavior of metallic materials. However, the effect of oxidation films on the wear resistance of Alloy 690 has not yet been studied.

As a first step to investigate the effect of formation of oxidation film on the Alloy 690 during operation of SG, we conducted the wear tests at room temperature for pre-oxidized Alloy 690 to verify whether the structure and thickness of oxidation film affect the wear behavior or not. The morphology, structure and thickness of the oxidation film were confirmed by using scanning electron microscopy (SEM), Auger electron spectroscopy (AES) and Raman spectroscopy. Wear tests were conducted in the amplitude range from 25 to 300 μm at a frequency of 30 Hz.

2. Experimental procedure

A commercialized Alloy 690TT tube was used for the wear test. SUS 409SS, which is generally used for anti-vibration structures in steam generators, was used as the mating material. The chemical compositions of Alloy 690TT and SUS 409SS were confirmed by optical emission spectroscopy and are presented in Table 1. The oxidation treatment was performed at a high temperature in a static autoclave made of SUS 316. The samples were exposed to 320 °C for 50 to 2000 h under a hydraulic pressure of 2.5 ksi. After the oxidation treatment, the morphology of the oxidation film was observed with SEM. Raman analysis was done on the film with a laser wavelength of 514 nm for an acquisition time of 60 s in an Ar gas atmosphere. Auger electron spectroscopy (AES) analysis was conducted on the oxidized surface to measure the film thickness with an Ar sputter depth rate of 1.9 nm/min. The thickness was measured by identifying the depth where the oxygen profile reached zero. The wear test was conducted on the oxidized surface mated with SUS 409 by using a modified fretting wear tester, as

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http://dx.doi.org/10.1016/j.wear.2016.10.009
0043-1648/

Table 1
Chemical compositions of Alloy 690TT and SUS 409SS.

Specimen	Element (wt%)								
	Ni	Cr	Fe	Co	C	Si	Mn	Ti	S
Alloy 690TT	bal.	28.95	10.85	0.030	0.020	0.18	0.09	0.236	0.002
SUS 409SS	0.28	11.9	Bal.	–	0.016	0.622	0.192	0.135	0.026

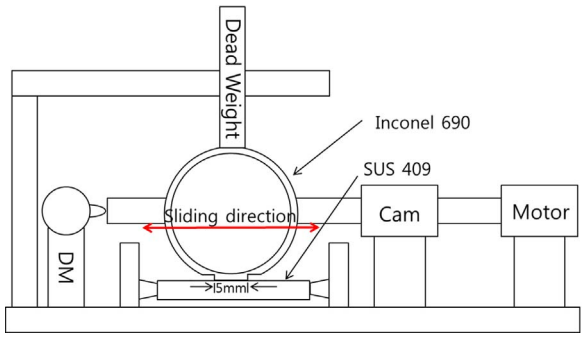

Fig. 1. Schematic of the custom-designed fretting wear test apparatus.

shown in Fig. 1. In case that the contact area is changed during wear test, not only oxidation film but also the changes in applied stress affect the wear behavior. Therefore, the tube surface was machined into a rectangular shape (5 mm × 20 mm) to make the contact stress constant during the test. The wear test was conducted with amplitudes from 25 to 300 μm which is a maximum value of fretting wear amplitude in general [7]. The testing normal load of 20 N was selected far below the peak force between the tube and support plate (90 N, [8]) to maximize the effect of oxidation film on the wear behavior. According to the previous research [9], the effect of frequency on the wear mode and wear coefficient of Alloy 690 was negligible. Therefore, the testing frequency was fixed to 30 Hz which is a similar value to the minimum frequency of steam generator tube (33 Hz [10]). More than three tests were performed for each set of conditions to obtain reliable data. The relative deviation in the amount of wear loss between tests was about ±9%. The worn surface was observed and the local composition of the worn surface was analyzed using SEM and energy dispersive spectroscopy (EDS).

3. Results and discussion

Fig. 2 shows the surface morphology of Alloy 690 after the oxidation treatment at 320 °C under a hydraulic pressure of 2.5 ksi. Before the oxidation treatment, a relatively rough surface was observed, as seen in Fig. 2(a). At the early stage of the oxidation treatment, as shown in Fig. 2(b), Alloy 690 was oxidized uniformly on the surface and the roughness was decreased. After 100 h of the oxidation treatment, discrete polyhedral-shaped oxide particles were formed locally; these particles are known as spinel oxide [1]. The area of the spinel oxide increased with increasing oxidation treatment time, as shown in Fig. 2(c)–(g).

To confirm the phases present in the oxidation film, Raman analysis was conducted. The Raman spectra in Fig. 3 show that after 50 h of the oxidation treatment, the peak at 587 cm^{-1} was dominant; this peak reveals the presence of Cr_2O_3 [1,11]. As the oxidation treatment time increased to 2000 h, the peak at 587 cm^{-1} became less dominant and the peak at 701 cm^{-1}, which reveals that the presence of $NiFe_2O_4$ [1,11] became more dominant. This confirms that, at the early stage of the oxidation treatment, Cr_2O_3 preferentially formed on the inner layer. Later, $NiFe_2O_4$ spinel was formed on the outer layer, as has been reported previously [1].

As shown in Fig. 4, the thickness of the oxidation film on the Alloy 690 after the oxidation treatment was measured by AES with Ar sputtering. The thickness increased rapidly until an oxidation treatment time of 100 h was reached. After 100 h, the thickness increased linearly with increasing oxidation treatment time.

Fig. 5 shows weight loss as a function of the test distance at a frequency of 30 Hz for various amplitudes and heat treatment times. The weight loss increased linearly as the test distance increased in all test specimens. The slopes in the weight loss graphs did not show significant changes for amplitudes ranging from 50 to 150 μm. This indicates that the wear mode did not change in this range. The wear mode in this range has been reported as gross slip [9]. However, the slope did increase as the amplitude increased from 150 to 300 μm as the wear mode changed from gross slip to sliding [9]. Additionally, the slope decreased with increasing oxidation treatment time from 0 to 2000 h. This shows that the oxidation film formed before the wear test increased the wear resistance of Alloy 690.

To quantitatively analyze the wear behavior of the specimens, wear coefficients were calculated from the weight loss data in Fig. 5 by using the Archard equation, as shown in Eq. (1):

$$V = KFS \quad (1)$$

Here, V is the wear volume, F is the applied normal load, K is the wear coefficient, and S is the sliding distance. As mentioned above, the wear coefficient values in Fig. 6 showed similar values as the amplitude was increased from 50 to 150 μm. These values then increased at an amplitude of 300 μm due to the change in the wear mode. Additionally, the wear coefficient decreased by about 40–50% as the oxidation treatment time increased. At amplitudes of 50, 100, and 150 μm, the wear coefficient of the gross slip region decreased from $(2.4 \pm 0.2) \times 10^{-13}$–$(2.6 \pm 0.2) \times 10^{-13}$ m^3/Nm to $(1.0 \pm 0.07) \times 10^{-13}$–$(1.6 \pm 0.12) \times 10^{-13}$ m^3/Nm. At an amplitude of 300 μm, the wear coefficient of the sliding region decreased from $(5.5 \pm 0.2) \times 10^{-13}$ m^3/Nm to $(3.4 \pm 0.25) \times 10^{-13}$ m^3/Nm. These results show that, as the oxidation treatment time increases, the thickness of the oxidation film increases and the wear resistance of Alloy 690 increases (regardless of the test amplitude).

To identify the effect of the oxidation film on the wear resistance of Alloy 690, the worn surfaces were analyzed via SEM. As shown in Fig. 7(a), a large disturbed layer was formed on the surface of the non-oxidized specimen during the wear test at an amplitude of 300 μm. As the oxidation treatment time increased to 2000 h, the size of the disturbed layer decreased and the roughness of the worn surface also decreased (Fig. 7). The disturbed layer on the worn surface was usually formed by material transfer. It has been reported that, under friction conditions, two metallic materials adhere locally via free electron transfer; this can be described by the Jellium model [12]. Material transfer occurs due to the adhesion force and a disturbed layer is formed [13–15]. However, when an oxidation film exists on the surface, metal-to-metal contact is prevented and material transfer is hindered [3]. Therefore, in this study, the adhesion tendency of Alloy 690 decreased with increasing oxidation treatment time by preventing direct metal-to-metal contact. This causes an increase in the wear resistance. However, it is doubtful that the oxidation film still exists on the surface after a 2 h wear test. Therefore, the local chemical compositions of worn specimens were measured by using EDS.

Fig. 8 and Table 2 show the quantitative analysis of the worn surface of non-oxidized Alloy 690. At many EDS points in the disturbed layer, the Fe compositions were measured to be between 30 and 50 wt% Fe, despite the fact that Alloy 690 contains only

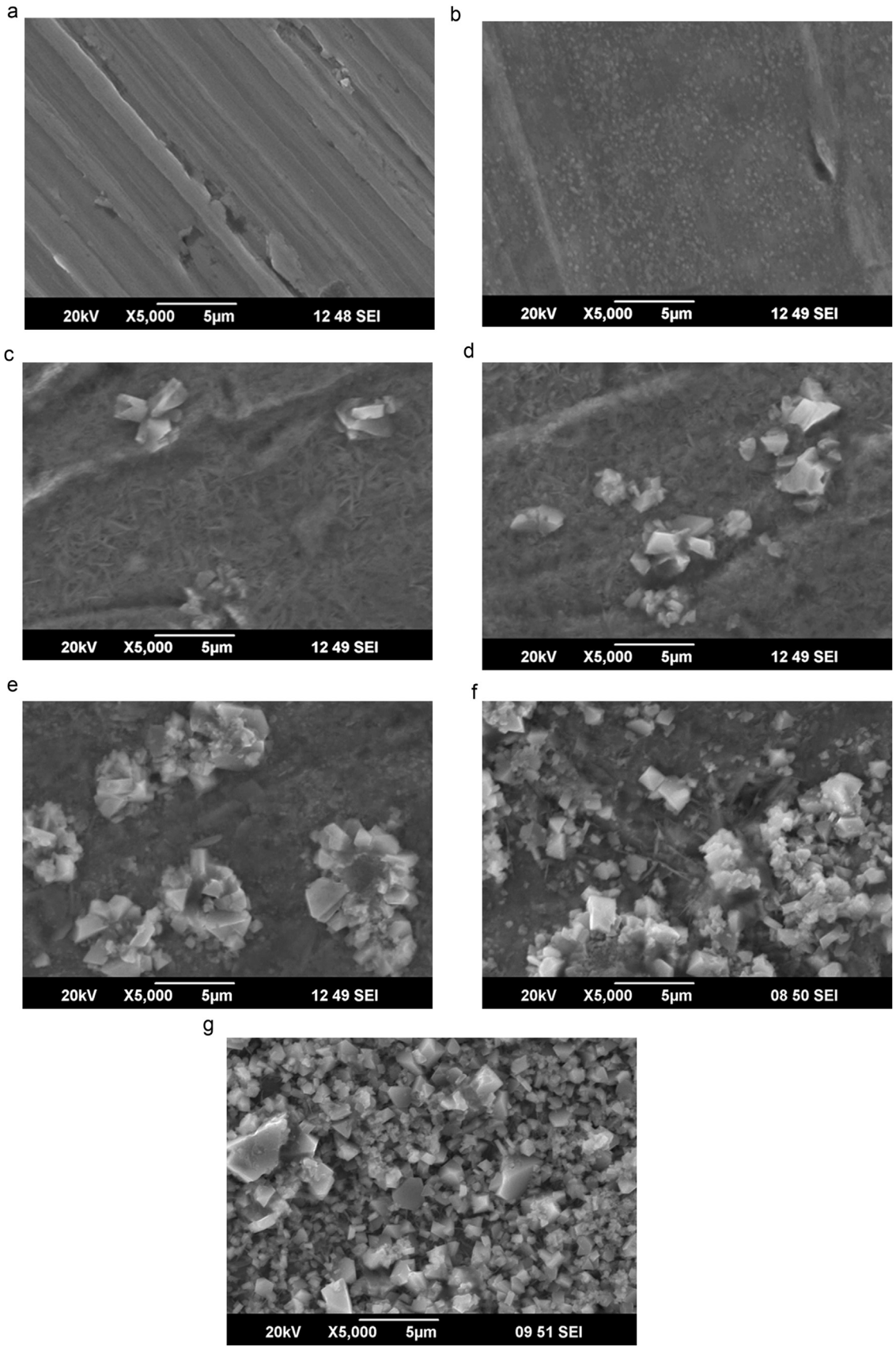

Fig. 2. SEM images of Alloy 690 at various oxidation treatment times of (a) 0 h, (b) 50 h, (c) 100 h, (d) 200 h, (e) 500 h, (f) 1000 h, and (g) 2000 h at 320 °C under a hydraulic pressure of 2.5 ksi.

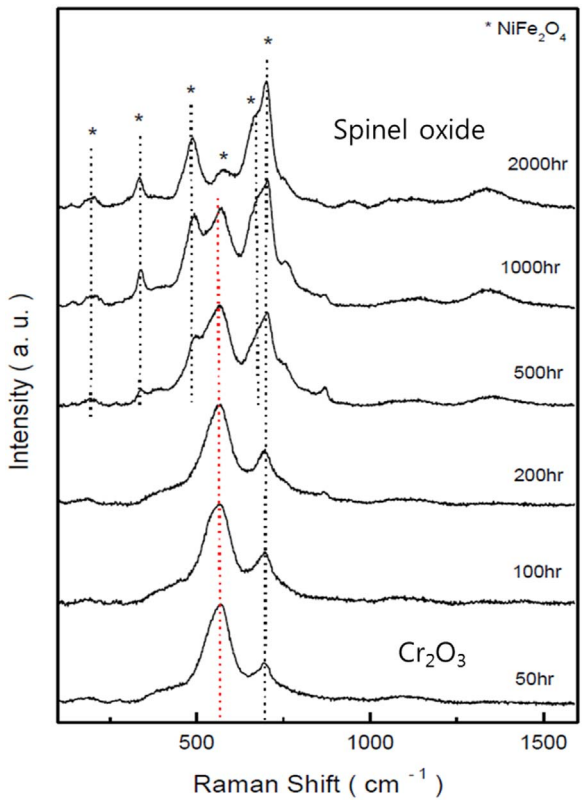

Fig. 3. Raman spectroscopy of Alloy 690 autoclaved at 320 °C, 2.5 ksi for various oxidation treatment times.

10 wt% Fe (Table 1). This shows that, as predicted above, material transfer occurred (from the mating material; SUS 409) and a disturbed layer was developed. As for the oxygen concentration, some parts of the surfaces contain about 5 wt% of oxygen, which is believed to be formed by tribo-oxidation. However, most of the surface contained minimal amount of oxygen.

Fig. 9 and Table 3 show the quantitative analysis of the worn surface of the Alloy 690 sample that was oxidized for 2000 h. Contrary to the EDS analysis results of the non-oxidized Alloy 690, the Fe compositions were measured to be between 9 and 17 wt% (except for two of the EDS points). As for the oxygen concentration, most of the surfaces contain more than 1.5 wt% of oxygen, which is considered to be formed by the oxidation treatment before the wear test. This shows that material transfer and formation of the disturbed layer were hindered by the residual oxide formed during the oxidation treatment; this caused the wear resistance of Alloy 690 to increase.

The results in this study were drawn from the wear tests of 'pre-oxidized' and 'rectangular-shaped' Alloy 690. In the SGs, 'cylindrical-shape' tubes are consistently oxidized due to high temperature and pressure of coolant, and so the results cannot be used directly to predict or simulate the lifetime of tube. However the results tell us that oxidation of Alloy 690 in SG can enhance the wear resistance by preventing metal-to-metal contact and material transfer, and this can be applied to the study of SG design or lifetime expectation as a fundamental research. To simulate the wear behavior during operation, further study for wear test under autoclaved environment is needed.

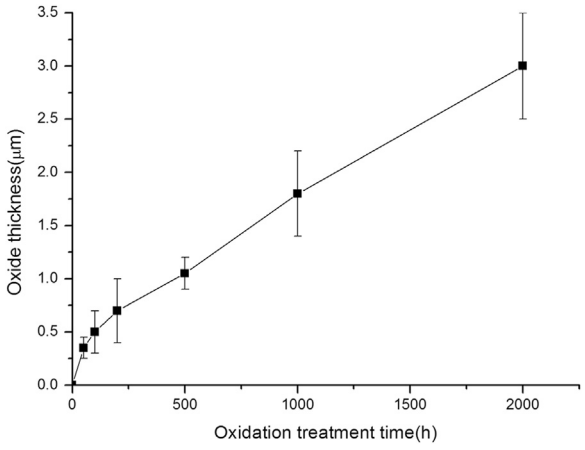

Fig. 4. Oxide thickness as a function of oxidation treatment time at 320 °C under a hydraulic pressure of 2.5 ksi.

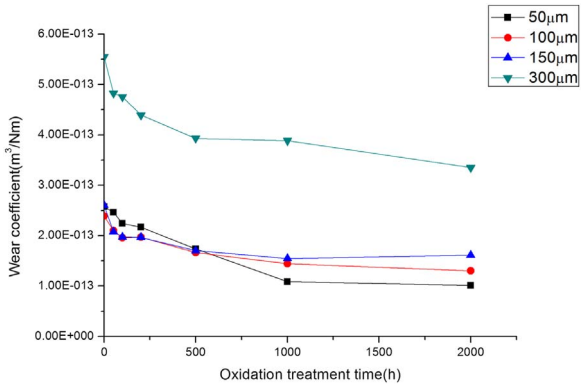

Fig. 6. Wear coefficient as a function of the oxidation treatment time at various amplitudes.

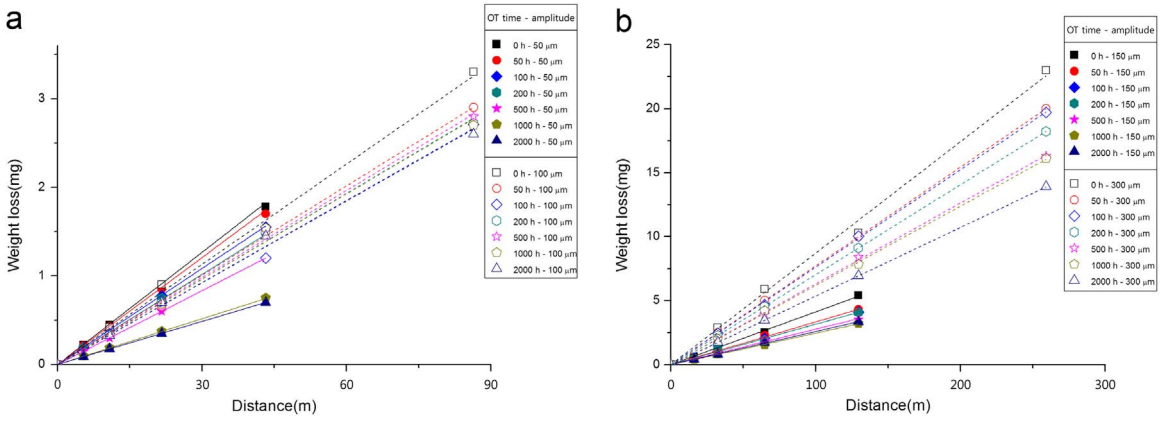

Fig. 5. Weight loss behavior as a function of the test distance at various oxidation treatment(OT) times; at amplitude of (a) 50 and 100 μm; and (b) 150 and 300 μm.

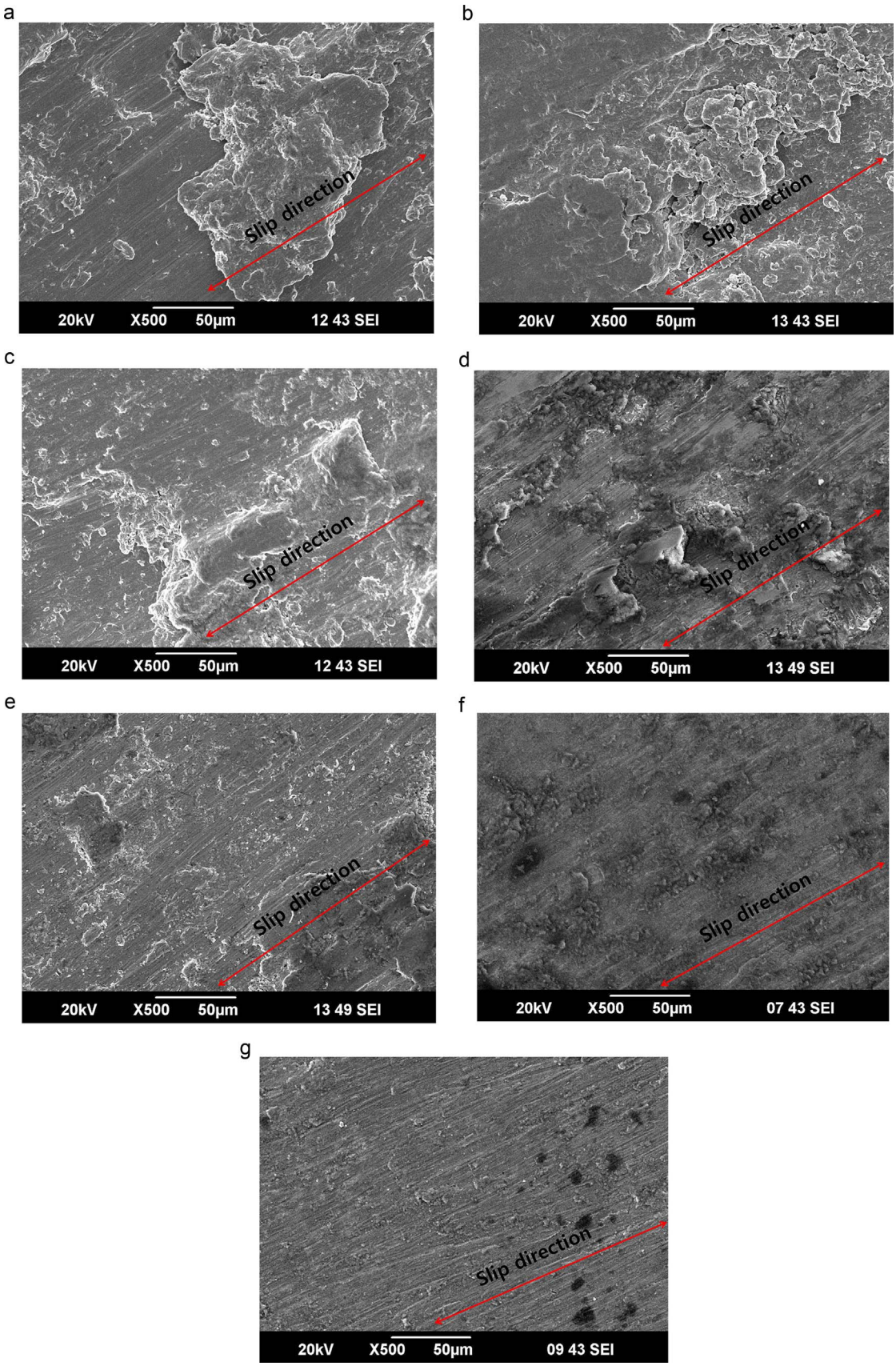

Fig. 7. SEM images of worn surfaces after 2 h (259.2 m) wear test at an amplitude of 300 μm, frequency of 30 Hz and various oxidation treatment times of (a) 0 h, (b) 50 h, (c) 100 h, (d) 200 h, (e) 500 h, (f) 1000 h, and (g) 2000 h.

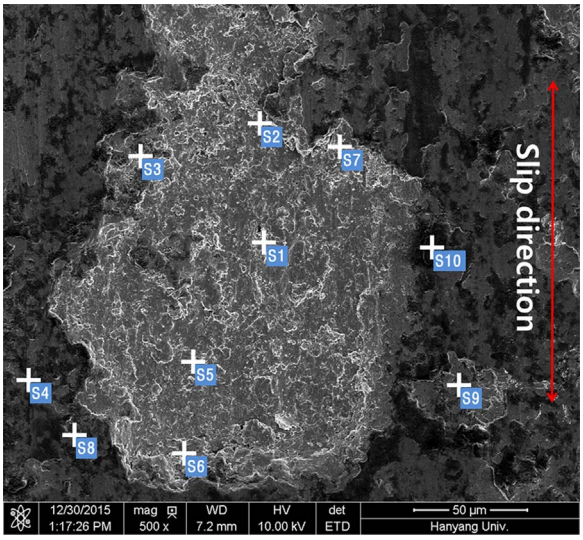

Fig. 8. Observation of the worn surface of the non-oxidized specimen at an amplitude of 300 μm and a frequency of 30 Hz.

Table 2
Quantitative EDS analysis of the worn surface of the non-oxidized specimen at an amplitude of 300 μm and a frequency of 30 Hz.

Composition (wt%)	O	Cr	Fe	Ni
S1,	0.52,	30.51,	11.08,	57.89,
S2,	0.33,	30.89,	17.17,	51.61,
S3,	5.55,	18.51,	48.64,	27.29,
S4,	4.13,	19.7,	44.67,	31.51,
S5,	0.04,	31.21,	10.86,	57.89,
S6,	0.14,	20.26,	40.77,	38.84,
S7,	0.45,	21.02,	30.91,	47.62,
S8,	0.48,	31.3,	10.9,	57.33,
S9,	0.35,	28.27,	31.75,	39.62,
S10,	0.43,	29.7,	15.05,	54.82,

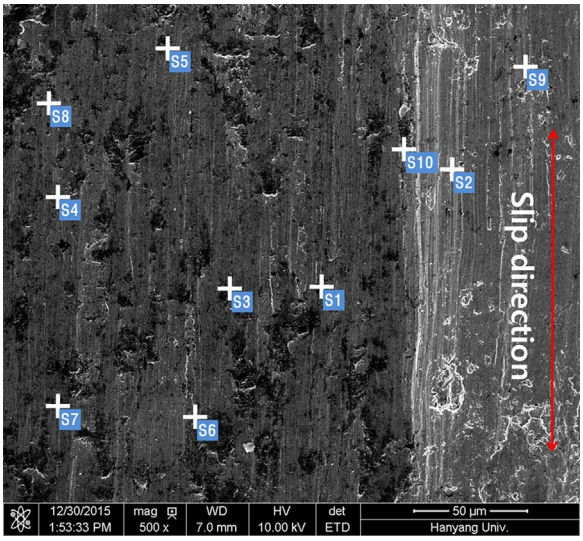

Fig. 9. Observation of the worn surface of the 2000 h oxidized specimen at an amplitude of 300 μm and a frequency of 30 Hz.

Summary

1. The results of Raman analysis and SEM observation confirm that, at the early stage of oxidation of Alloy 690, Cr_2O_3 is formed on the inner layer. Then, polyhedral-shaped $NiFe_2O_4$ is formed after an oxidation treatment of 100 h.
2. The thickness of the oxidation film increased rapidly until 100 h of oxidation. After 100 h, the thickness increased linearly with increasing oxidation treatment time.
3. The results of the wear tests show that, as the oxidation time increased, the wear resistance also increased due to the fact that formation of the disturbed layer was hindered. The disturbed layer of the non-oxidized specimen contained Fe concentrations of 30–50 wt%, which were transferred from the mating materials whereas the worn surface of the specimen oxidized for 2000 h contained residual oxide that was formed by the oxidation treatment; this prevented metal-to-metal contact and material transfer.

Table 3
Quantitative EDS analysis of the worn surface of the 2000 h oxidized specimen at an amplitude of 300 μm and a frequency of 30 Hz.

Composition (wt%)	O	Cr	Fe	Ni
S1,	2.56,	29.99,	10.2,	57.25,
S2,	2.65,	30.25,	9.94,	57.15,
S3,	1.54,	30.82,	10.8,	56.84,
S4,	4.75,	21.14,	40.93,	33.18,
S5,	2.84,	29.43,	10.69,	57.04,
S6,	2.27,	29.16,	10.33,	58.23,
S7,	9.08,	20.14,	50.38,	19.68,
S8,	5.36,	28.25,	15.05,	51.34,
S9,	2.7,	29.17,	10.41,	57.72,
S10,	9.94,	27.89,	17.15,	45.02,

Acknowledgements

This work was supported by the Human Resource Development Program (No. 20134030200360) of the Korea Institute of Energy Technology Evaluation and Planning (KETEP) Grant funded by the Korean government Ministry of Trade, Industry and Energy.

This work was also partially supported by the National Research Foundation of Korea (NRF) Grant funded by the Korea government (MSIP).

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