Effect of Plasma Nitriding on the Surface Characteristics of Al-Cr Diffusion-Treated Steels

S.Y. Lee, J.H. Yang, G.S. Kim, B.S. Kim, B.Y. Lee[+], H.B. Eun[++], J.H. Lee[•] and S.Y. Lee[••]

Department of Materials Engineering, [+]Faculty of Mechanical Engineering,
[++]Department of Flight Operation, Hankuk Aviation University,
KoYang, KyungKi-Do, 412-791, Korea
[•]Materials Characterization & Evaluation Group,
[••]Metal Working and Plasticity Group,
KIMM, Changwon, KyungNam, 641-010, Korea

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ABSTRACT

Plasma nitriding on simultaneously Al-Cr diffusion-treated AISI H13 and AISI 403 steel was performed and analysis of microstructure, microhardness, cyclic oxidation behavior and high temperature wear resistance of these duplex-treated steels was made. The results were compared with those from steels treated by either plasma nitriding or by duplex treatment of single element (Al) diffusion and plasma nitriding. Both steels showed a FeAl compound layer of approximately 350 μm thickness on the surface after simultaneous diffusion coating and nitrided layer of approximately 70~80μm formed after the subsequent plasma nitriding process. The microhardness was significantly improved by the duplex surface treatment (approximately 1500~1600 Hv(0.5N)) more than only by plasma nitriding (approximately 1000~1100 Hv(0.5N)) by a factor of 1.5 to 1.6. In addition the duplex treated specimens showed a much-improved high temperature wear resistance. Results from the cyclic oxidation test at 1173K showed that much improved oxidation resistance could be observed from the specimens treated by Al-Cr diffusion and plasma nitriding and this could be attributed to formation of a Cr_2O_3 layer as an additional protective layer on the surface.

1. INTRODUCTION

Many surface treatment processes including plasma assisted chemical vapor deposition (PACVD), ion plating for hard coating, and gas and plasma nitriding /1-5/ have been extensively studied to improve the service life of mold and high alloy steels for high temperature applications. One of the promising processes for this purpose includes a duplex plasma surface treatment process /6-8/, which was designed to improve wear and corrosion/oxidation resistance at high temperature at the same time. A series of this duplex plasma surface treatment process which consisted of single element diffusion coating such as Al /6,7/ and Cr /8/ followed by plasma nitriding were previously reported by Lee and co-workers. Much improvement of the surface properties such as high temperature wear resistance, oxidation resistance was reported in the duplex-treated mild and alloy steels such as AISI 1020, AISI H13, ASTM A213.

However, a further improvement is expected of the high temperature surface properties by a duplex plasma surface treatment consisting of multi-element diffusion coating such as Al-Cr or Al-Si and plasma nitriding.

In this study, the duplex treatment of multi-element diffusion coating and plasma nitriding (i.e., plasma nitriding on simultaneously Al-Cr diffusion-treated AISI H13 and STS 403 steel) was performed as one of many attempts to develop a duplex treated process to enhance the elevated temperature wear resistance and the thermal stability at the same time. Analyses of microstructure, microhardness, cyclic oxidation behaviors and high temperature wear resistance of these duplex-treated steels were conducted. The results were compared with those from steels treated by either plasma nitriding or by duplex treatment of Al diffusion and plasma nitriding.

2. EXPERIMENTAL

In this work AISI H13 and AISI 403 disks (diameter: 25mm and 50 mm; thickness: 3mm and 5 mm) were cut and prepared for oxidation and wear tests, respectively. Simultaneous Al-Cr diffusion coating on cleaned and degreased specimens was performed by a two-step pack cementation process (first step: 5 hours at 1023 K; second step: 10 hours at 1333 K). The pack composition was 20wt%Cr, 5wt%Al, 72wt%Al_2O_3, and 3wt%NH_4Cl. Sputter cleaning was performed prior to plasma nitriding for 30 minutes under Ar/H_2 atmosphere and plasma nitriding on the Al-Cr diffusion coated specimens was performed in a 50%N_2-50%H_2 atmosphere for 1.5 hour at 803 K. Specimens were cooled in the nitriding chamber under N_2.

The microstructure was studied by SEM/WDS and EDS analysis using Oxford Link ISIS with Li-doped Si window at an accelerating voltages of 20 keV. The comparative quantitative analysis was made using ZAF method. Microvickers hardness was measured using a load of 0.5 N and an average of twelve readings was taken. A diffractometer using CuK_0 radiation was used for XRD analysis. Ball-on-disk type wear tests were performed at 500°C. Applied load was 15 N and the sliding distance was 5 km with a linear velocity of 0.4m/sec. Alumina ball (99.99% purity) with 8 mm in diameter was used as counterface material and the relative humidity was 50 - 60%.

Cyclic oxidation test up to 100 cycles was performed and one cycle consisted of exposure at 1173 K for 45 minutes and 15 minutes at room temperature.

3. RESULTS AND DISCUSSION

3.1. Microstructural Analysis

Fig. 1 shows cross-sectional micrographs of specimens after simultaneous Al-Cr diffusion treatment. For the AISI H13 specimen, a fine tempered martensite microstructure, typical of quenched and tempered AISI H13 steel, along with a thick and featureless Al-Cr diffusion layer was observed as shown in Fig. 1a). Thickness of the Al-Cr diffusion layer was of the order of 350~360μm. A thin layer with small pores underneath the surface was identified and this layer was removed for improving the quality of the following plasma nitriding process. Having approximately 0.37wt% C and 5.0wt% Cr, AISI H13 steel was expected to form Cr carbides at the surface during diffusion treatment /8,9/, but it was not observed. After Al-Cr simultaneous diffusion treatment under the same processing conditions, the thickness of the Al-Cr diffusion layer in the AISI 403 steel was similar to that in the AISI H13 steel, but thin layer at the surface with a thickness of approximately 10μm was observed.

EDS results from the different locations in the Fig. 1a) and 1c) are shown in Fig. 1b) and d). In AISI H13 steel, the highest concentration of approximately 25wt%Al and 15wt%Cr at near the surface area was measured and continuous decrease in the composition toward the matrix was observed. With high concentration of Cr and Al at the surface area excellent oxidation and corrosion resistance could be expected. In AISI 403 steel, however a different compositional profile was observed as shown in Fig. 1d). EDS analysis on the thin layer at the surface showed an high concentration of Cr and C with relatively low Al content, comparing with the compositions in the other area. Especially high carbon content of approximately 3.25wt%C was measured. This indicates that high content of chromium carbides was formed in this thin layer and later it was confirmed to be $Cr_{23}C_6$ carbide by x-ray diffraction analysis. As this thin layer could interfere with proper plasma nitriding, it was removed before nitriding.

Plasma nitriding on the Al-Cr diffusion treated specimens was performed for 1.5 hour at 803 K. The cross-sectional microstructure after the duplex treatment

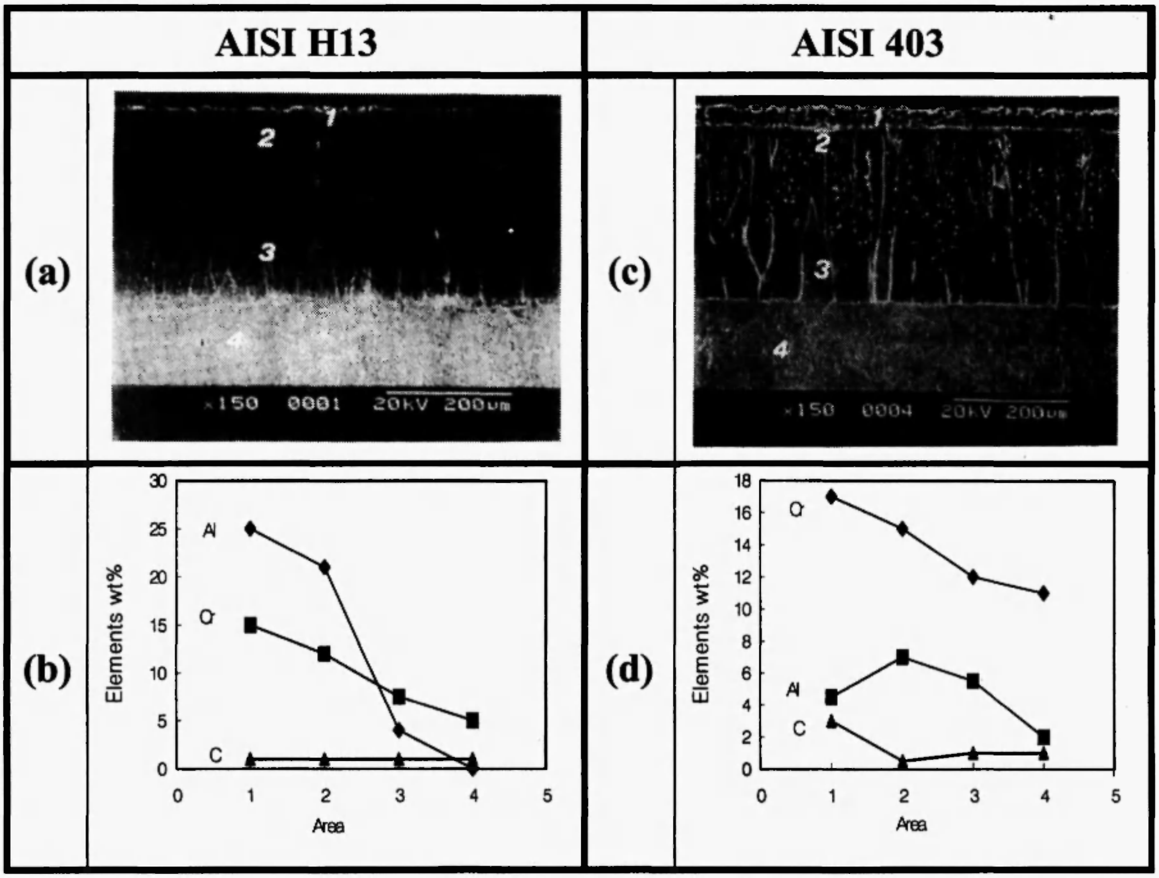

Fig. 1: Cross-sectional SEM micrographs and EDS analysis of simultaneously (Al+Cr) diffusion treated specimens, (a) & (b) AISI H13, (c) & (d) AISI 403

is shown in Fig. 2. Clear layer structure with duplex treated layer at the surface, Al-Cr diffusion layer at the middle, and matrix was observed. Duplex treated layers with a thickness in the order of 70~80μm and 90~100μm were observed in AISI H13 and AISI 403, respectively. Considering the heat of formation of AlN and CrN at 500 K are -266.1kJ/mole and -78.7kJ/mole, respectively /9/, a slightly thinner duplex treated layer in the AISI H13 steel could be attributed to the higher content of Al, which is considered to be an easy nitride forming element. However either nitrides of AlN or CrN were not observed from the XRD measurements.

After plasma nitriding on the Al-Cr diffusion treatment, the surfaces of the specimens were analyzed using XRD and the results are shown in Fig. 3. It showed that the surface consisted of only FeAl compound without forming any nitrides. It was noted that the diffraction peaks from the duplex treated specimens in Fig. 3 became broad and the 2θ values of the peaks were shifted by a small degree. Similar line broadening phenomena in an extended solid solution were previously reported /10/. Therefore, it could be explained by the strain produced by interstitial nitrogen solutionized into the FeAl.

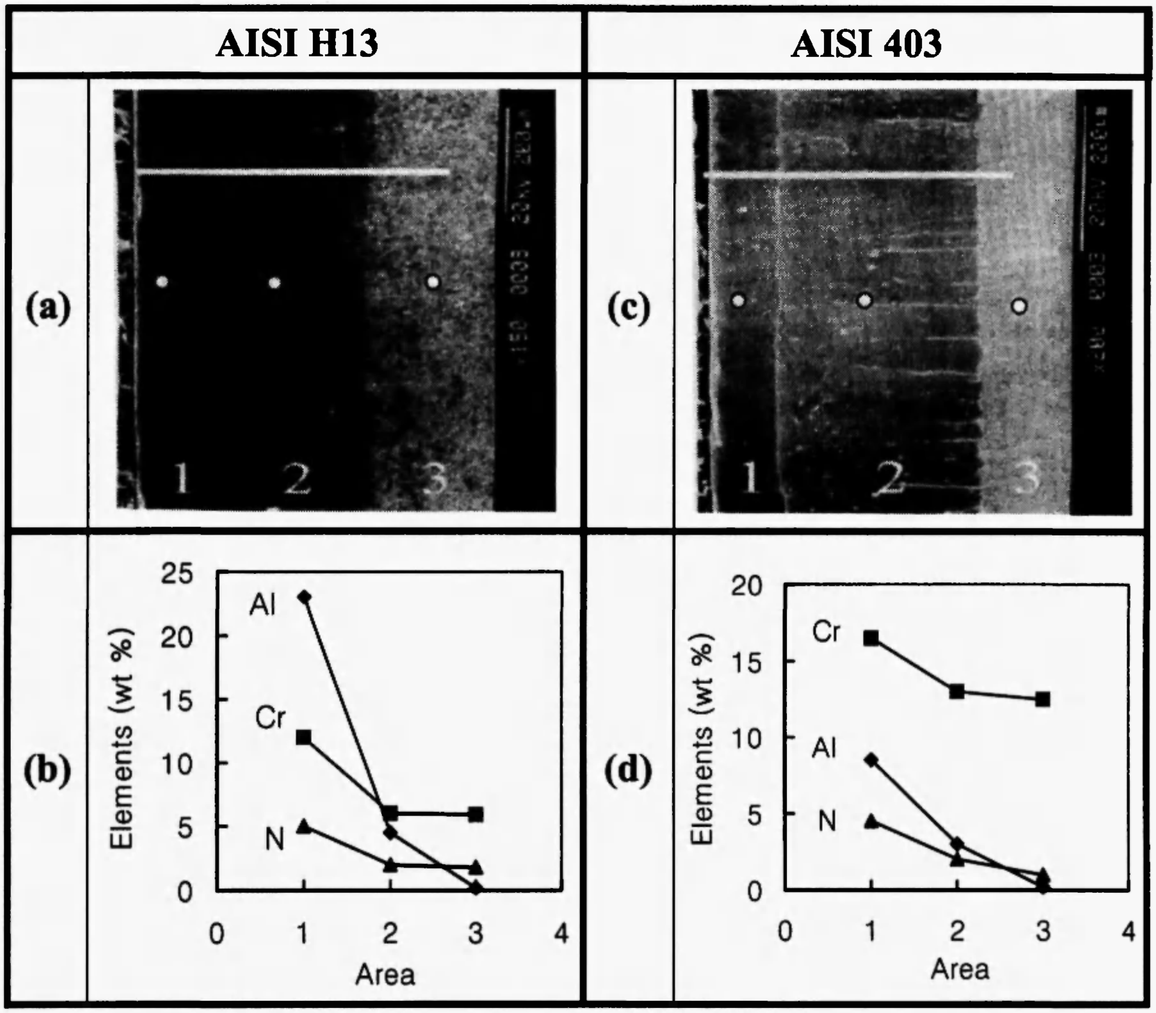

Fig. 2: Cross-sectional SEM micrographs and EDS analysis of specimens treated by simultaneously (Al+Cr) diffusion and plasma nitriding, (a) & (b) AISI H13, (c) & (d) AISI 403

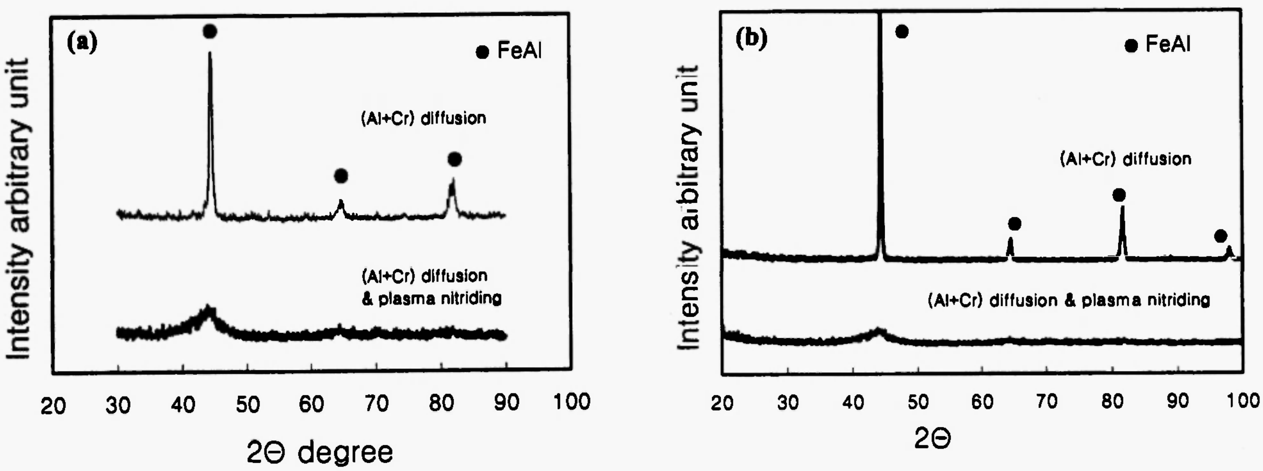

Fig. 3: Results from X-ray diffraction analysis on (a) AISI H13 (b) AISI 403

3.2 Microhardness and wear behavior at 773 K

The microhardness profiles of the specimens after duplex treatment of Al-Cr diffusion treatment and plasma nitriding are shown in Fig 4. Surface microhardness of the duplex treated AISI H13 was measured to approximately 1600Hv and it decreases continuously as the amount of nitrogen decreases toward the matrix as shown in Fig. 4a). The surface hardness of the duplex treated specimens showed marked improvement, compared with the specimens treated by nitriding only. This was explained in the previously reported publications /6,7,11/. It is noted, however, that the multi-element diffusion treatment of Al-Cr before plasma nitriding in the duplex treatment did not seem to affect the surface microhardness much because the microhardness measured from the specimen treated by single element diffusion treatment of Al and plasma nitriding /7/ was similar to that from the multi element diffusion treatment and plasma nitridng.

Similar microhardness distribution was observed in the duplex treated AISI 403 steel, but the surface microhardness was measured to be approximately 1400Hv, which is slightly lower than that measured in the AISI H13 steel. This could be attributed to the fact that a smaller amount of aluminium was solutionized in the duplex treated AISI 403 steel, which contains higher Cr and lower Al in the duplex treated layer at the surface than AISI H13 steel. Al, having a relatively larger atomic radii than Cr, seemed to induce more solid solution strengthening effect.

The results from the ball-on-disk type wear test at 500°C are summarized in Table 1. The wear volume in Table 1 was calculated from the wear track measured using a profilometer. Much improved high temperature wear resistance could be obtained by duplex treatment. In the duplex-treated specimen the wear volume was measured approximately 6 times smaller than that in the diffusion treated. Excellent surface stability provided by Al-Cr diffusion treatment and high surface hardness induced by plasma nitriding could be attributed to the much-improved high temperature wear resistance.

The wear tracks after wear test at 500°C on the duplex-treated specimens were investigated. Regardless of the alloy compositions the wear tracks of the duplex-

Table 1

Results from the wear test at 773 K

	Wear volume (mm^3) of disc	
	AISI H13	AISI 403
Al-Cr diffusion only	14.9	15.7
Al-Cr diffusion treatment and plasma nitriding	2.3	2.0

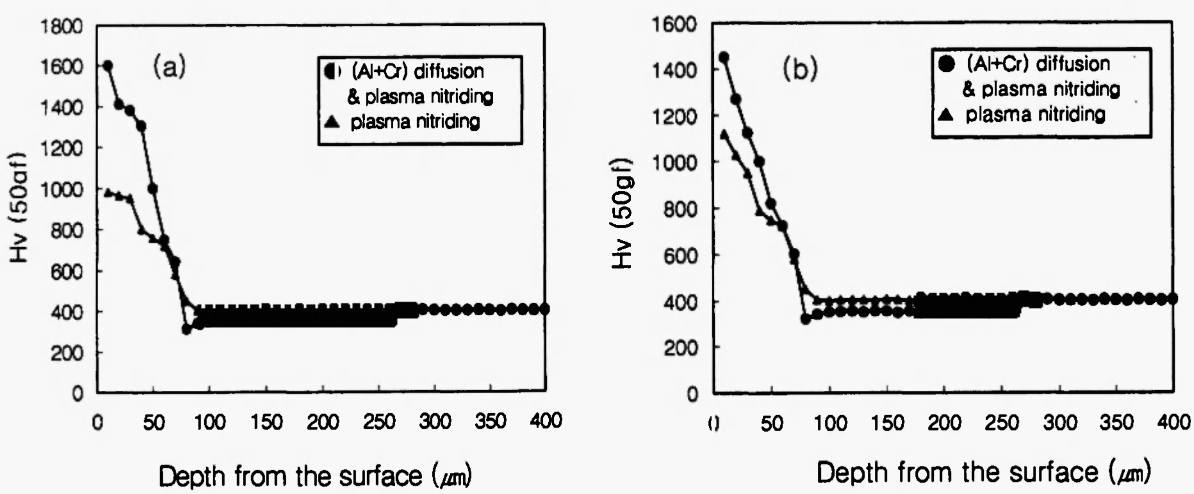

Fig. 4: Cross-sectional microvickers hardness profiles on (a) AISI H13 (b) AISI 403

treated specimen showed an abrasive type wear while the only diffusion treated specimens showed an adhesive wear. Compared with specimens treated by single element diffusion treatment and plasma nitridng, the specimens treated by dual element diffusion treatment and plasma nitriding did not show much difference in the high temperature wear track. An abrasive type wear track was observed in the specimens treated by Al diffusion (calorizing) /6,7/ or Cr diffusion (chromizing) /8/ and plasma nitriding was reported previously. High surface hardness in the duplex treated specimens was attributed to the abrasive wear behaviors in the previous publications/6-8/.

3.3. Cyclic oxidation behaviors

Cyclic oxidation test at 1173 K up to 100 cycles on specimens treated by Al-Cr diffusion treatment and plasma nitriding was performed and the results were compared with those from specimens treated by single element diffusion treatment of Al and plasma nitriding in order to illuminate the effects of dual element diffusion treatment on the oxidation properties of the final duplex treated surface layer. Results from the x-ray diffraction analysis on the duplex treated AISI H13 steel after cyclic oxidation test up to 40 cycles at 1173 K are shown in Fig. 5. In the specimen treated by duplex treatment of single element (Al) diffusion and plasma nitriding diffraction peaks from Al_2O_3 and Fe_2O_3 phases were detected, while additional chromium oxide (Cr_2O_3) peaks were detected in the specimen treated by duplex treatment of Cr-Al diffusion and plasma nitriding.

Weight change per unit area as a function of oxidation cycles in AISI 403 steel is shown in Fig. 6.

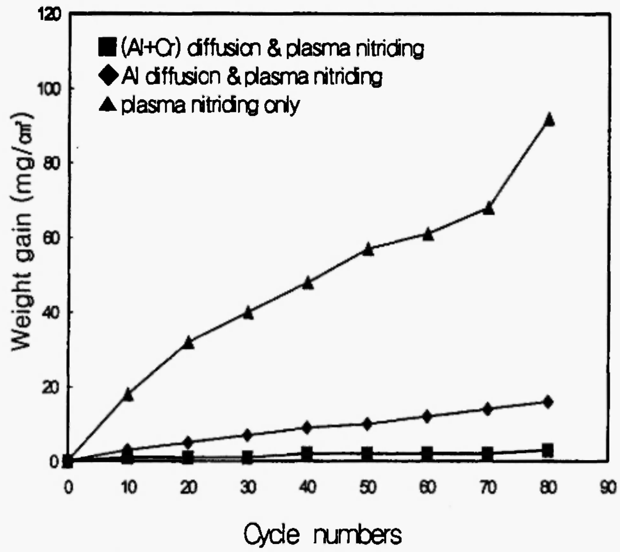

Fig. 6: Weight change per unit area vs. oxidation cycle for AISI 403 oxidized in air at 1173 K

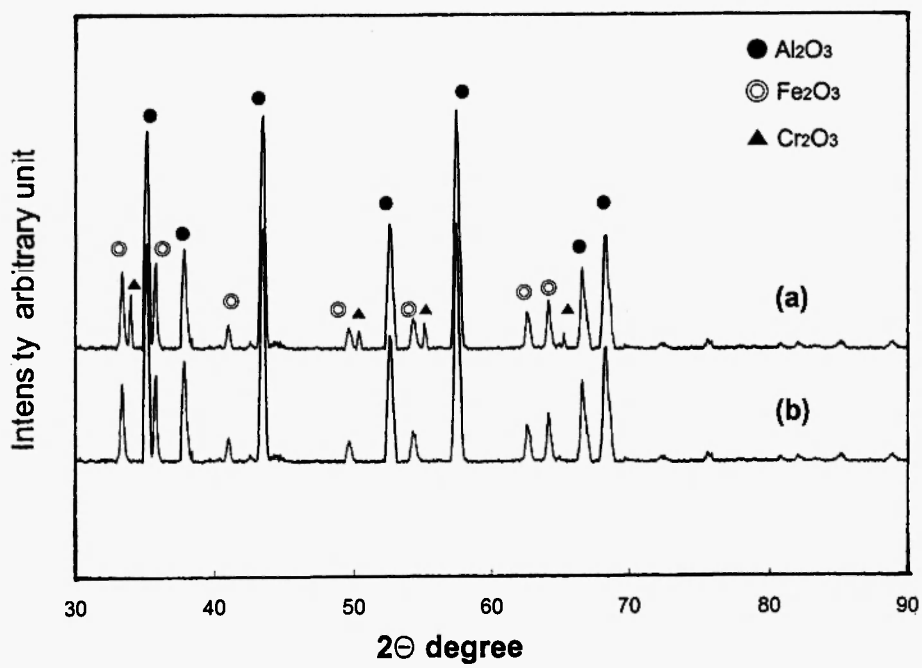

Fig. 5: X-ray diffraction patterns of duplex treated AISI H13 after cyclic oxidation test up to 40 cycle at 1173 K (a) (Al+Cr) diffusion and plasma nitriding (b) Al diffusion and plasma nitriding

The duplex treated specimens regardless of the number of elements in the diffusion process showed much improved oxidation resistance than the plasma nitrided specimen as shown in Fig. 6. Yet still further improved oxidation resistance could be confirmed in the specimen treated by duplex treatment of Al-Cr diffusion and plasma nitriding than the specimen treated by single element (Al) diffusion and plasma nitriding. This additional improvement could be explained by an additional protective oxide film (Cr_2O_3) provided by Cr in the dual element diffusion treatment, as confirmed in the x-ray diffraction analysis.

Both types of duplex treated specimens were subjected to cyclic oxidation at 1173 K up to 100 cycles and cross sectional micrographs of each specimens are shown in Fig. 7 Oxidation behavior varied depending upon the type of the diffusion treatment before plasma nitriding. In the specimen treated by single element (Al) diffusion and plasma nitriding, oxidation by penetration along an interface in the duplex treated layer was observed after 20 cycles, and oxidation penetration depth as well as oxidation width increased as the number of cycles increased as shown in Fig. 7. As this type of oxidation by penetration was not observed under the isothermal oxidation atmosphere /7/, it could be attributed to the cyclic stress generated from the cyclic heating and cooling during cyclic oxidation test. It is suggested that the cyclic stress might have assisted an enhanced diffusion of oxidizing element along a weak interface in the duplex treated layer and eventually an accelerated oxidation along the interface. On the contrary, however, general surface oxidation without extensive penetration at the duplex treated layer was observed in the specimen treated by Al-Cr diffusion and plasma nitriding, showing much improved cyclic oxidation resistance. Even after 80 cycles, only the surface layer was spalled away while the intermediate layer underneath the duplex surface layer and the matrix remained intact.

Results from the EPMA mapping after cyclic oxidation are summarized in Fig. 7. In the case of the specimen treated by single element (Al) diffusion and plasma nitriding, almost all the Al element was consumed away while an extensive amount of Al as well as Cr still remained in the duplex treated layer and in the intermediate layer between the duplex treated layer and the matrix, providing the continuous formation of a protective film of Cr_2O_3 and Al_2O_3 in the specimen treated by Cr-Al diffusion and plasma nitriding as shown in Fig. 7. Similar cyclic oxidation behavior was observed in the AISI 403 specimen treated by Cr-Al diffusion and plasma nitriding.

4. CONCLUSIONS

1. By performing plasma nitriding on Al-Cr diffusion treated specimens for 1.5 hour at 803 K, duplex treated layer with a thickness in the order of 70~80μm and 90~100μm could be obtained in AISI H13 and AISI 403, respectively and the duplex treated layer was determined to be of FeAl compound with high degree of nitrogen solutionized.
2. Surface microhardness of approximately 1600Hv and 1400Hv could be obtained in the duplex treated AISI H13 and AISI 403, respectively. It is noted, however that single or dual elements in the diffusion treatment before plasma nitriding did not affect the surface microhardness much.
3. The duplex treated specimens regardless of the number of elements in the diffusion process showed much more improved oxidation resistance than the plasma nitrided specimen. Further improved oxidation resistance could be confirmed in the specimen treated by Al-Cr diffusion and plasma nitriding than the specimen treated by single element (Al) diffusion and plasma nitriding due to an additional protective oxide film (Cr_2O_3) provided by Cr in the dual element diffusion treatment.

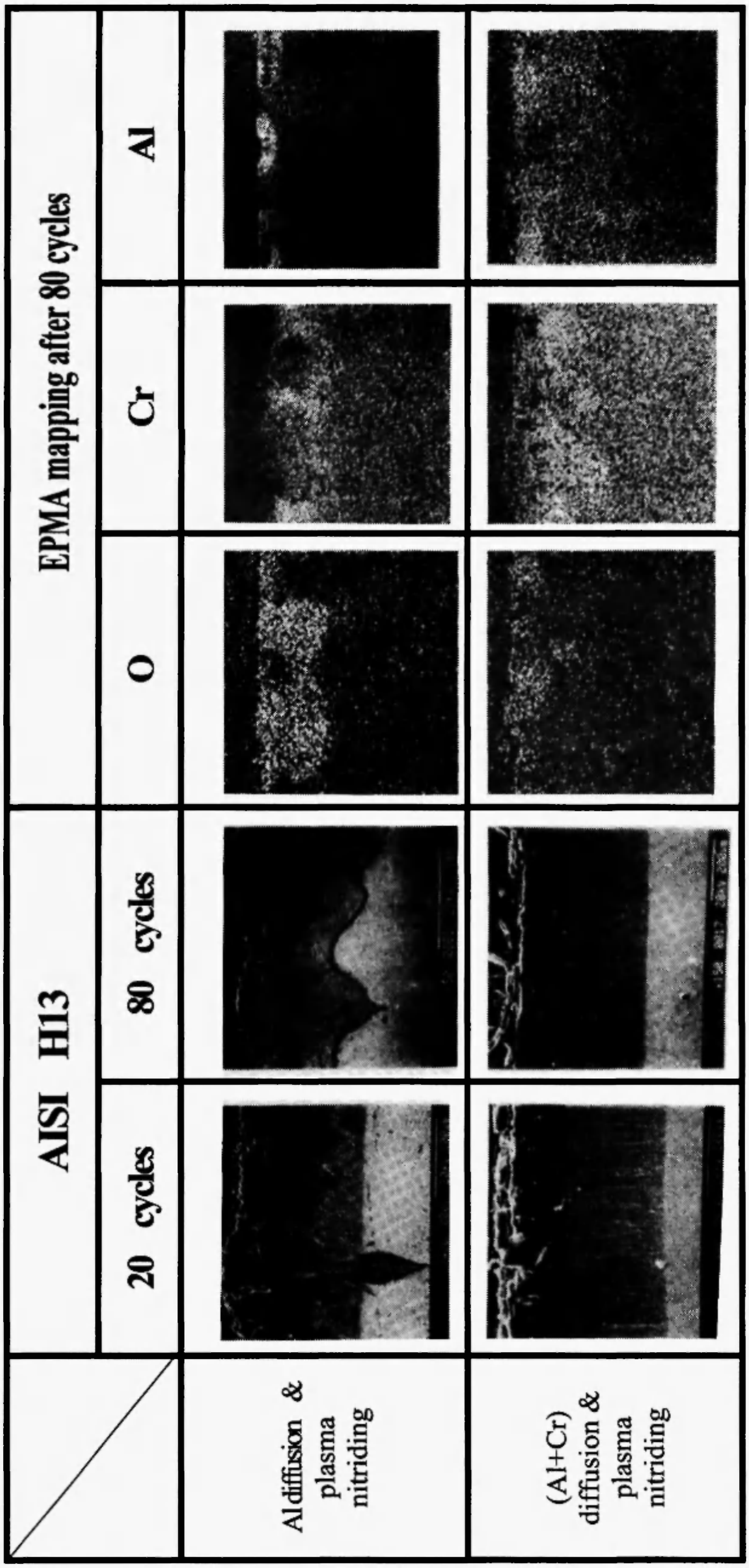

Fig. 7: Cross-sectional SEM micrographs and EPMA mapping after cyclic oxidation test up to 80 cycles at 1173 K

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