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Chromizing-Siliconizing Coating on Austenitic Stainless Steel by Pack Cementation Method

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The simultaneous deposition of chromium and silicon on austenitic stainless steel SUS310S using a halide-activated diffusion coating process was performed to improve oxidation and wear properties at high temperatures. The sample was placed in an Al₂O₃ crucible filled with Cr and Si powder, a halide activator of NH₄Cl, NaF and AlF₃, and an inert Al₂O₃ filler powder. The diffusion coating treatment was conducted at two different temperatures of 1073 and 1323 K for a constant time of 18.0 ks in argon atmosphere. A chromizing-siliconizing diffusion coating layer, which exhibits high hardness and high oxidation resistance, was mainly characterized into two zones: an outer compound layer of chromium silicide and a diffusion layer of alpha ferrite. Moreover, the 'two-step' chromizing-siliconizing process is more advantageous than the 'one-step' process since the mass increase was lower for the two-step sample in the oxidation tests.

Keywords: diffusion coating, chromizing, siliconizing, pack cementation, simultaneous deposition, stainless steel

1. Introduction

Materials used in industrial plants should be resistant to environmental attack. They must have appropriate creep strength and corrosion resistance, in particular when used at high temperature. Austenitic stainless steels have been used in these environments; however, their corrosion resistance needs to be improved by surface modifications.¹⁻⁴⁾ Among the various surface modification methods, pack cementation has been used for many years to enrich chromium, silicon and aluminum at the alloy surfaces. The increase in the amount of Cr in steel improves corrosion resistance; however, this has an adverse effect on mechanical properties of steel; for example, it increases the brittle transition temperature. It has been reported that the addition of Si to stainless steels could improve their high-temperature oxidation resistance.⁵⁻⁸⁾

Therefore, simultaneous deposition of two kinds of different elements by pack cementation is very effective in protecting substrates from hot corrosion and oxidizing environments at high temperature.^{6,9-14)} However, a one-step process, keeping the temperature and time constant, has been used for simultaneous diffusion coating.

In this study, chromium and silicon were simultaneously deposited by diffusion into an austenitic stainless steel substrate SUS310S, which is generally used in high-temperature environments, using a halide-activated pack cementation in two different heat-treatment cycles.

2. Experimental procedure

2.1 Material

The material used in the present investigation was an austenitic stainless steel, SUS310S. Its chemical composition is listed in Table 1. The sample disc was 10 mm in diameter and 5 mm in thickness. The sample was mechanically polished with 800-grit SiC, ultrasonically cleaned, and further degreased ultrasonically in acetone and dried in air.

2.2 Processing

Cr and Si were used as agents of pack powders, Al₂O₃ as a filler, and NaF, NH₄Cl and AlF₃ as halide activator salts. The composition of pack powders is shown in Table 2. After placing the Al₂O₃ crucible containing the substrates and pack powders in an electric tube furnace, the furnace was evacuated to ~3 Pa. Argon was then introduced into the furnace until atmospheric pressure is reached. The crucible temperature was monitored using a chromel-alumel (type-K) thermocouple, which was in contact with the crucible, and connected to the furnace temperature controller. The simultaneous chromizing and siliconizing treatments were conducted at two different temperatures of 1073 and 1323 K for a constant time of 18.0 ks as shown in Table 3. After coating, the packs were cooled to room temperature in the same furnace, and the samples were ultrasonically cleaned to remove any loosely entrapped pack material on the surface.

2.3 Characterization

After coating, X-ray diffraction (XRD) was used to determine the phase structures at the surface layer. The cross sections of each sample were cut using a low-speed saw and polished for examination using optical microscopy, scanning electron microscopy (SEM) and energy dispersive X-ray spectrometry (EDS). In addition, room temperature hardness and hot hardness tests of the surface layer were conducted. The latter method was designed such that tests could be performed in a protective atmosphere of Ar. A diamond tipped steel indenter with a Vickers pyramid geometry was heated to the same temperature as the sample. Five indentations were made at each test temperature ranging from 300 K to 1073 K under 0.98 N loads. To investigate oxidation characteristics, the samples were subjected to 11 cycles of oxidation in air for 86.4 ks at 1073 K for a total oxidation time of 1000 ks. After every heating cycle, the samples were cooled to room temperature, then weighed using a microbalance.

3. Results and discussion

Figure 1 shows the cross-sectional microstructure and

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Table 1 Chemical composition of SUS310S substrate (wt%).

C	Si	Mn	P	S	Ni	Cr	Fe
0.020	0.28	1.13	0.028	0.002	19.64	24.15	balance

Table 2 Composition of pack powders (wt%).

Cr agent	Si agent	Al ₂ O ₃ filler	NH ₄ Cl activator	NaF activator	AlF ₃ activator
66.8	7.4	24.8	0.08	0.25	0.67

Table 3 Treating condition for chromizing-siliconizing coating.

Treating condition
1073 K, 18.0 ks
1073 K, 7.2 ks + 1323 K, 10.8 ks
1323 K, 18.0 ks

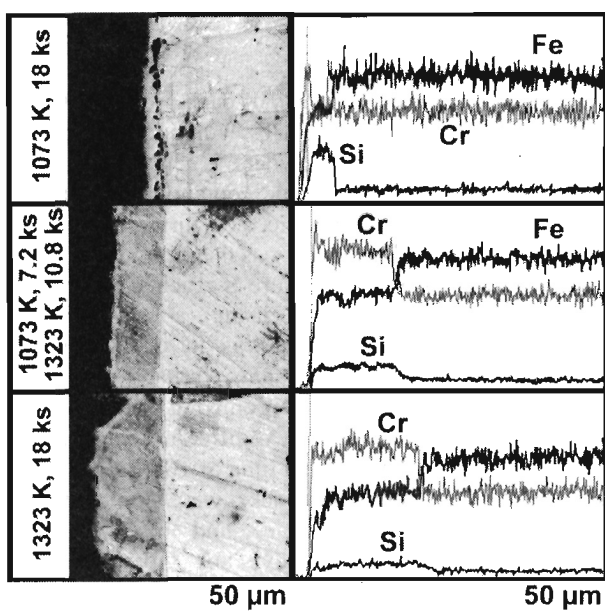


Figure 1 Cross-sectional microstructure and the EDS line analysis for samples treated by the chromizing-siliconizing coating process.

the EDS line analysis for the samples treated by the simultaneous chromizing-siliconizing diffusion coating process. At 1073 K, it was observed that the reactions of AlF with Si and NH₄Cl with Si and Cr resulted in voids and Si enrichment on the treated layers, as the treatment time increased. At 1323 K, all components of the activator are likely to bind with Si and Cr. Therefore, Si would show a predominant effect at 1073 K compared with 1323 K. The domination of Si at 1073 K would cause inhomogeneous diffusion of Fe and Si, resulting in the formation of voids and Si enrichment in the coating layer. Therefore, a two-step process at different treatment temperatures of 1073 K and 1323 K for a given holding time is required for Si enrichment and for penetration into the substrate.

On the basis of the XRD results for samples treated by the simultaneous chromizing-siliconizing diffusion coating process, Cr₃Si and α-Fe were identified in each sample. Cr₃Si was identified in the surface layers for all treatment

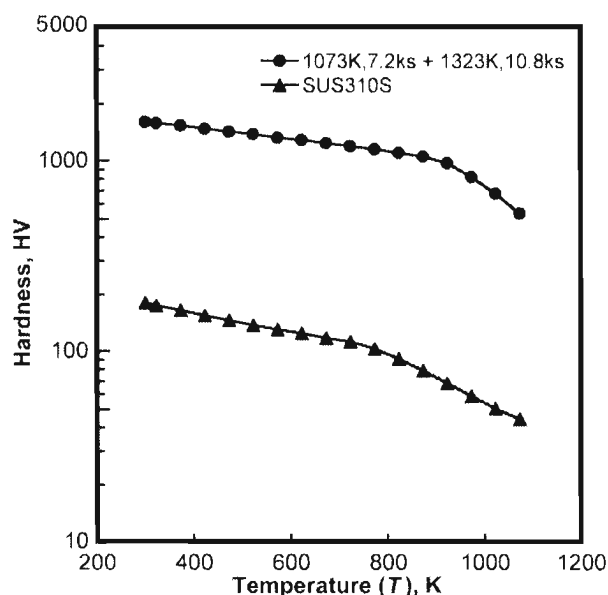


Figure 2 Hot hardness result for chromizing-siliconized and untreated sample surfaces.

conditions and is explained as follows. At 1073 K, Si and Cr were deposited on the surface of the substrate because of their low diffusion rates. However, at 1323 K, the diffusion rates of Si and Cr were greater than those at 1073 K, and therefore they partly penetrated into the substrate. The elements also partly form silicide (Cr₃Si) on the surface of the substrate. The phase transformation from γ-Fe to α-Fe was observed in the substrate. It was concluded that this phase transformation was induced because of the penetration of Si and Cr into the substrate as both the elements promote the formation of ferrite.

The hardness of the chromizing-siliconized and untreated sample surfaces is 1600 HV and 165 HV, respectively. Figure 2 shows a hot hardness result tested at temperatures ranging from 300 K to 1073 K for treated and untreated samples. The treated sample showed higher hardness than the untreated sample, even at high temperature. A gradual decrease in hardness up to a transition temperature, followed by a rapid drop above the temperature in both samples was observed, as shown in Figure 2. Transition temperatures of treated and untreated samples were 930 K and 750 K, respectively. This result indicates that the hardness of the treated sample is higher than 1000 HV relatively up to 930 K. Therefore, it was concluded that the chromizing-siliconizing coating process could be applied to some parts that require wear resistance at high temperature.

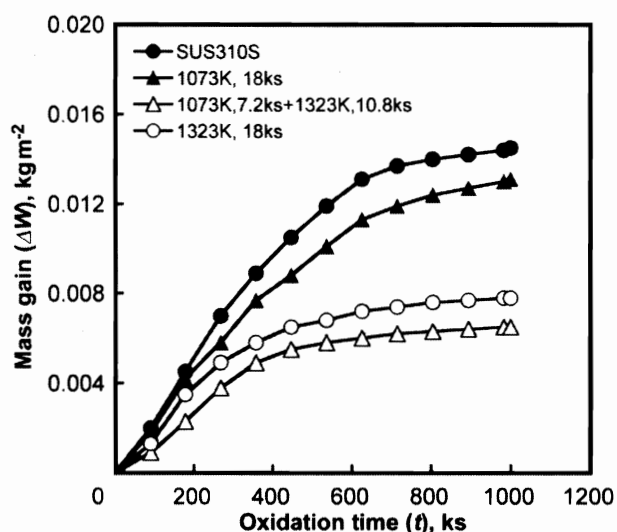


Figure 3 Oxidation characteristics of the chromizing-siliconizing sample for a high-temperature oxidation test conducted at 1073 K.

Figure 3 shows the relationship between oxidation time and mass increase for a high-temperature oxidation test conducted for 1000 ks at 1073 K. Comparison of the treated samples and the untreated SUS310S sample reveals that the mass increase was lower and the high-temperature oxidation resistance was higher for the treated samples in both cases. Comparison of the sample treated by the two-step process and the samples treated by the one-step process reveals that the mass increase was lower and the high-temperature oxidation resistance was greater for the sample treated by the two-step process in both cases. This result indicates that the two-step chromizing-siliconizing process is more advantageous than the 'one-step' process. However, for the sample treated by the one-step process for 18.0 ks at 1073 K, which showed the most significant Si enrichment near the surface as shown in Figure 1, the mass increase was higher and the high-temperature oxidation resistance did not improve significantly. This was because the treatment at the lower temperature of 1073 K causes inhomogeneous diffusion of Fe and Si and void formations in the coating, resulting in the coating becoming ineffective for anti-oxidation.

4. Conclusions

The simultaneous deposition of chromium and silicon on austenitic stainless steel SUS310S using a halide-activated diffusion coating process was performed to improve oxidation and wear properties at high temperatures. The effects of treatment conditions on the properties of coated layers were investigated and the results revealed that by applying a two-step process (at 1073 K for 7.2 ks and at 1323 K for 10.8 ks), relatively large quantities of Si penetrated into the substrate, enriching it to produce a homogeneous coated layer. The result of hot hardness test revealed that the treated sample maintained high hardness up to 900 K. Moreover, the result of an oxidation test indicated that the high-temperature oxidation resistance of the sample treated by the two-step process was higher than

that of an untreated sample and samples treated only by a one-step process.

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