

Effect of Aluminizing Treatment on the Oxidation Properties of 12Cr Heat Resisting Steel

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In order to investigate the effect of aluminization on the oxidation properties of 12Cr martensitic heat resisting steel, a specimen was prepared by forging after centrifugal casting. After aluminizing treatment under various conditions, scanning electron microscopy observation, and hardness, line profile and x-ray diffraction analysis of the alloy layer were performed. The results confirmed that the thickness of the layer of $Al_{13}Fe_4$, with a Vickers hardness of over 880, increased with increasing aluminizing temperature and time. Moreover, it was concluded from the results of the oxidation experiment that the oxidation properties of the aluminized specimen were improved by up to approximately 30 %.

Keywords: alloys, surface modification, diffusion, SEM, aluminizing treatment

1. INTRODUCTION

The diaphragm of a steam generator plays an important role, since it forces vapor from the steam generation turbine to flow in a certain direction and thereby helps to transform heat energy to kinetic energy. To make steam flow in the optimum direction, the power blades are assembled on a rotor that is rotated by controlling the edge angle of the partition; then, electrical power is supplied when operating the generator. This diaphragm consists of outer and inner rings. 9-12Cr martensitic heat resisting steel has superior oxidation properties as well as an excellent high temperature property. The latter is important because the diaphragm is exposed to water vapor when used.

Accordingly, it is preferable to increase the amount of Cr in order to improve the oxidation properties. However, since δ ferrite is formed in the martensitic matrix with increasing amounts of Cr, a dual phase is obtained. When the dual phase is formed, the high temperature properties can be problematic due to the variation of the microstructure. Therefore, a method to maintain the oxidation properties without increasing the amount of Cr in heat resisting steel has been suggested. Immersing Al in the steel matrix is generally known to improve the oxidation, corrosion resistance, heat resistance and wear-resistance properties of steel [1,2].

Many methods [3-6] for pack cementation, such as hot dipping, vacuum deposition and spray coating, have been investigated, with hot dipping being the simplest method for mass production. This is mainly carried out on carbon steel and cast iron but, in addition, can be used in many applications of stainless steel because of advantages [7] such as improvement of corrosion resistance and wear-resistance at high temperature, and prevention of stress corrosion cracking.

In the present study, in order to investigate the oxidation properties of heat resistant aluminized steel, the effects of variations of thickness of alloy layer, structure and hardness on the oxidation properties have been examined.

2. EXPERIMENTAL PROCEDURE

The specimens were prepared by means of centrifugal casting and 30 % forging after melting in a high-frequency melting furnace. Afterwards, the samples were water-washed after removing any grease using 20 % NaOH solution and then picked and water-washed with diluted HCl. After eliminating impurities such as oxide from the surface, the specimens were treated with a water-soluble flux containing NH_4HF , NaF and KCl. As a drying pre-treatment, aluminizing treatment was carried out in a vessel filled with molten aluminum.

The flux containing KCl, NaCl and AlF_3 was placed on molten aluminum to prevent the oxidation of the aluminum during aluminizing. The microstructure and oxidation prop-

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Table 1. Chemical composition of the specimen

Elem.	Cr	Si	Mn	C	P	S	Fe
wt.%	11.6	0.6	0.41	0.12	0.003	0.002	Bal.

erties were then evaluated after water-washing and pickling. The aluminizing treatments were carried out in molten aluminum at controlled temperatures of 700, 750 and 800 °C over periods from 1 minute to 30 minutes to examine the effects of aluminizing temperature and time. Table 1 shows the chemical composition of the specimens. A scanning electron microscope (SEM, S-2400) was used to observe the thickness of the alloy layer. In addition, line profiles of the chemical compositions in each specimen were determined with an electron probe micro-analyzer. In order to evaluate the structure of the alloy layer as a function of depth from the surface, x-ray diffraction analysis was conducted. The oxidation properties were evaluated by measurement of the specimen weight gain under air and water vapor at 600 and 800 °C for 100 hours.

3. RESULTS AND DISCUSSION

3.1. Observation of alloy layer

Fig. 1 shows SEM micrographs for specimens air-cooled after immersing in molten aluminum at 700, 750 and 800 °C for 10 minutes. As can be seen in this figure, an alloy layer (B) was formed between the aluminum (A) and the matrix (C), and the thickness of the layer increased with increasing aluminizing treatment temperature.

Fig. 2 shows the effect of aluminizing treatment time on the formation of the alloy layer at 750 °C in 12Cr martensitic

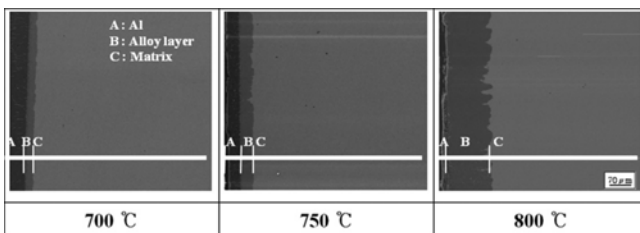


Fig. 1. SEM micrographs showing the effect of the aluminizing treatment temperature for 10 minutes on the alloy layers in 12Cr heat resisting steel.

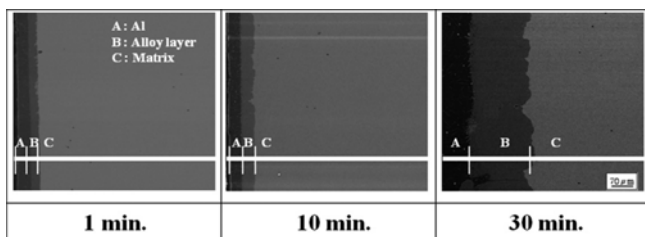


Fig. 2. SEM micrographs showing the effect of aluminizing treatment time on the alloy layers at 750 °C in 12Cr heat resisting steel.

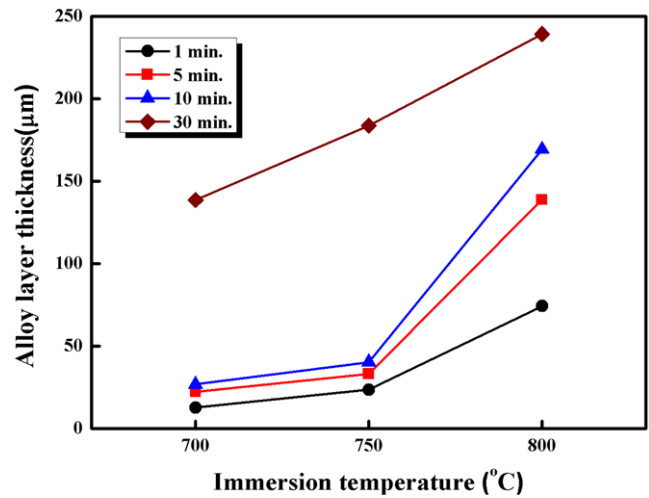


Fig. 3. Variation of alloy layer thickness in aluminizing treatment at various temperatures and for various times in the centrifugal casting and forged 12Cr heat resisting steel.

heat resisting steel. It can be observed that the thickness of the alloy layer increased with the increase in the aluminizing treatment time.

Fig. 3 shows that with increasing aluminizing treatment temperature and time, the thickness of the alloy layer increased. It is suggested that the increase is caused by the increase of Al diffusion velocity as well as by the increase of time for immersion of Al into matrix. The results of the present study are in good agreement with those of other well-known studies [7-13] in that the thickness of the alloy layer formed by hot dipping can be varied depending on the composition of the matrix, the activation treatment of the surface, the chemical composition of the molten aluminum, the immersion temperature and time, and so on.

3.2. Hardness of the alloy layer

Fig. 4(a) and (b) illustrates the variation of hardness of the alloy layer and matrix in aluminized specimens after aluminizing at different temperatures and times, respectively. The thickness of the alloy layer, having a hardness of over 880 Hv, was increased with the increase of the aluminizing temperature and time. It is suggested that this increase of hardness can be caused by the formation of an intermetallic compound. Accordingly, in order to characterize the intermetallic compound formed due to the aluminizing treatment, an XRD analysis was conducted, with results as shown in Fig. 5.

3.3. XRD analysis

To examine the structure of the alloy layer for a specimen aluminized at 750 °C for 30 minutes, XRD analysis was conducted at various depths, namely at the surface, and at 100 µm and 200 µm below the surface. As can be seen in Fig. 5,

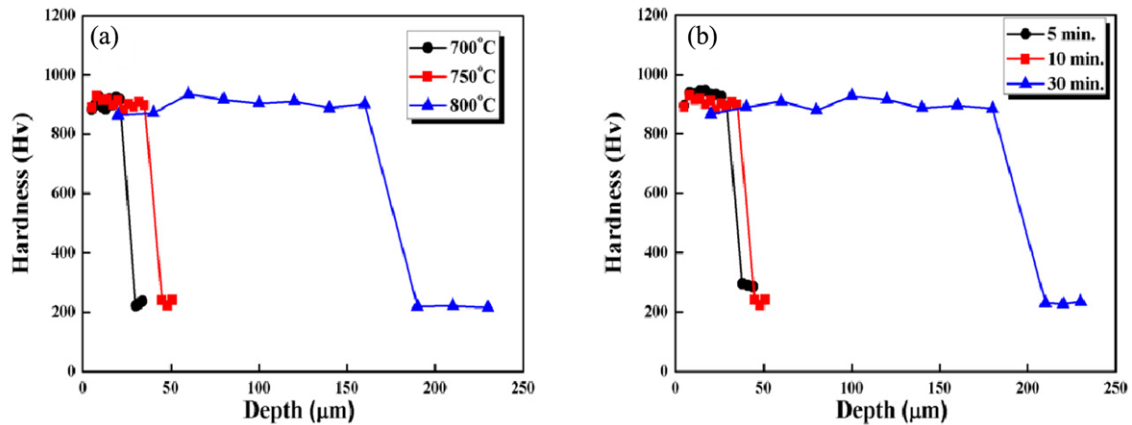


Fig. 4. Hardness as a function of the depth below the surface in 12Cr heat resisting steel for various aluminizing conditions. (a) as a function of temperature with 10 minutes aluminizing (b) as a function of aluminization time at 750 °C.

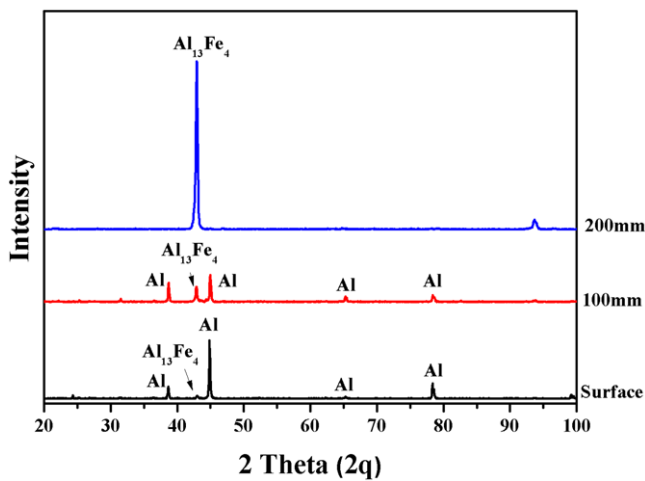


Fig. 5. XRD spectra from the surface of the alloy layer after aluminizing treatment at 750 °C and 30 min. of a centrifugal cast and forged 12Cr heat resisting steel sample.

there exist peaks for both Al and Al₁₃Fe₄ at the surface and at 100 μm below the surface. However it was confirmed that the only peak present below 200 μm depth was that of Al₁₃Fe₄. It is suggested that diffusion of aluminum into the interior of the specimen during the aluminizing treatment contributed to this result. Therefore, the Al concentration decreased from the outside to the inside, as confirmed in this figure.

Although only Al₁₃Fe₄ was formed in the present study, other studies of the aluminization of carbon steel and stainless steel have reported the existence of a variety of compounds, such as FeAl, FeAl₂, FeAl₃ and Fe₂Al₅ [14-16].

3.4. EPMA measurement

When a heat resisting steel is aluminized, an alloy layer is formed during the immersion in Al and this diffuses into the matrix, substituting Al for Fe and Cr. In addition, it is predicted that, as a result, a variation of the C and Cr concentrations will result as the Al diffuses into the specimen.

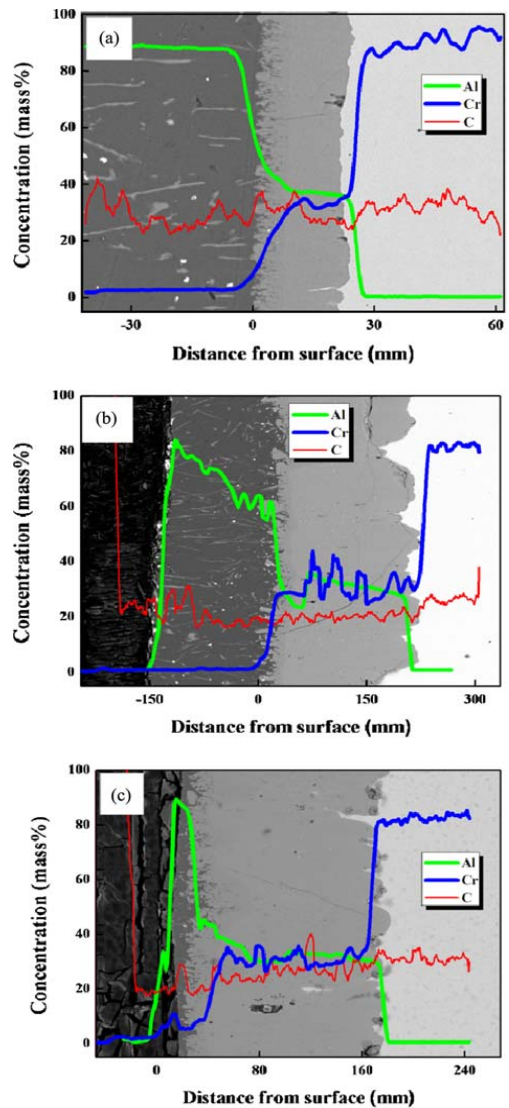


Fig. 6. Cross-sectional micrographs and EPMA line profiles showing the effect of aluminizing treatment temperature and time for 12Cr heat resisting steel.

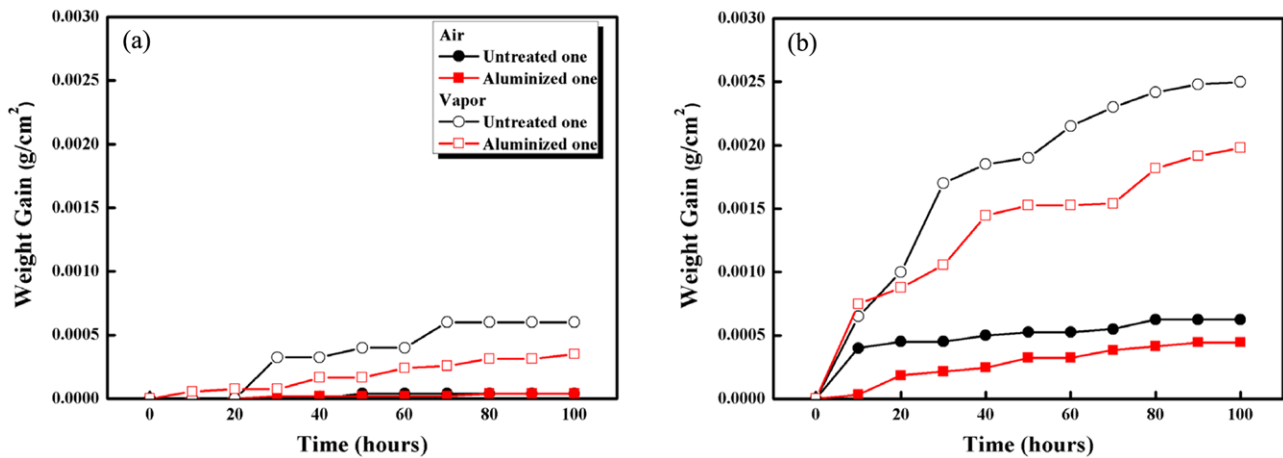


Fig. 7. Weight gain curves during isothermal oxidation exposed to air and water vapor at (a) 600 °C and (b) 800 °C for untreated and aluminized 12Cr heat resisting steel.

To investigate this, EPMA was carried out on a specimen subjected to different aluminizing conditions of temperature and time in order to investigate the immersion and diffusion mechanism for each element. The results are shown in Fig. 6. In both figures, there was no variation of C, which is an interstitial atom, even though Al atoms become immersed in the matrix. However, the Cr concentration in the alloy layer was reduced due to the replacement of Cr with Al.

3.5. Oxidation properties

Fig. 7(a) shows the weight gain curves during isothermal oxidation under air and water vapor at 600 °C for 100 hours for untreated and aluminized 12Cr heat resisting steel in order to investigate the oxidation properties at high temperature. In air, both specimens showed a tendency to increase weight very slightly. However, it was confirmed that there was no difference in weight gain for the untreated and the aluminized specimen. It is suggested that little oxidation occurred since the specimen includes a large concentration of Cr, which provides excellent oxidation properties; also, the experimental temperature was not high enough to lead to oxidation. On the other hand, in water vapor, both specimens suffered similar weight gains until 20 hours of exposure; after that, there was a slight further increase. Compared to that for air, the weight gain from oxidation was slightly higher. In addition, the aluminized specimen exhibited a smaller weight gain than the untreated one, which is the same result as for treatment in air.

Fig. 7(b) shows the weight gain curves during isothermal oxidation in air and water vapor at 800 °C for 100 hours for the untreated and aluminized 12Cr heat resisting steel. Both specimens showed identical behavior, namely that the weight gain from oxidation sharply increased for the first 80 hours and then slightly increased thereafter. It was also confirmed that the weight gain for the aluminized specimen was 30 %, which is as low as that of the untreated sample. The results

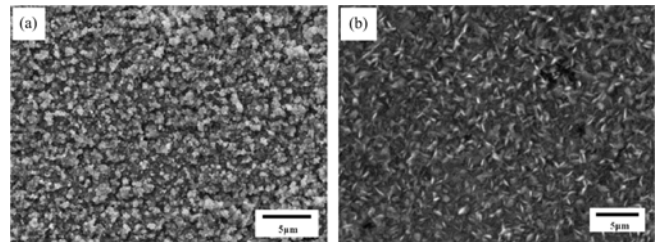


Fig. 8. SEM micrographs of (a) the untreated and (b) the aluminized specimen after the oxidation experiment at 800 °C for 100 hours in air.

can be explained in terms of the formation of a stable Al_2O_3 , Al and $\text{Al}_{13}\text{Fe}_4$ alloy layer, which is well-known to hinder and delay the oxidation [17].

Fig. 8 shows the variation of the surface morphology for the untreated and aluminized specimens, showing that there were considerable variations in the degree of oxidation in air at 800 °C. It is suggested that mainly Cr_2O_3 and Fe_2O_3 oxide scales were formed at the surface of the untreated specimen (the EDX results are not shown in this paper) while Al_2O_3 oxide scales were predominantly formed on the surface of the aluminized specimen. This suggestion is in good agreement with Pillai's report [18]. In addition, it was confirmed that the quantity of scales on the aluminized specimen was lower than was present on the untreated specimen.

4. CONCLUSIONS

In the present study, the effects of an aluminizing treatment on the oxidation properties of 12Cr martensitic heat resisting steel were investigated for the various aluminizing temperatures and times. The conclusions are as follows:

- (1) With an increase in the aluminizing temperature and time, the thickness of the alloy layer increased.
- (2) The alloy layer, formed by means of aluminizing treatment, consisted of $\text{Al}_{13}\text{Fe}_4$ with a hardness of over 880.

(3) When heat resisting steel is aluminized, an alloy layer is formed on immersion in Al, which diffused into the matrix, substituting Al for Fe and Cr. Accordingly, the Cr concentration decreased while the Al concentration increased, going from the surface to the inside of the specimen.

(4) From the results of isothermal oxidation experiments and SEM observations, the oxidation properties in water vapor, as well as in air, were found to have been improved by up to approximately 30 % when the alloy layer was formed during aluminizing treatment.

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