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Microstructure and Oxidation Resistance of Cr–Al–Si Alloys for High-Temperature Applications

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Abstract: Cr–Al alloys are attracting much attention as heat- and corrosion-resistant coating materials due to their excellent high-temperature properties. In order to investigate the effect of aluminum content on the microstructure and oxidation resistance of Cr–Al–Si alloys, cast specimens were prepared by using a vacuum-arc melting furnace, and high-temperature oxidation tests were conducted with the specimens, for 1 h, at 1100 °C, in air. In the case of cast microstructure of Cr–Al–Si alloys, it consists mainly of Cr single phase, up to 5 at.% Al, and AlCr phases were additionally formed in alloys containing 10% Al or more. In the specimen with 20% Al added, CrSi phase was also found in addition to the AlCr phase. The weight change of the specimens heated for 1 h, at 1100 °C, indicated that all had excellent oxidation resistance. However, when the Al content was less than 10%, the weight gain tended to be a little lower than that of 10% or more.

Keywords: high temperature; metal coating; Cr–Al–Si, microstructure

1. Introduction

The demand for alloys that surpass the high-temperature properties of Ni-based superalloys is steadily increasing as the operation temperature of high-temperature components increases. It is a refractory-based alloy having a melting point higher than 1900 °C that is promising as an alternative metallic material [1]. Especially since Cr and Cr–Al alloys are excellent in high temperature oxidation resistance, they are suitable as materials for high-temperature components or oxidation-resistant coating, and related research has been conducted [2–8]. For instance, some research has been carried out to apply Cr or Cr–Al powders to the surface coating of the nuclear fuel cladding by using a laser surface-melting method [8,9]. Recently, a study was conducted that focused on Cr–Al alloys containing Si for the purpose of enhancing the high-temperature hardness and strength of the Cr–Al alloys [10]. Thermal stability of Cr₃Si phase and the possibility of improvement of high-temperature strength due to formation of it have already been reported; however, only a few research studies have been done on the formation of Cr₃Si phase in Cr–Al–Si alloys [11,12]. In addition, although the oxidation resistance due to the formation of Cr and Al oxides in Cr–Al–Si alloys has been studied to some extent [13,14], the microstructure changes due to the addition of Si are still insufficient. For example, it has been reported that, when a certain amount of silicon is added, a Cr₃Si phase is formed, but the critical Si content is related to the amount of Al added, which requires further investigation [10,15].

Various properties, such as oxidation resistance and high-temperature strength, of Cr–Al–Si alloys seem to be closely related to the chemical composition and microstructure. Thermodynamically, SiO₂ is more stable than Cr₂O₃, but Cr oxide can be formed predominately due to a higher activity and faster diffusion in Cr phase. The addition of Si to Cr has been known to improve the oxidation resistance [1]. The formation of Al₂O₃ on the surface of Cr alloys through the addition of aluminum may be also desirable depending on the conditions of use of the material. Although Al and Cr are

oxidized simultaneously during oxidation of Al-added Cr alloys, the replacement of Cr_2O_3 with Al_2O_3 can occur, since the free energy for Al_2O_3 formation is much more negative than that for Cr_2O_3 at high temperatures [3]. However, for most cases, a sufficient amount of Al should be added for continuous surface Al_2O_3 , but it is obviously undesirable to form relatively low melting point AlCr phases in terms of heat resistance. Therefore, knowledge about the microstructure of Cr–Al–Si alloys is the prerequisite for the actual practical use of them. In this study, Cr–5% Si (at.%) alloy was selected as the basic composition, and the difference of the microstructure after casting and high-temperature isothermal heating, according to the amount of Al added, was investigated.

2. Materials and Methods

Cr–5% Si (at.%) with different Al contents (0, 5, 10, and 20 at.%), which are candidates for high-temperature coating materials, were vacuum-arc melted (KHAM-500, Misung S & I, Cheonan, Korea) and cast to produce 35 g of button-shaped ingots. Commercially pure Cr, Al, and Si materials (99.9 wt.%, NeoDM, Daejeon, Korea) were used for the vacuum melting. Then, $10 \times 10 \times 5$ mm plate specimens were prepared by electric-discharge machining the ingots and used for microstructure investigation and a high-temperature oxidation test. Two cast ingots were fabricated for the same composition, and four plate specimens were prepared for each ingot. Cross sections of the plate specimens were mechanically polished by using sandpaper and diamond suspension, with a diameter of 1 μm , to a mirror surface.

In the case of the high-temperature oxidation test, a method of examining and comparing the weight change of the specimen during isothermal heating up to 1 h in an air atmosphere of 1100 °C was applied. Thermogravimetric analysis (TGA, Mettler-Toledo, Zurich, Sweden), with about 200 mg of alloy specimens, was used for the test, and the weight change was measured every 4 s, after reaching the target temperature of 1100 °C.

The alloy microstructure before and after the high-temperature heating was investigated by using a scanning electron microscope (JEOL, Tokyo, Japan) equipped with an energy-dispersive X-ray spectrometer (EDS, JEOL, Tokyo, Japan), and the oxides on the surface of the alloys after the oxidation test were analyzed by using an X-ray diffractometer (XRD, Rigaku, Tokyo, Japan). Cu $K\alpha$ radiation was used for XRD. Micro-hardness of the specimen was measured by using a micro-Vickers tester (Duramin-40, Struers, Cleveland, OH, USA). The applied load condition was 0.2 N for 10 s, and the representative hardness values were determined by randomly measuring 10 times of various specimen parts and averaging them.

3. Results and Discussions

3.1. Microstructure of As-Cast Cr–Al–Si Alloys

Figure 1 shows typical SEM micrographs of as-cast Cr–xAl–5%Si alloys. According to the Cr–Si binary diagram, about 5% Si is expected to be completely dissolved in the Cr matrix, at a high temperature, above 1000 °C. However, as the temperature decreases, the solid solubility decreases, and thus, a Cr_3Si phase may be formed at room temperature [15,16]. On the other hand, the solubility of Al element in Cr matrix is relatively high, and it is expected to be completely dissolved in matrix up to 10% Al, even at room temperature [16]. Virtually, single Cr-phase is observed in the case of 0% and 5% Al-added alloys. Due to the small size of the cast specimens produced by vacuum-arc melting, the solidification rate is comparatively high, and the alloying elements are considered to be slightly supersaturated. In the case of alloys containing 10% or 20% Al, dark phases were formed on the Cr base, showing a different microstructure from that of the low Al alloy.

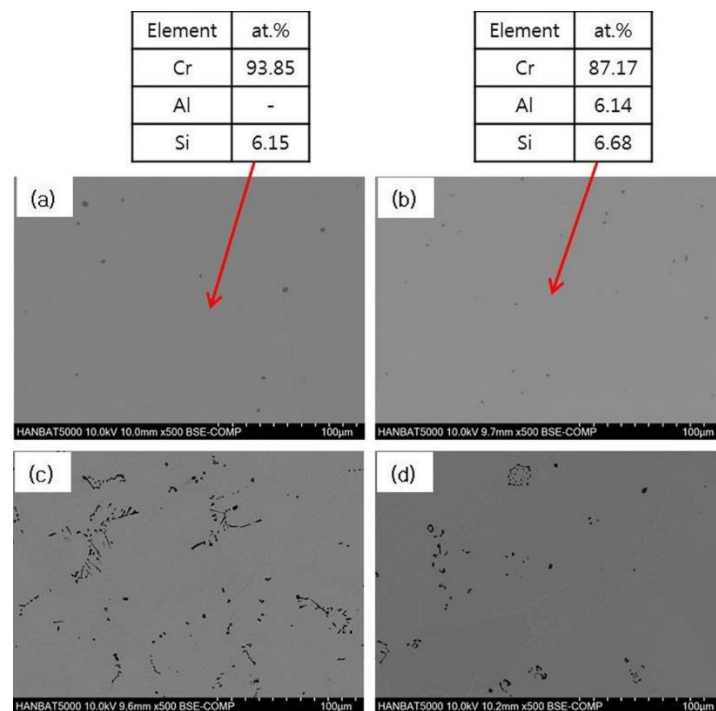


Figure 1. SEM-EDS analyses of as-cast Cr-xAl-5%Si alloys (500X): (a) 0% Al; (b) 5% Al; (c) 10% Al; and (d) 20% Al.

The microstructure of Cr-Al-Si alloys containing 10% or 20% of Al was observed and analyzed at higher magnification, as shown in Figure 2. Considering the literature and the EDS analysis results, the dark phase is assumed to be Al_8Cr_5 or Al_9Cr_4 [17]. Al_9Cr_4 phase is sometimes treated as an extension of the Al_8Cr_5 phase [15,18]. The maximum amount of Si dissolved in Al_8Cr_5 phase was known to be 5.6%, but an amount smaller than that, about 2.3%, was measured in this study [18]. Meanwhile, it was observed that a large amount of CrSi phase was formed, in addition to some AlCr phase in the alloy containing 20% Al, and the CrSi phase is considered to be Cr_3Si , based on the literature and EDS analysis results [16]. It is interesting to note that, although Al content is further increased, the amount of AlCr phase is not increased and instead a large amount of CrSi phase is formed. This phenomenon is presumed to have occurred because the element of Si dissolved in the Cr matrix was released from the base due to the precipitation of the CrSi phase when the Al content was increased above a certain amount.

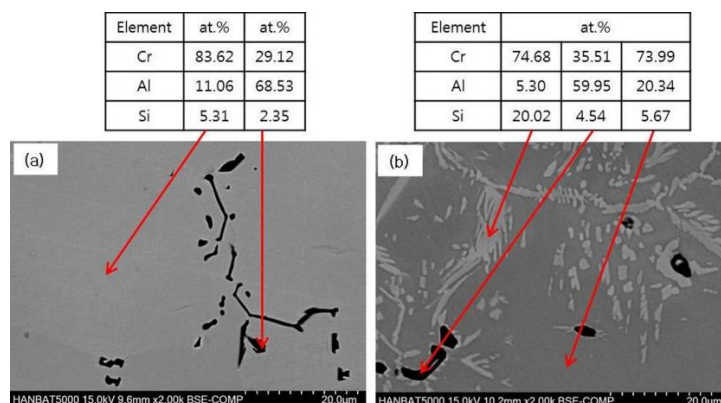


Figure 2. SEM-EDS analyses of as-cast Cr-xAl-5%Si alloys (2000X): (a) 10%Al; (b) 20%Al.

Figure 3 indicates that the micro-hardness of Cr–Al–Si alloys increases in proportion to the aluminum content. Since aluminum and silicon added as alloying elements are completely dissolved in the Cr–xAl–5%Si alloys' matrix up to 5% Al, solid solution hardening seems to be the main reason for the increase in hardness of the 5% Al-added alloy. In the case of 10% Al-added alloy, the increase in hardness due to the formation of the AlCr phase may be added. A more significant increase in hardness was observed at 20% Al, which seems to be associated with the formation of Cr₃Si phase. Cr₃Si is a very hard phase, and the hardness of Cr₃Si phase on VHN basis has been reported to be more than eight times that of Cr phase [19]. Since the Cr₃Si is stable at high temperatures [11,12], formation of the Cr₃Si phase is expected to improve not only the wear resistance but also the strength of the Cr–Al–Si alloys at high temperatures.

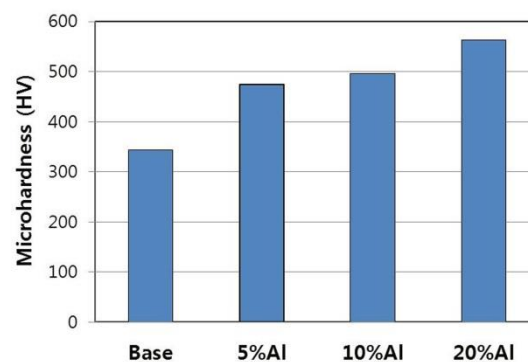


Figure 3. Micro-hardness of as-cast Cr–xAl–5%Si alloys.

3.2. Microstructural Change after the High-Temperature Oxidation Test

The microstructure of Cr–xAl–5%Si alloys with 5% and 10% Al after 1 h in air at 1100 °C is shown in Figure 4. The isothermally heated microstructure of 0% Al-added alloy is composed of virtually single Cr-phase structure, as in the cast state. In the case of 5% Al-added alloy, a few AlCr phases were formed after high-temperature heating, unlike the casting state, and it is presumed that this phase was mainly formed during the cooling process. In the case of 10% Al-added alloy, more AlCr phases were formed than in 5% Al-added alloy, and any CrSi phases were not observed in both alloys.

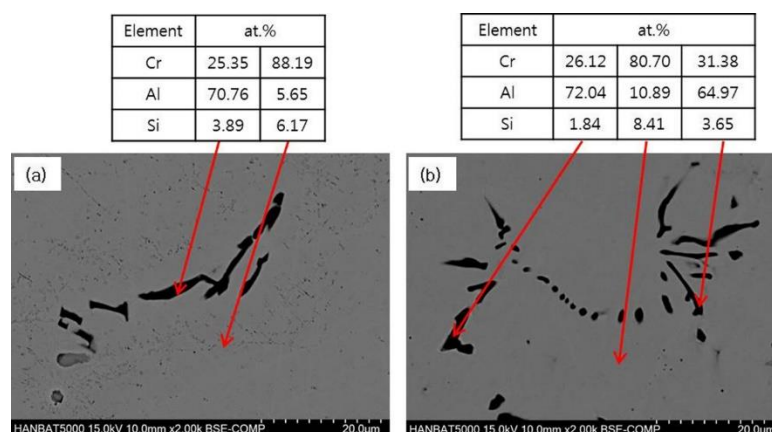


Figure 4. SEM-EDS analyses of isothermally heated Cr–xAl–5%Si alloys (2000X): (a) 5% Al, (b) 10% Al.

Figure 5 shows the microstructure after heating 20% Al-added alloy at 1100 °C, and it can be seen that a large amount of Cr₃Si phase, which is seen as a bright color, was formed. Occasionally, Al-rich phases were observed in some regions, but the Al₈Cr₅ (or Al₉Cr₄) phases, which were observed in the cast microstructure, could no longer be found. Due to solidification segregation, there can be regions with high Al concentration in the cast specimen, where small liquid pools may be formed

during the high-temperature heating. It is estimated that a few Al-rich phases were formed during the solidification of the liquid parts.

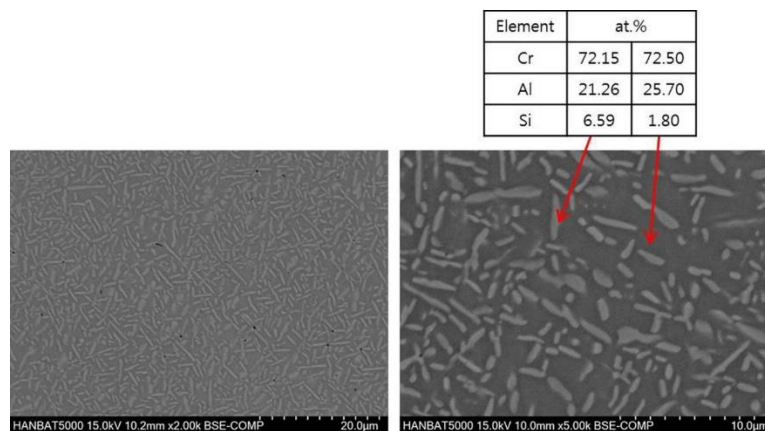


Figure 5. SEM–EDS analyses of isothermally heated Cr-20%Al-5%Si alloys (2000X).

3.3. Oxidation Resistance of Cr–Al–Si Alloys

Even after 1 h heating at 1100 °C in air, the surface of the specimens was relatively good, as shown in Figure 6, and the excellent oxidation resistance of these alloys was confirmed. However, a slight spalling occurred in some parts of the specimen, and this may affect the weight of the specimens a little. This spalling is thought to occur mainly during cooling because of the large difference in coefficient of thermal expansion between surface oxide and alloy substrate.

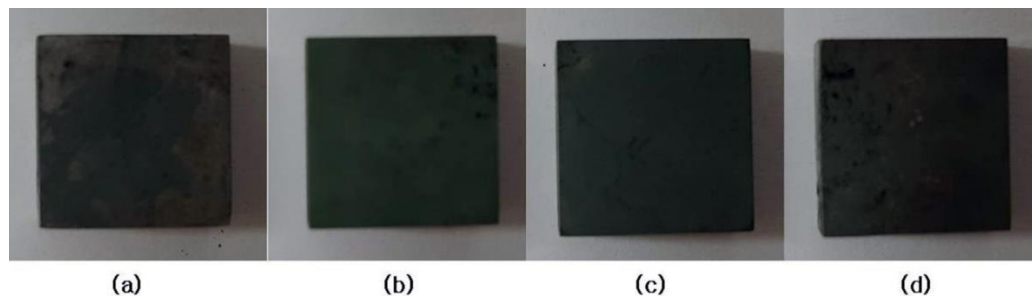


Figure 6. Appearance of Cr–xAl–5%Si alloy surfaces after the isothermal heating: (a) 0% Al; (b) 5% Al; (c) 10% Al; and (d) 20% Al.

As indicated in Figure 7, when the oxidation resistance was evaluated based on the weight change, the increase of Al addition did not increase the oxidation resistance of the Cr–Al–Si alloys, but rather decreased slightly. The weight increase of 5% Al alloy was slightly lower than that of base alloy (0% Al), and those of other high Al alloys was apparently larger. When spalling occurs in the oxidation process, it is not accurate to evaluate oxidation resistance only by weight increase. On the other hand, the reason why the weight gain is higher in the high-Al alloys is believed to be partly due to the formation of alumina in addition to Cr oxide.

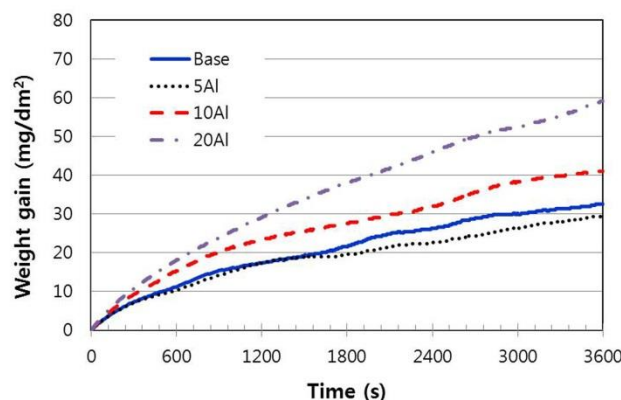


Figure 7. Oxidation behavior of Cr-xAl-5%Si alloys during the isothermal heating at 1100 °C.

The largest difference between the surface oxides of high- and low-Al alloys is the presence or absence of alumina, as shown in Figure 8. In alloys with less than 10% Al, most of the oxides were Cr_2O_3 , while in more than 10% Al-added alloys, additional Al_2O_3 was observed. In particular, a significant amount of Al_2O_3 was formed on the surface of the 20% Al-added alloy. Both Cr_2O_3 and Al_2O_3 are generally stable at high temperatures, but Al is known to have more oxidation tendency and to be more stable. Thus, if the Al content and the heating time are sufficient, Al_2O_3 may form a continuous external layer over most of the specimen's surface [8,20]. Under the oxidation condition of the current study, 20% Al of the experiment alloy was considered to be insufficient to give a complete external scale of Al_2O_3 . However, if exposed to a high temperature for a long time, it is expected that the corrosion resistance of the high-Al alloy can be superior to those of low-Al alloys.

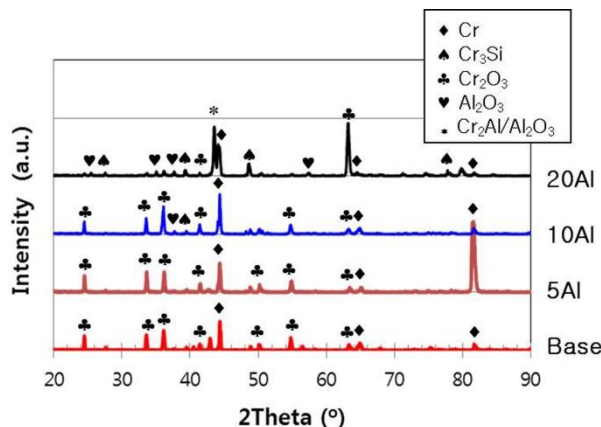


Figure 8. XRD analysis results for the surfaces of Cr-xAl-5%Si alloys after the isothermal heating.

4. Conclusions

It was observed that the as-cast microstructure of Cr-xAl-5%Si alloys was mainly composed of Cr single phase, up to 5% Al, and Al_8Cr_5 phase was additionally formed in the case of 10% or more of Al. When 20% Al was added, Cr_3Si phase were also found. Meanwhile, the weight change of the specimens heated for 1 h at 1100 °C in air showed that all experiment alloys had excellent oxidation resistance. Although the microstructure change of the most alloys after the isothermal heating was not remarkable, it is noteworthy that Al_8Cr_5 phase disappeared and a large amount of Cr_3Si phase was formed in the 20% Al-added alloy.

The results of XRD analysis showed that the Al_2O_3 oxide film was formed with Cr_2O_3 in the high Al alloys, whereas only the Cr_2O_3 oxide film was mainly formed on the surfaces of the lower Al containing alloy specimens. It is expected that high Al containing Cr-Al-Si alloys, such as 20%

Al, can be made into powders and utilized as high-oxidation and wear-resistant coating materials for thermal spraying or laser coating.

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Conflicts of Interest: The authors declare no conflict of interest.

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