Preparation of Ti Ternary Alloys by Addition of Si to Ti-Mo Alloy Scraps for Carbonitride Application

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In this study, Ti-Mo-Si ternary alloy ingots were prepared by the addition of Si (0.25–2.0 mass%) to Ti-10Mo alloy scraps in order to produce the raw materials for titanium carbonitride composites. To investigate the effects of Si addition, the prepared alloys were subjected to hardness, tensile strength, grain size, and phase analyses. The Si-added alloys showed no major changes in their O, N, and C impurity contents. Their hardness increased remarkably in proportion to an increase in the Si content, from 435 Hv to 601 Hv at 2.0 mass%. The tensile strength increased with Si addition up to a maximum of 1.0 mass%, reaching 883 MPa, but after this peak, it decreased sharply because of the brittleness that arose by the formation of titanium silicide.

Keywords: titanium-molybdenum-silicon alloys, titanium carbonitride, recycling, silicide

1. Introduction

Cermets, which are cutting tool materials, are manufactured by mixing titanium carbide and carbonitride, both of which have excellent mechanical characteristics like high hardness, with high-toughness metals such as Ni and Co. Although titanium cermets have advantages in terms of high hardness, their major drawback is their low toughness.1,2,3,4 Given this fact, mixing titanium carbide and carbonitride with secondary carbides and carbonitrides, including those of Mo, Ta, and W, has attracted attention as a method to enhance the toughness and thermal stability of cermets. In particular, Mo has an advantage over Ta and W because of its lower melting point, convenient processing, and cost effectiveness. In titanium and titanium carbonitride, Ti-Mo alloys are known to show an improved wear property because of the formation of a MoO3 lubrication film on the high-hardness wear track as a result of the solid solution strengthening by Mo.4,5 Unlike Ni and Co, which are not capable of forming carbides and carbonitrides, Mo, a titanium alloying element, forms carbonitride composites such as in the forms of (Ti, Mo)C or (Ti, Mo)CN. This formation of the carbonitride composites is expected to contribute to improvements in the properties of titanium cermets. In addition, there have been many attempts to enhance the mechanical properties of cermets to meet the rapidly growing industry requirements. The production of multicomponent alloys is one of these, and Si, in particular, has emerged as a promising candidate for such alloys.6,7 Jeon et al.8 reported that high-hardness titanium nitride coating materials with significantly improved hardness were successfully manufactured by adding Si to Ti-Mo alloy.

In this study, titanium alloy scraps were used to investigate the properties of the raw materials for such carbonitride composites utilizing titanium alloy scraps. Experiments were conducted in which Ti ternary alloys were produced by adding 0.25–2.0 mass% of Si to Ti-10Mo alloy scraps, and the effects of the Si addition were examined by analyzing its hardness, tensile strength, grain size, and phase.

2. Experimental

The Ti-Mo alloy scraps that were used as a base material were consumable-electrode cuttings from the vacuum arc remelting (VAR) process. The alloys were prepared at a ratio of 9 : 1 (w/w). Si granules (High Purity Chemicals, 99.9%) at 0.25, 0.5, 0.75, 1.0, 1.5, and 2.0 mass% were added to Ti-10Mo alloy scraps, and then 35 g button-type ingots were manufactured. This was followed by four cycles of back and forth melting process to assure the homogeneity of the alloys. The gas impurity content of each ingot was analyzed using a LECO gas analyzer (TCH-600, CS-600). The hardness changes, in response to the amount of added Si, were measured by applying a load of 250 g for 10 s using a Vickers hardness tester (Akashi, MVK-E). The tensile strength and elongation were assessed by applying a load of 2 tons at a tension speed of 1.5 mm/min, utilizing a universal tester (MTDI UT-100). An optical microscope was used to examine the changes in the grain size. Specimens were polished with SiC paper and micro-cloth, and were etched with a solution of HF : HNO3 : H2O = 3 mL : 6 mL : 18 mL. An X-ray diffraction (XRD, Rigaku RTP 300 RC) analysis was performed to investigate the changes in the ingot phase with respect to the Si addition.

3. Results and Discussion

Figure 1 shows the results of the O, N, and C impurity analyses with respect to the Si content in the Ti-Mo-Si alloys. Even though gaseous impurities in small quantities, when present at interstitial sites, improve titanium’s specific mechanical properties, at high concentrations, they are major

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(Received August 5, 2014; Accepted October 22, 2014; Published November 29, 2014)
impurities that cause brittleness in titanium. This is especially true in carbonitride manufacturing as the amount of C and N to be added is determined during the synthesis, and addition of correct amounts is of paramount importance. The baseline contents of O, N, and C in the Ti-10Mo were 1480, 47, and 97 ppm, respectively. On an average, O, N, and C contents were measured to be 1450, 50, and 75 ppm, respectively, in the Si-added alloys, manifesting no significant changes. Meanwhile, we confirmed that no contamination or degassing of the impurities in the titanium alloys occurred during the vacuum arc melting in an Ar atmosphere. Consequently, only the amount of added Si was considered in the next mechanical property analyses, without considering the effects of gas impurities.

Figure 2(a) shows the hardness values of the Ti-Mo-Si alloy specimens, as measured with a Vickers hardness tester. The hardness of the base material Ti-10Mo alloy was found to be 435 Hv. The 0.25 mass% and 2 mass% Si-added alloys showed increased hardness values of 459 Hv and 601 Hv, respectively. In others words, the hardness of the 2 mass% Si-added Ti-10Mo alloy showed an increase of 38%. The improved hardness by adding Si to titanium alloys may be explained by the following effects. First, the Si atoms enhance the solid solution strength of the alloying elements in the matrix. It is known that the added Si atoms restrict the intra-matrix dislocation, thereby increasing its hardness. Second, Si-addition is believed to enhance the grain refinement. Bermingham et al. found that Si in titanium is one of the largest grain refinement elements, exceeded in ability only by B and O.

The tensile strength and elongation of the Ti-Mo-Si alloy specimens were measured, and the results are listed in Fig. 2(b). The initial Ti-10Mo alloy possessed a tensile strength and elongation of 753 MPa and 21.2%, respectively. The tensile strength increased to 883 MPa when 1.0 mass% Si was added to the Ti-10Mo alloy, whereas a remarkably decreased tensile strength, down to 423 MPa, was observed in the 2.0 mass% Si-added alloy. The tensile strength of the Ti-Mo-Si alloy was gradually elevated in proportion to the amount of added Si and resulted in an increase of approximately 17% on 1.0 mass% Si addition. The elongation, on the other hand, decreased from 21.2% to 10.4%. It is a generally recognized fact that an increase in tensile strength induced by solid elements during the alloying of metals entails a decrease in the elongation. As shown in Fig. 2(b), a markedly decreased elongation of 11.2% was measured at 0.5 mass% Si addition, and then no major changes were observed up to 1.0 mass%. To explain this phenomenon, it may be assumed that the elongation is relatively less influenced by Si, which has a smaller atomic diameter than titanium and Mo, because of the enlarged β phase, i.e., the BCC structure, by adding Mo. In the 1.5 mass% and 2.0 mass% Si-added alloys, the tensile strength and elongation were reduced sharply. This result is in agreement with a study conducted by Li et al., reporting that the strength and elongation decreased with the addition of a certain amount of Si. According to the study by Li et al., an excessive Si addition increased the production of the α’ phase within the β-titanium matrix, thereby decreasing the strength and elongation. In this context, Yang et al. reported that the formation of titanium silicide is the main cause of this reduced strength and elongation when an excessive amount of Si is added. In order to clarify these causes, we investigated the grain size and phase changes in the Ti-Mo-Si alloys in the present study. Figure 3 shows the changes in the grain size with respect to the amount of added Si. It was observed that the grain size of the Ti-10Mo alloys ranged approximately between 500 and 700 µm on average and then slightly decreased with an increase in the Si content. The grain size tended to decrease to around 300–400 µm at 0.75 mass% and ultimately down to 100–150 µm at 2.0 mass% Si addition. Such a reduction in grain size, which is drastically lower than that of pure titanium, is presumably because of solid solution strengthening induced by the Mo addition. Therefore, a continuous decrease in the grain size in the Ti-Mo-Si alloys with respect to the Si addition is observed up to
2.0 mass%, which appears to have influenced the increase in the hardness and tensile strength. However, the mere function of a grain size reduction by adding Si was not sufficient to clarify the causes of the decreased tensile strength and elongation in the Ti-10Mo-1.5Si and Ti-10Mo-2.0Si alloys. To clearly elucidate the causes, we examined the phase changes in the Ti-Mo-Si alloys in response to the Si addition. Figure 4 illustrates the XRD patterns. First, $\alpha$, $\alpha''$, and $\beta$-titanium peaks were observed in the Ti-10Mo alloys, and there were no major changes in the peaks in the Si-added alloys. On the other hand, the alloys with the 1.5 mass% and 2.0 mass% Si additions showed the generation of the Ti$_5$Si$_3$ peak. As mentioned in a study by Yang et al.,$^{13}$ this may be because of the brittleness induced by distributed titanium silicide within the matrices. From the above result of our hardness measurement, it can be also considered that the lineal increase of the hardness was affected by the Ti$_5$Si$_3$ precipitates observed at the Ti-10Mo-1.5Si and Ti-10Mo-2.0Si alloys as well as the grain refinement. Through the analysis of the mechanical properties listed above, we confirmed that the mechanical properties of the Ti-Mo-Si alloys were improved when Si was added up to 1.0 mass%. Specifically, the Ti-10Mo-1.0Si alloy showed superior mechanical properties with a hardness of 502 Hv, tensile strength of 883 MPa, and elongation of 10.4%, which is a great improvement, even surpassing Ti-6Al-4V, which is a representative titanium alloy. In addition, adding Si to titanium is known to enhance its thermal property. Thus, the Ti-10Mo-1.0Si alloy would also be suitable as a thermal structural material in the production of gas turbines and engine covers, in addition to its use as a raw material for titanium carbonitride composites. Furthermore, Li et al. observed improved fracture toughness in composites when the titanium silicide Ti$_5$Si$_3$ was synthesized with titanium carbide, and ascribed this to the dispersion strength of the Ti$_5$Si$_3$ and titanium carbide composites.$^{14}$ In the present study, the raw materials for complex carbonitride composites were prepared utilizing titanium alloy scraps, which may contribute to ensuring the homogeneity of the constituents when manufacturing carbonitride composites, as well as to resource recycling. In a follow-up study, complex carbonitrides will be prepared using Ti-Mo-Si alloys as raw materials, and their properties will be analyzed.

4. Conclusions

In this study, we assessed the applicability of carbonitride composites by preparing Si-added ternary alloy ingots as raw
materials, while utilizing titanium alloy scraps. When 0.25–2.0 mass% Si was added to Ti-10Mo alloys, the hardness was observed to improve substantially as a result of solid solution strengthening and grain refinement. The tensile strength of each ingot also increased, reaching its peak increase at the 1.0 mass% Si addition, followed by a sharp decrease afterward because of the brittleness induced by the formation of titanium silicide within the ingot. The elongation tended to decrease in proportion to the increase in the Si addition.

Acknowledgments

This research was supported by the Basic Research Project of the Korea Institute of Geoscience and Mineral Resources (KIGAM) funded by the Ministry of Knowledge Economy of Korea and this research was partially supported by Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education (No. 2014R1A1A2058656).

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