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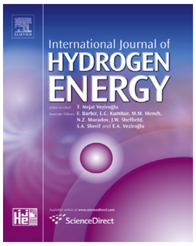

Review Article

Brief review of removal effect of hydrogen-plasma arc melting on refining of pure titanium and titanium alloys

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ABSTRACT

In this study, the effect of hydrogen-plasma arc melting (HPAM) on the removal of metallic and gaseous impurities from pure titanium and titanium alloys is briefly reviewed according to the previous results and a newly added experiment. The highest removal degree (RD) of metallic impurities from pure titanium by HPAM with an Ar-20 vol.% of H_2 gas is 84.8%. In the titanium alloys, the RD values of the metallic impurities of the Ti–Ni, Ti–Mo, Ti–Al, and Ti–6Al–4V alloys regarding HPAM with an Ar-20 vol.% of H_2 gas are 82.6%, 86.2%, 49.1%, and 76.6%, respectively. The total amount of gaseous impurities such as O, N, C, and H was decreased to 962 ppm from 2697 ppm, whereby a high RD value of 64.6% is shown despite the strong affinity of titanium regarding gaseous elements. It is suggested that HPAM exerts a dramatic effect on the removal of metallic impurities from pure titanium and titanium alloys, and it is appropriate for the refining of titanium alloys whereby a significant weight loss needs to be avoided. Thereby, HPAM process can be applied to industrial refining of commercial titanium and titanium alloys.

Contents

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Introduction

In recent years, high-purity metals have been commercially prepared for the electronics and aerospace industries [1–8]. In the purification process of various metals and alloys, plasma arc melting (PAM) is well known as a melting method that is more practical and useful than electron beam melting (EBM) and vacuum arc melting (VAM) [9–12]. The advantages of the PAM method are an operating cost that is lower than that of EBM and a purification effect that is higher than that of VAM. In general, Ar gas is used as the plasma-generating element for PAM [13–16], and therefore a significant refining effect cannot be expected; alternatively, the addition of H_2 to Ar-plasma gas enhances the removal of numerous metallic impurities from molten metals such as Zr, Nb, Mo, and Ta [17–21]. In addition, the addition of H_2 to Ar-plasma gas has removed gaseous impurities such as O, N, and C from ferrous and refractory metals [22–24]. This Ar–H_2 PAM is called “Hydrogen-plasma Arc Melting (HPAM).” For the removal of metallic impurities from raw metals during HPAM, impurities that are more volatile than a molten metal can be reduced more quickly, and the reduction rates are enhanced with increases of the H_2 content in the plasma gas [13,18,21,25]. HPAM is therefore considered a very attractive method for the refining and purification of refractory metals with high-temperature melting points because almost all metallic impurities are considerably more volatile than molten refractory metals.

During the purification of titanium, the removal of the gas impurities from titanium is very important but also difficult when compared to the removal processes regarding other metals; this is especially the case for oxygen, as the maximum solubility of oxygen is approximately 30 at.% in titanium, and dissolved oxygen largely affects the physical, mechanical, and electrical properties of titanium [26–30]. Oxygen removal from titanium is very difficult, because the solubility of titanium is very large and its affinity with oxygen is strong; furthermore, the titanium-oxide layer on the surface of titanium is very strong and stable [31,32]. The most common process of oxygen removal regarding titanium involves the use of a deoxidation agent that has a higher affinity with oxygen such as Ca [33–39]; therefore, the effect of HPAM on the removal of metallic impurities from pure titanium and titanium alloys with binary [40,41] and ternary systems has been clarified in this paper through a newly added experiment as well as previous studies. In addition, the reduction effect of HPAM on gaseous impurities such as O, N, and C with respect to pure titanium was also evaluated.

Experimental methods

In the case of HPAM for pure titanium, commercial titanium sponges (above a 99.7% purity according to the supplier) were used as the raw material. The titanium sponges (30 g) were placed on a water-cooled Cu crucible, where they melted for 10 min–60 min with the use of only-Ar (10 vol.%) and Ar–H_2 (20 vol.%) PAM. For a comparison with the refining effect of titanium sponges that is obtained at the same power for the only-Ar and Ar–H_2 PAM, the power of the plasma arc was set as 4.3 kW. The specimen after the first melting was melted again for the same time duration after it was turned upside down for a uniform refining; therefore, the melting time is a total of both of the times. The flow rate of the plasma-generating gas that was introduced to the plasma torch was constantly 5 L/min [40]. The impurity concentrations in the titanium before and after the HPAM were determined using GDMS (VG ELEMENTAL, VG-9000). For the HPAM of the titanium alloys, the Ti–Ni, Ti–Mo, Ti–Al, and Ti–6Al–4V alloys were used. The Ti–Ni and Ti–Mo alloys were the cutting scraps of consumable electrodes that are used for the vacuum arc-remelting (VAR) process. The weight ratios of the Ti–Ni and Ti–Mo alloy compositions are 7:3 and 9:1, respectively, while the Ti–Al alloy was a sputtering target scrap with a weight ratio of 65:35 and the Ti–6Al–4V alloys were post-production rod scraps. For the HPAM-refinement process, 35 g of each of the titanium alloys were inserted into the HPAM chamber. At the beginning of the melting, only Ar-plasma gas used, and this was followed by the introduction of H_2 after the formation of a molten pool. The Ar and H_2 gases were mixed and introduced into the plasma torch at a flow rate of 15 L/min. The H_2 content in the plasma gas is 20 vol.%. The total melting time for each specimen is 10 min and 20 min, respectively [41]. An X-ray diffraction (XRD) analysis (Rigaku, RTP 300 RC) was performed to analyze the phases before and after the refining of the titanium alloys. The concentrations of the metallic impurities in the titanium alloys before and after the HPAM were determined using GDMS (Autoconcept GD90, MSI Ltd.). The Autoconcept GD90 has a higher resolution and transmission than those of VG9000, and GD90 provides a precisions of 1% RSD (relative standard deviation) and accuracies better than 2% RSD. Alternatively, it is kwon that VG90 instruments provide reliable quantitative data to sub-ppb levels with reproducibility of about 10% [42]. For the reduction of the gaseous impurities from the pure titanium, commercial titanium sponges of ASTM 3 grades (above a 99.9 mass % purity, Sigma–Aldrich, Inc.) were used as the starting material. After the insertion of 30 g of the titanium sponge into the HPAM chamber, the chamber was evacuated to a vacuum of 1×10^{-3} torr. After the evacuation, ultra-pure Ar was introduced into the melting chamber under a pressure of 500 torr–600 torr. The ultra-pure Ar and H_2 gases were then mixed and introduced into the plasma torch at a flow rate of 10 L/min. The H_2-gas content in the plasma gas is 20 vol.%. The titanium sponge was melted for 5 min–30 min by the HPAM with 10 kW of electric power. The gaseous impurities, including the O, N, C, and H concentrations, in the refined ingots and raw titanium were measured using a LECO gas analyzer (TCH-600, CS-600).

Results and discussion

First, the metallic-impurity-removal amount was evaluated for the pure titanium. The GDMS results of the pure titanium that was melted by the only-Ar PAM for 40 min and by the Ar-10%-H_2 and Ar-20%-H_2 PAM for 10 min, 20 min, 40 min, and 60 min were reported in previous work [40]. The removal

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