



Temperature-dependent Ta hydride formation for recycling of Ta scraps: Experimental and thermodynamic investigations



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ABSTRACT

We report on the theoretical and experimental investigations about the Ta-hydride formation depending on the temperature for recycling of Ta scraps. The structural investigations based on scanning electron microscope and X-ray diffraction (XRD) showed that the amount of hydrogen incorporated into the Ta matrix varied with hydridation temperature. The XRD measurement showed that the H/Ta mole ratio in Ta-hydride increased with increasing the hydridation temperature up to 700 °C and then decreased with increasing the temperature furthermore. Depending on the hydridation temperature, various phase of Ta-hydride, such as TaH_{0.93} and Ta₂H were formed and this hydride process was verified by thermodynamic analysis.

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1. Introduction

Tantalum (Ta), a refractory metal, has been regarded as a fascinating material for electronic, thermal and structural applications due to its excellent properties, such as low temperature coefficient of resistance, stable specific resistance, large density of electrical charges, high density (16.65 g/cm³), high melting temperature of 2996 °C, and strong corrosion resistance [1]. Because of their remarkable performances, high purity Ta powder materials are demanded in many applications, including capacitors, surface acoustic wave filters, dental implants, and heat exchangers [2]. Even though its applications are becoming widened, the production of Ta is limited due to its rarity associated with production only in the conflict regions [2–4]. Therefore recycling the Ta from the scraps and wastes becoming an important part in the production of pure Ta, for instant, around 15–30% of the total global Ta supply in 2000 and 2001 were from the recycled Ta [3,4]. As a fabrication process of high purity Ta powders, wet process based on the solvent extraction, Na reduction, Ma vapor reduction and dry process based on e-beam melting and vacuum arc melting methods have been developed [4–7]. However, those methods are suffering from the problems related with non-eco friendly, highly cost, and complicated processes. To circumvent

these problems, a hydride-dehydride (HDH) process has been recognized and well established for the production of titanium as well as zirconium and vanadium materials [8]. This method possesses low price and easily applicable for the mass production. This process necessarily comprises the formation of brittle metal hydrides that can be easily crushed, milled, and screened to produce fine metal powders. However, in the case of Ta, the formation of Ta-hydride has not been fully understood in experiments as well as in thermodynamics [9]. According to the previous study about the thermodynamic study on the Ta-hydride system, nine ordered phases of Ta-hydride with different composition have been shown to exist at low temperatures [10]. Therefore, to establish the HDH process for the high purity Ta powders by recycling process, Ta-hydride formation should be fully understood based on thermodynamic analysis as well as experiment in the practical atmosphere. In this study, we investigated the temperature-dependent Ta-hydride formation process by hydrating the Ta scrap in hydrogen atmosphere and studied theoretically based on a thermodynamic calculation.

2. Experimental procedure

Ta turning scrap (purchased from Korea Platinum Group Metals Co., Ltd.) was used for the Ta-hydride formation. Before the hydridation process, the Ta turning scrap was cut into small pieces with size around

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5 mm length. These small pieces of Ta scrap samples were chemically cleaned by using acetone and ethanol to remove cutting oil and dusts in ultrasonic bath. Purity of the initial Ta scrap measured by X-ray fluorescence (XRF) was 99.6% including impurities mostly composed of Al and Fe. To remove these impurities, mixed solution of HCl, H₂SO₄, and HNO₃ was used as a pickling solution. The cleaned Ta scraps were loaded into the hydrogen charging chamber for hydridation process. The hydridation process was conducted at the pressure of 10⁻⁵ mbar for 3 h in the hydrogen atmosphere at different temperature. The hydridation temperature was varied from 200 to 900 °C. After hydridation process, Ta-hydride was milled for 5 min at room temperature. The structural properties of the Ta-hydride powders were investigated by field emission-scanning electron microscopy (FE-SEM, Hitachi S-4800) and X-ray diffraction (XRD, Rigaku D/MAX 2200H) by using Cu-K α radiation at 50 kV and 100 mA.

3. Results and discussions

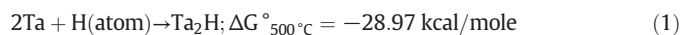
Fig. 1(a) shows the image of Ta turning scrap before hydridation process. The turning scrap used in this study is high purity of 99.6% including Al and Fe impurities which would be incorporated during cutting process from the cutting tools. Before the hydridation process, the Ta scrap was ductile and difficult to cut into powders. After hydridation process, the Ta-scrap became brittle and was easy to fabricate the powder by milling and sieving processes as shown in Fig. 1(b).

Fig. 2 shows FESEM images of the Ta powders after hydridation process at different temperature. At temperature lower than 300 °C, it was difficult to fabricate the powder due to difficulty in milling process. As shown in Fig. 2(a)–(d), edge of the Ta particles are sharp even after the milling process. This indicates that the Ta is not brittle. However, as the hydridation temperature increased above 500 °C, the particle shape showed dull edge. This is due to that the Ta particle was brittle and easy to mill into small powder. Therefore, the shapes of the particle imply whether the metal incorporates the hydrogen well or not.

Fig. 3(a) shows the XRD results of the Ta scrap and powders after hydridation and milling process. It should be noted that the XRD results were obtained after cooling the Ta samples from hydridation temperature to room temperature and hydrogen would be desorbed or the hydrides may be transformed to ordered phases during cooling process. The hydridation process was performed at temperature range from 200 to 900 °C. As shown in Fig. 3(a), Ta scrap shows typical pure Ta metal pattern and do not show any trace of Ta or impurity-related compounds. Crystalline structure of Ta is body-centered cubic (BCC) structure with lattice constant of 3.305 Å (space group Im3m). With increasing the hydridation temperature up to 400 °C, there is no significant change in the diffraction patterns

but slightly changing the peak position to lower angle side. As the hydridation temperature increased above 500 °C, the peak position changed greatly and additional peaks started to appear. Fig. 3(b) shows the small range XRD patterns near Ta (110) peak. As the hydridation temperature increases to 500 °C, the Ta (110) peak shifted to lower angle side. This indicates that the crystalline lattice of Ta is distorted by incorporation of hydrogen atoms. It has been known that the hydrogen atoms are randomly distributed in the tetrahedral and octahedral interstitial sites of BCC crystalline lattice at temperatures above 323 K forming disordered α -Ta hydrides [11,12]. However, as the hydridation temperature increased above 500 °C, new peaks started to appear. As indexed in Fig. 3(b), Ta₂H is dominated around 500 °C. Here, Ta₂H is orthorhombic structure (space group C222) with lattice constants of a = 4.738 Å, b = 3.398 Å, and c = 4.763 Å. With increasing the hydridation temperature up to 700 °C, new TaH_{0.93} phase dominates with small amount of Ta₂H phase. Crystalline structure of the TaH_{0.93} phase is face-centered orthorhombic structure (space group F222) with lattice constants of a = 4.791 Å, b = 4.831 Å, and c = 3.468 Å. This indicates that the hydrogen incorporation is enhanced with increasing the hydridation temperature increased to 700 °C because the TaH_{0.93} phase contained more hydrogen than Ta₂H phase. However, with increasing the hydridation temperature further up to 900 °C, the proportion of the TaH_{0.93} phase decreases and the Ta₂H and Ta incorporating hydrogen phases increase. Therefore, the H/Ta mole ratio increases with increasing the hydridation temperature up to 700 °C, while decreases with increasing the temperature furthermore. This indicates that the hydrogen-rich hydride are unstable at higher temperature and turning point of the hydride and dehydride temperature exists at temperature around 700 °C. Fig. 3(c) shows the hydridation time-dependent Ta hydride formation. At hydridation temperature of 500 °C, the hydridation time has been increased from 3 to 5 h. As shown in the XRD results, there was no visible change in the crystalline structure and lattice constant. Therefore, the hydridation process at this temperature range depends strongly on temperature not on time. This implies that the hydridation process is limited by chemical reaction between Ta and H atoms not by diffusion process because the H atom is small enough to penetrate easily through the Ta lattice.

To further investigate the temperature dependence of the chemical reaction between Ta and H, we calculated the Gibbs free energy change (ΔG) by using thermodynamics software, HSC chemistry 8 (Outotec Research). Fig. 4 shows the thermodynamic comparisons between hydride and de-hydride behaviors between Ta and H. Under 1 atm pressure of H₂ gas condition, Ta₂H could be formed at temperature between 0 and 1100 °C. At the same time, thermodynamic calculation predicts that the Ta₂H can be also easily decomposed to Ta and H₂ gas. As shown in Fig. 4, ΔG of the Ta₂H formation is increased continuously while that of the decomposition of Ta₂H decreases with increasing the temperature. Thereby the ΔG of two reactions shows cross-over point around 500 °C. The ΔG for these two processes calculated at 500 °C is presented as follows;



It should be noted that the diffusion of H atoms through the Ta lattice sites has not been considered. Although ΔG for the dehydride process becomes more negative value than that of the hydride process at higher temperature, diffusion of H atoms in Ta metal matrix occurs more effectively with increasing temperature. And the



Fig. 1. Images of Ta turning scrap (a) before and (b) after hydridation at 500 °C and milling processes.

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