Preparation of Ultra-Fine Titanium Powder by Arc-Plasma Process

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Preparation of ultra-fine titanium powder was tried by subjecting molten titanium to an arc-plasma generated in the argon-hydrogen atmosphere. The arc voltage, current and hydrogen/argon ratio were varied to optimize the powder generation. The optimum conditions were obtained at 40 V and 150 A for stabilizing arc and the hydrogen/argon ratios of 0.5 to 0.7 for achieving the generation rates of 0.18 to 0.30 g/min over reasonable periods of time. The powder generated under optimum conditions have a surface area of approximately 22 m²/g, and the average particle size of 65 nm calculated from the surface area measurement coincides with TEM observations. XRD confirmed that particles are mostly titanium hydride (TiH_{1.924}) containing small amounts of titanium (Ti) and its oxides (TiO and Ti₂O₃). All of the particulate sizes for these phases are less than 20 nm. Powder can be dehydrogenated by heating in vacuum above 673 K, the activation energy for dehydrogenation being determined to be 95 ± 5 kJ/mol by DSC experiments. This activation energy value matches well with the sum of diffusion energy of hydrogen in α -Ti and the hydrogenation energy of α -Ti. Also the dehydrogenation treatment does not provoke grain growth. It is therefore concluded that ultra-fine titanium powder of nano-sized crystallite sizes can be produced at a reasonable yield rate by a plasma arc process in hydrogen/Argon atmosphere and dehydrogenating the product between 673 and 873 K.

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I. Introduction

The preparation methods of ultra-fine particles may be classified roughly into two categories; the break-down method that produces ultra-fine particles from the bulk by mechanical grinding and the build-up method that creates ultra-fine particles from atomic or molecular states. As one of the physical routes in the build-up methods, the arc-plasma method (gas condensation employing hydrogen-argon, nitrogen or oxygen atmosphere) has been developed at National Research Institute for Metals⁽¹⁾⁻⁽⁸⁾ and Advanced Materials Laboratory, Nisshin Steel Co., Ltd.⁽⁹⁾⁻⁽¹²⁾ for producing ultra-fine metal and ceramic powders. Since a mixture of hydrogen and argon gases is introduced in the evaporation chamber, the evaporated atoms collide with each other in the vicinity of the molten metal surface and are condensed to form ultra-fine metal particles. They are then transported by the draft of a mixture of gases to the powder collection filter. Since hydrogen is employed, hydrogen atoms dissociated in the arc-plasma first dissolve into the molten metal and then enhance the evaporation of metal atoms when they are emitted from the molten metal. The formation rate of ultra-fine particles is expected much higher than that in an inert gas. The formation rate of ultra-fine particles and their size depend predominantly on the input power and hydrogen content in the mixture. The present paper concerns with the optimum conditions for forming titanium ultra-fine powder and the characterization of produced powder.

II. Experimental

A ultra-fine powder production apparatus (Fuji Electronic Industrial) was employed to produce titanium ultra-fine powder, which composed of a ultra-fine powder generation furnace, a powder transport system, a powder collection chamber, a gas circulation system, a vacuum system and a power supply system. The ultra-fine powder generated in the arc furnace were transported by a carrier gas to the particle collection filter which is installed in a glove box so that the collected ultra-fine powder could be handled in an inert gas atmosphere. The power supply from TC-150S (Daiden) was employed that could produce stable arc states up to 50 V even when the hydrogen concentration was increased. A 40 g titanium button was first prepared as the starting material by arc-melting titanium sponge (High-purity Chemicals) in pure argon.

After a titanium button was placed on a water-cooled copper hearth, the powder generation furnace was evacuated by a rotary pump to 1 Pa and then back-filled with a hydrogen-argon mixture of the predetermined ratio to 0.1 MPa. The distance between the tip of tungsten electrode and button surface was set to be 13 mm throughout the entire experiments. Once the button was arc-melted, the voltage and current values were set to the predetermined. Soon after the button was arc-melted, the metal fume was generated from the surface of a molten pool, and it was transported by a carrier gas stream to the collection filter. The generation rate of ultra-fine particles was calculated from the weight loss of

a button before and after a generation experiment since all of the generated powder could not be collected at the filter leaving some on the walls of the furnace and transport conduit.

The surface area of the produced powder was measured using Multisorb-12 (Yuasa Ionics) and the morphology was observed using a TEM JEM-400 (JEOL). The phase identification by XRD was carried by using a RINT-1200 unit (Rigaku) and the detailed analysis of XRD spectra was made by employing a non-linear curve-fit software, *Peakfit*[®] by Jandel Scientific. The thermal analysis of as-produced ultra-fine powder was made by using a differential calorimeter, Dupont 2200 (Dupont) to identify the dehydrogenation temperature and the activation energy for dehydrogenation was determined by varying the heating rate.

III. Results and Discussion

To sustain a stable arc for generating metallic fume from the molten bath, the applied voltage has to be optimized that depends on the distance between a tungsten electrode and the molten metal surface (the target electrode), the angle of the arc to the molten pool and the atmosphere. It is naturally expected that the applied voltage increases with increasing the distance. Figure 1 depicts the relation of the applied voltage versus the electrode distance as a function of the hydrogen content at a constant arc current of 150 A. It is seen in this figure that the higher the hydrogen content the higher applied voltage is required, the effect of the hydrogen content being greater than that of the electrode distance. It is, however, not very desirable to immensely increase the applied voltage since a large power supply would be required. On the other hand, if the electrode distance is too short, the sputtering of molten titanium onto tungsten electrode produce a low melting phase to de-stabilize the arc. Ac-

cordingly it appears that there should be an optimum window for the applied voltage (25–45 V) and electrode distance (10–20 mm).

Figure 2 shows the results for the amount of powder generated during the first one hour by varying the arc current while the atmosphere, applied voltage and electrode distance were kept constant to be 60% hydrogen–40% argon, 40 V and 13 mm, respectively. Although an increase in power (by increasing the arc current) rapidly increases the yield to reach a maximum at 150 A, the yield drops rather quickly to saturate beyond 200 A. Although it is expected that an increase in the arc current would increase the molten pool size, it appears that the amounts of the hydrogen absorption to the molten titanium and emission of hydrogen from the molten pool more strongly influence the powder generation rate. And this result suggests a current larger than 150 A does not necessarily produce better yield, but the hydrogen content would have a more significant effect on the yield. Accordingly the arc voltage of 40 V and arc current of 150 A are set as the optimum power input in the future experiments. Okada *et al.*⁽¹³⁾ found a similar phenomenon. They explained it by a change in the concentration of the arc; at the arc current for the maximum yield the arc was concentrated on the anode spot while at the larger arc current the arc spread over the molten metal surface.

The relation of the yield versus the hydrogen content is shown in Fig. 3, where it is clearly seen that the yield increases rapidly once the hydrogen content exceeds 50%. Accordingly it may be concluded that the absorption to the molten titanium pool and emission of hydrogen from it, which primarily depend on the hydrogen content in atmosphere, dictate the powder production. First gaseous hydrogen dissociates in the arc plasma and enters into the molten titanium. Atomic hydrogen, probably in the proton state moves quickly to encounter each other and

Fig. 1 Voltage to applied to maintain arc versus electrode distance as a function of the hydrogen content.

Fig. 2 Powder yield during the first one hour versus applied current under a condition of 60% H₂–40% Ar, 40 V arc voltage and electrode distance of 13 mm.

Fig. 3 Powder yield during the first one hour versus hydrogen content under a condition of 150 A arc current and 40 V arc voltage.

Fig. 4 Specific surface area measured versus hydrogen content for powder produced under a condition of 150 A arc current and 40 V arc voltage.

produce molecular hydrogen in the molten pool. Because of low gas solubility at high temperatures, hydrogen gas in a bubble form escapes from the molten pool accompanying titanium atoms to the outside of the arc. Then, titanium atoms of the gaseous state collide each other and are cooled down to form a powdery product. During this cooling process, hydrogen atoms in the atmosphere may be absorbed again into solid titanium. It is therefore expected that the direct product from the present process is ultra-fine powder of titanium hydride.

The powder particle size was first evaluated from the surface area measurements. The surface area measured per gram is plotted against the hydrogen content in Fig. 4. It is seen here that the surface area decreases from about $90 \text{ m}^2/\text{g}$ at 30% hydrogen–70% argon down to approximately $22 \text{ m}^2/\text{g}$ at and above 50% hydrogen–50% argon. This trend suggests that if the hydrogen content is less than 50%, the absorption of hydrogen into the molten pool is very much limited. A very small amount of very small particle sizes are produced since the emission rate of gaseous hydrogen atoms is also limited. Although the production rate steadily increases with increasing hydrogen content beyond 50%, the specific surface area (similarly particle size) remains almost constant beyond 50% hydrogen content. The reason is considered that the current system is not a closed one so that the product is being perpetually removed from the reacted zone.

Assuming the particle is of a spherical shape and the density of 3.72 g/cm^3 for titanium dihydride (TiH_2), the average particle size d_p is calculated from

$$d_p = 6W/Sp \quad (1)$$

where (S/W) is the measured particle surface area per gram, S is the total area and W is the sample weight, and ρ is the density. The results are shown in Fig. 5 as a func-

Fig. 5 Average particle size calculated from the surface area measurements versus hydrogen content. An assumption was made on spherical particle shape for calculation.

tion of the hydrogen content, where it is seen that the particle size increases with increasing the hydrogen content to saturate at approximately 60 nm above 50% hydrogen. Definitely the powder generation rate linearly increases with increasing the hydrogen content (Fig. 3) while the particle size growth above 50% hydrogen is minimal. The particle size growth occurs by collision of gaseous metal atoms only in the vicinity of the arc where the temperature is still very high, and once they leave the heated zone no particle size growth can be expected. At lower hydrogen concentrations, the collision probability of titanium atoms is lowered due to lower evaporation

rates so that the formation of solid powder particles discontinues before reaching the critical particle size. When the generation rate is increased with increasing the hydrogen content, the collision probability accordingly increases to grow the particle size up to somewhat a critical size but no further growth is expected. It is because the grown particles are forced to leave the hot zone by the draft.

Figure 6 is a typical example of transmission electron micrographs obtained for powder generated under a condition of 40 V, 150 A and 60% hydrogen–40% argon. The morphology of powder is of fairly spherical to elliptical shapes and the particles are somewhat agglomerated. The overall particle size distribution appears rather narrow (20 to 100 nm). The average particle size of approximately 60 nm agrees with that estimated from the particle surface area measurement.

Depicted in Fig. 7 is the major part of an X-ray diffraction spectrum for as-produced powder obtained using a copper target ($K\alpha$) from 10 to 90 degrees for 2θ at 40 kV and 30 mA with a scanning speed of 0.02 degrees/s. The

Fig. 6 TEM micrograph to show the powder particle morphology.

Fig. 7 XRD spectrum for as-prepared powders.

major peaks are at about 35, 41, 59, 70 and 74 degrees. The first four peaks roughly match with 2θ values for $\text{TiH}_{1.924}$ of (111), (200), (202) and (311) planes. The last peak does, however, not match with any for $\text{TiH}_{1.924}$ but does match well with that for $\text{TiO}(311)$, indicating a possibility that the powder thus produced are mostly titanium hydride, $\text{TiH}_{1.924}$ and partly titanium oxide produced either during the powder generation process or powder transferring to the X-ray unit. If $\text{TiO}(311)$ does exist, there is also a possibility that titanium oxides of other forms such as Ti_2O_3 and TiO_2 may also exist. But their peaks may be hidden within the aforementioned major peaks because of their weak intensities. In order to fully analyze the phases existing in the presently produced powder, a non-linear curve-fitting software, *Peakfit*® from Jandel Scientific was employed. In this program the experimentally obtained spectrum is deconvoluted into 8 possible peaks for various phases and planes. A Gaussian curve for a peak is assumed. The 2θ value for a specific plane of a specific phase obtained from JCPDS⁽¹⁴⁾ and a tentative width value for the peak are fed into the *Peakfit* program so that it sums up all of the peak curves to simulate the experimentally obtained XRD spectrum.

Figures 8(a), (b) and (c) present the simulation results. The entire spectra shown in Fig. 7 are now separated into

Fig. 8 Deconvoluted XRD spectra for precise identification of phases. (a) at lower angles, (b) at intermediate angles and (c) at higher angles.

three regions. The region (a) represents the major peak at lower angles of 33 to 37 degrees for 2θ , which can be deconvoluted into at least 3 noticeable peaks at 34.84° , 34.92° and 35.07° for $\text{Ti}_2\text{O}_3(110)$, $\text{TiH}_{1.924}(111)$ and $\text{Ti}(010)$, respectively. The region (b) represents the major peak at the intermediate angles of 37 to 45 degrees which can be deconvoluted into 6 peaks at 38.41° , 40.14° , 40.26° , 40.54° , 40.98° and 42.11° for $\text{Ti}(002)$, $\text{Ti}(011)$, $\text{Ti}_2\text{O}_3(113)$, $\text{TiH}_{1.924}(200)$, $\text{TiH}_{1.924}(002)$ and $\text{TiO}(200)$, respectively. The last region (c) represents 2 major peaks situated at higher angles of 55 to 70 degrees. Similarly these three peaks are deconvoluted into 4 separated peaks at 58.22° , 58.80° , 62.98° and 70.04° for $\text{TiH}_{1.924}(220)$, $\text{TiH}_{1.924}(202)$, $\text{Ti}(110)$ and $\text{Ti}(103)$, respectively.

It is rather obvious from these three figures that the predominant peaks are for a $\text{TiH}_{1.924}$ phase, followed by an elemental Ti phase. The presence of titanium suboxides of TiO and Ti_2O_3 cannot be neglected, but their actual amounts would be much smaller than those roughly estimated from their intensities; the precise calculation of the volume fractions of these suboxides must be based on the areas under their peaks. No equilibrium titanium oxide phase, TiO_2 could not be detected. Accordingly, a possibility of being oxidized from long exposure to air during the X-ray measurement should be excluded. Titanium hydride $\text{TiH}_{1.924}$ itself is a rather stable compound that cannot be easily oxidized simply by exposing to air.

However, the formation of titanium suboxides is suspected during preparation of ultra-fine powder using a plasma arc in the aforementioned atmosphere. Precise oxygen analysis of the mixture gas was not made, but it is suspected that a very small amount of oxygen might have existed in the chamber. The trials of a 100% conversion of ultra-fine powder to $\text{TiH}_{1.924}$, by exposing powder in the glove box to pure hydrogen gas for a long period of time, were often failed since thus hydrogenated powder often caught fire by exposing to the ambient atmosphere. A literature⁽¹⁵⁾ indicates the perfect hydrogenation of titanium cannot be made as long as a small amount of oxygen exists.

Of interest is that another important information can be obtained from the above-mentioned peakfit analysis. That is the half width automatically obtained from analysis which is fed into the following equation⁽¹⁶⁾ for calculating the crystallite size, d_c .

$$d_c = 0.94\lambda / \beta \cos \theta_p \quad (2)$$

where λ is the X-ray wave length, θ_p one half of the 2θ for a peak and β is half width. The crystallite sizes averaged over various planes are 15.5 nm for $\text{TiH}_{1.924}$, 14.4 nm for Ti, 8.4 nm for TiO and 14.5 nm for Ti_2O_3 respectively. This crystallite size analysis along with the aforementioned particle size estimate definitely indicate that the present arc plasma process produces not only ultra-fine particle powder (approximately 60 nm in diameter) of $\text{TiH}_{1.924}$ but also with very fine crystallite size of less than 20 nm at a reasonable yield rate compared to other evaporation techniques.

Since the primary product from the present process is titanium hydride, $\text{TiH}_{1.924}$, it has to be dehydrogenated to obtain ultra-fine titanium powder. DSC experiments were carried out for powder produced under the condition of 40 V, 150 A and 60% hydrogen–40% argon at temperatures from the ambient to 873 K and heating rates of 0.167 to 0.500 K/s. An example of the DSC runs is shown in Fig. 9 with a 10 mg sample heated at 10 K/min (0.167 K/s) in the argon atmosphere which indicates a significant endothermic peak starting at 673 K and reaching the minimum at approximately 770 K. Temperatures at the endothermic start and the peak minimum increased with increasing the heating rate. To obtain the activation energy for this dehydrogenation reaction, the Kissinger plot⁽¹⁷⁾ is created in Fig. 10 by plotting $\ln [(dT/dt)/T_p^2]$ versus T_p^{-1} where (dT/dt) is the heating rate and T_p is the peak minimum temperature. It is clearly seen that the data points are on a straight line, which slope gives the activation energy of 95 ± 5 kJ/mol. To dehydrogenate $\text{TiH}_{1.924}$ to elemental Ti, first $\text{TiH}_{1.924}$ must be dissociated to Ti and hydrogen and hydrogen atoms diffuse out of the titanium matrix. Therefore the activation energy for dehydrogenation is the sum of hydride formation and diffusion of hydrogen through Ti matrix. The formation energy of $\text{TiH}_{1.924}$ has been reported by Dantzer⁽¹⁸⁾ to be 40 kJ/mol while the diffusion energy of hydrogen in Ti is given to 52 to 62 kJ/mol^{(19)–(21)}. The sum of these two energies gives 92 to 102 kJ/mol, which is close enough to the currently obtained 95 ± 5 kJ/mol.

Depicted in Fig. 11 is a part of XRD spectrum from 35 to 50 degrees for 2θ for powder dehydrogenated at 773 K for one hour in vacuum of approximately 10^{-1} Pa. The most dominant peak was $\text{Ti}(011)$, while, because of poor vacuum, TiO_2 of (100), (111) and (200) planes and TiO of (111) and (200) planes exhibit higher intensities compared to those of as-produced state. A peak for $\text{TiH}_{1.924}(200)$ still existed with a weaker intensity, implying a longer

Fig. 9 A typical example of DSC runs for as-produced powders of 10.0 mg from R.T. to 873 K at heating rate of 10 K/min.

Fig. 10 Kissinger plot of $(dT/dt)/T_p^2$ against T_p^{-1} to obtain the activation energy for dehydrogenation of $\text{TiH}_{1.924}$.

Fig. 11 A partial XRD spectrum for powder dehydrogenated at 773 K for 1 h.

heating at a higher temperature may be needed for complete conversion. Definitely dehydrogenation should be done in a better vacuum (at least 10^{-4} Pa) to eliminate oxidation. The result, however, clearly indicates that it is possible to dehydrogenate $\text{TiH}_{1.924}$ to ultra-fine powder of pure titanium. The Scherrer analysis for particulate sizes for respective phases after dehydrogenation treatment revealed that grain growth did not take place,

particulate sizes remaining unchanged.

IV. Conclusion

Ultra-fine titanium hydride ($\text{TiH}_{1.924}$) powder was produced by an arc-plasma process in the argon-hydrogen atmosphere. The optimum condition for powder generation was at 40 V and 150 A with hydrogen/argon ratios of 0.5 to 0.7. The powder generated under optimum conditions have a surface area of $22 \text{ m}^2/\text{g}$ and an average particle size of 60 nm. This ultra-fine powder is composed of mostly $\text{TiH}_{1.924}$ and very small amounts of $\alpha\text{-Ti}$, Ti_2O_3 and TiO . All of the crystallite sizes for these phases are less than 20 nm. Dehydrogenation of $\text{TiH}_{1.924}$ occurs when heated above 673 K to convert into $\alpha\text{-Ti}$ with an activation energy of $95 \pm 5 \text{ kJ/mol}$. This energy is equivalent to the sum of those for hydrogenation and diffusion of hydrogen in titanium. Also the dehydrogenation treatment does not provoke grain growth. It is therefore concluded that ultra-fine titanium powder of nano-sized crystallite sizes can be produced at a reasonable yield rate by a plasma arc process in hydrogen/argon atmosphere and dehydrogenating the product at temperatures below 873 K.

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