Hydrogen Sorption Property of $\text{Zr}_{55}\text{V}_{29}\text{Fe}_{16}$ Nanopowder Synthesized by the Plasma Arc Discharge Process

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The present study focused on the synthesis of a Zr-V-Fe-based nanopowder for investigating the possibility of synthesizing zirconium-based alloyed getter nanoparticles by the plasma arc discharge process. The chamber pressure and the mixing ratio of hydrogen:argon in the powder synthesis atmosphere were changed. The chemical composition, phase structure, particle size and hydrogen sorption property of the synthesized powders were analyzed using XRF, XRD, TEM, XPS and the ASTM-F798 method. The synthesized Zr-V-Fe-based powders have a different chemical composition than the raw material, $\text{Zr}_{57}\text{V}_{36}\text{Fe}_7$. The chemical composition of the synthesized Zr-V-Fe-based powders approached that of the raw material with an increasing hydrogen fraction in the powder synthesis atmosphere. The synthesized $\text{Zr}_{55}\text{V}_{29}\text{Fe}_{16}$ powder has a mixed phase structure of the Zr, ZrH_2 , FeV and $\text{Zr}(\text{V}_{1-x}\text{Fe}_x)_2$ phases. This powder has an average particle size of about 20 nm. The $\text{Zr}_{55}\text{V}_{29}\text{Fe}_{16}$ nanopowder synthesized by the plasma arc discharge process showed getter characteristics, even though it had a lower hydrogen sorption speed than the $\text{Zr}_{57}\text{V}_{36}\text{Fe}_7$ getter powder synthesized by the conventional hydride-dehydride method. [doi:10.2320/matertrans.MER2007031]

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1. Introduction

Nanoparticles can be produced by several different methods, such as colloidal precipitation, mechanical attrition, and vapor condensation process.^{1,2)} The latter is the most widely used method at present, based on its advantage of being relatively simple to scale-up to high-rate production. Vapor condensation processes typically involve nucleation and growth of nanosized particles from a supersaturated vapor produced either by the evaporation of bulk materials or by the chemical reaction of gas-phase precursors. The plasma arc discharge process can be used for preparing metal, ceramic, and their composite nanoparticles by vaporization-condensation of metals or alloys in an active atmosphere using a DC arc-plasma.³⁻⁸⁾ Generally, the degree of vaporization of the metal elements was depended on their equilibrium vapor pressure.⁹⁾ The higher melting temperature element has a lower equilibrium vapor pressure at the same temperature. It seems that precise control of the chemical composition was very difficult for the synthesis of alloyed nanoparticles with multi-elements compared to that of pure nanoparticles with a single element in the vapor condensation process. Thus, many studies on the synthesis of nanoparticles using the plasma arc discharge process have been done on pure metal particles and simple compounds; oxides, carbides and nitrides.⁵⁻⁸⁾

Zirconium-based alloy powders are of particular interest for hydrogen storage and “get” the active gases in vacuum technology, i.e., “getters”.¹⁰⁻¹³⁾ The zirconium-based alloy powders for hydrogen storage and getters have multi-element systems, for example, Zr-V-Fe, Zr-Ti-V, Zr-Al-Ni, etc. Generally, these powders have been made by the hydride-dehydride method, i.e., a combination of casting, hydrogenation-dehydrogenation and mechanical grinding processes. In order to improve the performance of the zirconium-

based alloy powders made by this conventional method, many researchers have studied the effects of alloying elements and the mechanical grinding.¹²⁻¹⁶⁾ However, the mechanical grinding method was difficult to effectively reduce the particle size below the sub-micrometer range without special equipment and contamination. The gas sorption properties of the particles strongly depend on the particle and surface characteristics, including size, morphology, surface area, surface oxide, and others. It was expected that nanopowders of the zirconium-based alloys with a diameter between 10 nm and 100 nm would have high gas sorption properties due to a high surface area. However, the synthesis and characterization of the zirconium-based nanopowders for the getter application have been rarely studied.

In the present study, the focus is the preparation of the Zr-V-Fe-based nanopowders by the plasma arc discharge process under various powder synthesis conditions to investigate the synthesis possibilities of the zirconium-based getter nanoparticles using the plasma arc discharge process.

2. Experimental Procedure

Figure 1 shows the apparatus for preparing the nanoparticles by the plasma arc discharge process. This apparatus basically consists of a vacuum chamber, a tungsten cathode, a copper anode, a gas flow system, and a DC power supply. $\text{Zr}_{57}\text{V}_{36}\text{Fe}_7$ bulk alloy with a button shape of 2×10^{-2} m diameter was used as the raw material. The vacuum chamber was evacuated to 133.32×10^{-5} Pa and then backfilled with a hydrogen/argon mixture gas to $399.96 \times 10^2 \sim 666.6 \times 10^2$ Pa. The arc plasma was then initiated between the tungsten cathode and the bulk $\text{Zr}_{57}\text{V}_{36}\text{Fe}_7$ on the copper anode under an arc current of 180 A and an arc voltage of 16 ~ 25 V. The mixing ratio of the hydrogen:argon was varied from 4:6 to 5:5. An atomic smoke was generated

Fig. 1 Schematic diagram of apparatus for producing nanoparticles by the plasma arc discharge process.

around the arc spot area of the molten specimen, and nano-sized particles were then formed by collisions between the quenched smoke atoms. The formed nanoparticles were then separated with a working gas. Before the particles were removed from the chamber, they were passivated in an argon/oxygen mixture atmosphere at room temperature for 3.6×10^4 s to prevent any rapid spontaneous reaction with oxygen. The variation in chemical composition, phase structure and particle size of the synthesized Zr-V-Fe-based particles with the changes in the mixing ratio of the hydrogen/argon and chamber pressure in the powder synthesis atmosphere were studied using XRF, XPS, TEM and XRD. The gas sorption property of the synthesized powder was characterized using the ASTM-F798 method.¹⁷⁾ The basic principle of this method is measuring the total pressure difference between the gas inlet and the sample chamber using the orifice method under flowing active gases. The sorption speed and the sorption quantity of the sample were calculated using equations (1) and (2), respectively.

$$S = Q(P_2 - P_{20}) \quad (1)$$

$$Q = C[(P_1 - P_{10}) - (P_2 - P_{20})] \quad (2)$$

Here, S is the sorption speed of the sample, Q is the sorption quantity, C is the conductance of the orifice, P_1 is the pressure of the gas inlet, P_2 is the pressure of the sample chamber, and P_{10} and P_{20} are the initial pressures of the gas inlet and sample chamber, respectively. The detailed contents of the measuring method were described in another paper.¹⁸⁾

3. Results and Discussion

Table 1 shows a summary of the chemical composition of

the synthesized Zr-V-Fe-based powders under various chamber pressures and mixing ratios of the hydrogen:argon in the powder synthesis atmosphere. The analysis of the chemical composition was carried out only on the zirconium, vanadium and iron elements using XRF. At a chamber pressure of 399.96×10^2 Pa and a mixing ratio of the hydrogen:argon of 4:6, the synthesized powder had a composition of about $\text{Zr}_{16}\text{V}_{48}\text{Fe}_{36}$ (Sample I). This chemical composition changes to about $\text{Zr}_{11}\text{V}_{40}\text{Fe}_{49}$ (Sample II) with increasing chamber pressure from 399.96×10^2 Pa to 666.6×10^2 Pa under a constant gas atmosphere in the chamber. At a mixing ratio of the hydrogen:argon of 5:5 and a chamber pressure of 399.96×10^2 Pa, the synthesized powder had a composition of about $\text{Zr}_{55}\text{V}_{29}\text{Fe}_{16}$ (sample III). Sample II showed a higher iron content than sample I. The melting temperatures of zirconium, vanadium and iron are 2125 K, 2173 K, 1809 K, respectively. Iron has a lower melting temperature compared to those of zirconium and vanadium. Generally, the degree of vaporization of the melt has been increased with decreasing melting temperature and chamber pressure.⁹⁾ In the melt mixture with a high melting temperature element and a low melting temperature element, the difference in vaporization between these elements is not as large under a low chamber pressure. However, vaporization of the element having a lower melting temperature is relatively easier than that of the element having a higher melting temperature with increasing chamber pressure. Thus, it was considered that sample II synthesized under the higher chamber pressure had a higher iron content than sample I synthesized under the lower chamber pressure due to the difference in the melting temperature of the constituent elements, zirconium, vanadium and iron. Sample III has a relatively higher zirconium and vanadium content than sample I in spite of the same chamber pressure. The chemical composition of sample III, $\text{Zr}_{55}\text{V}_{29}\text{Fe}_{16}$, shows a value closest that of the raw material, $\text{Zr}_{57}\text{V}_{36}\text{Fe}_7$, among the samples. During melting of the metals under the gas atmosphere, the gas components of the atmosphere dissolve into the molten metal in the single atomic state. The solubility of the gas component depends on its partial pressure in the atmosphere according to Sievert's law.¹⁹⁾ A molecular gas such as hydrogen decomposes to the single atomic state under the plasma.^{20,21)} These decomposed single atoms rapidly dissolve into the molten metal through the highest temperature region directly under the arc plasma column. The dissolved atoms in the molten metal diffuse to the peripheral region which has a lower temperature than the direct arc spot region. In that region, the dissolved atom in the molten metal is in a supersaturated state compared to the equilibrium solubility. To maintain the equilibrium solubility in the molten metal, the supersaturated atoms recombine at the

Table 1 Summary of the chemical composition of the synthesized Zr-V-Fe-based powders under various synthesis conditions.

Sample	Synthesis process parameters		Chemical composition (at%)		
	Chamber pressure (10^2 Pa)	Hydrogen:Argon	Zr	V	Fe
I	399.96	4:6	16	48	36
II	666.6	4:6	11	40	49
III	399.96	5:5	55	29	16

Fig. 2 X-ray diffraction pattern of the synthesized $\text{Zr}_{55}\text{V}_{29}\text{Fe}_{16}$ powder.

interface of the molten metal and atmosphere and then are released into the atmosphere in the molecular gas state. The released molecular gas contains the molten metal vapor. The hydrogen molecules in the atmosphere promote the evaporation of the metal vapor from the molten metal in the plasma arc discharge process by their dissolution and releasing action.^{7,8,21)} This promoting action of the hydrogen molecules increased with the increasing volume fraction of hydrogen in the powder synthesis atmosphere according to Sievert's law. The vaporization behavior of the molten elements by the promoting action of the hydrogen has no relation to the melting temperature of the constituent elements. Thus, it was considered that sample III synthesized in the highest hydrogen fraction in the powder synthesis atmosphere had a chemical composition closest to that of the raw material due to the promoting action of the hydrogen.

The control of the chemical composition of the particles was very important for the synthesis of Zr-V-Fe-based nanoparticles for functional applications. For the control of the chemical composition in the plasma arc discharge process, we changed the process parameters: the chamber pressure and the hydrogen fraction in the synthesis atmosphere. It seems that the control of the chemical composition by a change in the chamber pressure was very difficult, because the constituent elements, Zr, V and Fe, have a different equilibrium vapor pressure under the synthesis conditions. However, a Zr-V-Fe-based powder has a chemical composition closest to that of the raw material could be obtained using the promoting action of hydrogen molecules. Sample III's chemical composition, $\text{Zr}_{55}\text{V}_{29}\text{Fe}_{16}$, was closest to the designed chemical composition of the raw material, $\text{Zr}_{57}\text{V}_{36}\text{Fe}_7$. In spite of the remaining chemical composition problem, sample III was evaluated by investigating the application possibilities of the synthesized powder as a "getter".

Figure 2 shows the X-ray diffraction pattern of the synthesized $\text{Zr}_{55}\text{V}_{29}\text{Fe}_{16}$ powder (sample III). The synthesized powder showed diffraction peaks of the Zr, ZrH_2 , FeV and $\text{Zr}(\text{V}_{1-x}\text{Fe}_x)_2$ phases. Generally, the conventionally prepared Zr-V-Fe-based getter material, $\text{Zr}_{57}\text{V}_{36}\text{Fe}_7$, has a mixed phase structure of α -Zr and $\text{Zr}(\text{V}_{1-x}\text{Fe}_x)_2$ phases.^{10,22)} The $\text{Zr}(\text{V}_{1-x}\text{Fe}_x)_2$ phase was formed by the addition of Fe to ZrV_2 . For the application of the Zr-V-Fe-based alloys as a

Fig. 3 TEM micrograph of the synthesized $\text{Zr}_{55}\text{V}_{29}\text{Fe}_{16}$ powder.

getter in vacuum technology, a high gas sorption property and a low activation temperature are needed. Activation of the getter creates a fresh getter surface ready to react with the active gases usually present in vacuum devices (H_2 , H_2O , CO , CO_2 , N_2 and O_2).¹⁰⁾ In the case of Zr-V-Fe-based getters, the activation is carried out by properly heating the getter material and promoting the bulk diffusion of oxygen of the passivated surface layer until the surface is sufficiently clean to begin sorbing the active gases. The activation process is not only related to the temperature but also to time, even though it is more strongly dependent on the temperature, as is to be expected for the diffusion mechanism.²³⁾ The solid solution phase in the zirconium-based getters, α -Zr, acts to sorb the active gases, and the intermetallic compound phases, $\text{Zr}(\text{V}_{1-x}\text{Fe}_x)_2$, ZrV_2 , etc., act to decrease the activation temperature.^{10,22)} Thus, the formation of the mixed-phase structure of the zirconium solid solution and intermetallic compound is very important for preparing the zirconium-based getter. The synthesized $\text{Zr}_{55}\text{V}_{29}\text{Fe}_{16}$ powder by the plasma arc discharge process in this study has a mixed-phase structure of the Zr, ZrH_2 , FeV and $\text{Zr}(\text{V}_{1-x}\text{Fe}_x)_2$ phases as shown in Fig. 2. This phase mixture includes the zirconium solid solution and the intermetallic compound for promotion of the getter characteristic.

Figure 3 shows a TEM micrograph of the synthesized $\text{Zr}_{55}\text{V}_{29}\text{Fe}_{16}$ powder (sample III). The powder has a slightly agglomerated structure with nano-sized particles of about 20 nm. The specific surface area and oxygen content of this powder are about $0.73375 \times 10^5 \text{ m}^2 \text{ kg}^{-1}$ and about 3.487 mass%, respectively. It was known that the Zr-V-Fe-based alloy nanoparticles can be synthesized by the plasma arc discharge process. For verification of the chemical composition and phase structure of the individual particles, however, fundamental research is needed concerning the crystal structure and distribution of the elements in the future.

Fig. 4 Analysis results on the XPS peaks of the synthesized $\text{Zr}_{55}\text{V}_{29}\text{Fe}_{16}$ nanoparticles.

Figure 4 shows the analysis results of the XPS peaks of the synthesized $\text{Zr}_{55}\text{V}_{29}\text{Fe}_{16}$ nanoparticles. The analysis of the binding energy was carried out on Zr 3d5/2, Zr 3d3/2, V 2p3/2 and Fe 2p3/2 based on the Gaussian function. The binding energies of Zr 3d5/2 and Zr 3d3/2 of the zirconium, V 2p3/2 of the vanadium and Fe 2p3/2 of the iron were 178.8 eV, 181.1 eV, 512.1 eV and 706.8 eV, respectively. In the case of the Zr 3d5/2 and Zr 3d3/2, the measured peak could be separated into five peaks; a Zr peak at about 181.7 eV, an $(\text{Fe}_{0.9}\text{V}_{0.1})_2\text{Zr}$ peak at about 182.3 eV, an $\text{Fe}_{24}\text{Zr}_{76}\text{O}_2$ peak at about 183.1 eV, a V_2ZrO_2 peak at about 184.6 eV and a ZrO_2 peak at about 185.8 eV. In the case of V 2p3/2, the measured peak could be separated into two peaks; a V_2O_3 peak at about 515.7 eV and a V_2O_4 peak at about 516.5 eV. In the case of Fe 2p3/2, the measured peak could be separated into three peaks; an Fe peak at about 707.9 eV,

Fig. 5 Change in the hydrogen sorption speed of the synthesized $\text{Zr}_{55}\text{V}_{29}\text{Fe}_{16}$ nanopowder and $\text{Zr}_{57}\text{V}_{36}\text{Fe}_7$ powder versus sorption quantity.

an Fe_3O_4 peak at about 710.4 eV and an $\text{Fe}(\text{OH})\text{O}$ peak at about 711.8 eV. The surface oxide phases of the synthesized $\text{Zr}_{55}\text{V}_{29}\text{Fe}_{16}$ nanoparticles have the forms of $\text{Fe}_{24}\text{Zr}_{76}\text{O}_2$, V_2ZrO_2 , ZrO_2 , V_2O_3 , V_2O_4 , Fe_3O_4 and $\text{Fe}(\text{OH})\text{O}$. These oxide phases could not be identified by XRD. Generally, the metal nanoparticles synthesized by the plasma arc discharge process have a shell-core structure composed of the pure metal in the core and the oxides in the shell.^{3,7,8)} The thickness of the shell, even though it depended on the synthesis conditions, ranged over several nanometer (about 1 ~ 5 nm). This shell-core structure formed due to the passivation treatment in the dilute oxygen gas atmosphere. It is presumed that the synthesized $\text{Zr}_{55}\text{V}_{29}\text{Fe}_{16}$ nanoparticles also have the shell-core structure. The identified oxide phases in the XPS compose the shell, and the diffraction peaks of these oxides were not detected in the XRD diffraction patterns due to the thinness of the shell.

Figure 5 shows the change in the hydrogen sorption speed of the synthesized $\text{Zr}_{55}\text{V}_{29}\text{Fe}_{16}$ nanopowder with the sorption quantity. The hydrogen sorption speed was measured at room temperature after activation treatment at 723 K for 600 s under 133.32×10^{-9} Pa. For comparison, the sorption speed of the $\text{Zr}_{57}\text{V}_{36}\text{Fe}_7$ powder synthesized by the hydride-dehydride method also shown in the figure. This powder has a specific surface area of about $0.49649 \times 10^2 \text{ m}^2 \text{ kg}^{-1}$, an average particle size of about 10 μm and an oxygen content of about 0.798 mass%. At a sorption quantity of 1×10^{-2} LPa, the sorption speeds of the synthesized $\text{Zr}_{55}\text{V}_{29}\text{Fe}_{16}$ nanopowder and the $\text{Zr}_{57}\text{V}_{36}\text{Fe}_7$ powder were about $5.7 \times 10^3 \text{ Lm}^{-2} \text{ s}^{-1}$ and about $9.8 \times 10^3 \text{ Lm}^{-2} \text{ s}^{-1}$, respectively. The synthesized $\text{Zr}_{55}\text{V}_{29}\text{Fe}_{16}$ nanopowder showed a lower hydrogen sorption speed than the $\text{Zr}_{57}\text{V}_{36}\text{Fe}_7$ powder. Generally, the sorption speed of the getters decreases with increasing oxygen content.^{10,16,24)} In the case of the $\text{Zr}_{57}\text{V}_{36}\text{Fe}_7$ powder, the sorption speed at a sorption quantity of 1×10^{-2} LPa decreased from about $9.8 \times 10^3 \text{ Lm}^{-2} \text{ s}^{-1}$ to about $7.0 \times 10^3 \text{ Lm}^{-2} \text{ s}^{-1}$, with increasing oxygen content from about 0.798 mass% to about 3.312 mass%. It is postulated that the low sorption speed of the synthesized $\text{Zr}_{55}\text{V}_{29}\text{Fe}_{16}$ nanopowder is due to the mismatch of the chemical composition and the high oxygen content. How-

ever, the synthesized $Zr_{55}V_{29}Fe_{16}$ nanopowder showed a getter characteristic as shown in Fig. 5, even though it has a chemical composition problem. The getter characteristic of the synthesized $Zr_{55}V_{29}Fe_{16}$ powder comes not only from the mixed-phase structure of the zirconium and intermetallic compound but also from the nano-sized particle size. It is considered that the $Zr_{55}V_{29}Fe_{16}$ nanopowder synthesized by the plasma arc discharge process can be used as a getter material, in spite of the remaining chemical composition problem and high oxygen content. To increase the gas sorption property of the Zr-V-Fe-based nanopowder synthesized by the plasma arc discharge process, however, fundamental research is needed concerning the surface oxide, particle size, particle morphology and chemical composition in the future.

4. Conclusion

The present study focused on the synthesis of Zr-V-Fe-based nanopowder to investigate the possibility of synthesizing zirconium-based alloy getter nanoparticles by the plasma arc discharge process. The synthesized Zr-V-Fe-based powders have a different chemical composition from that of the raw material, $Zr_{57}V_{36}Fe_7$. The chemical composition of the synthesized powder changed with the synthesis process parameters; chamber pressure and mixing ratio of the hydrogen:argon in the powder synthesis atmosphere. The chemical composition of the synthesized Zr-V-Fe-based powders approached to that of the raw material with increasing hydrogen fraction in the powder synthesis atmosphere. The synthesized $Zr_{55}V_{29}Fe_{16}$ powder has a mixed-phase structure of the Zr, ZrH_2 , FeV and $Zr(V_{1-x}Fe_x)_2$ phases. This powder has an average particle size of about 20 nm. The synthesized nanoparticles have surface oxides; $Fe_{24}Zr_{76}O_2$, V_2ZrO_2 , ZrO_2 , V_2O_3 , V_2O_4 , Fe_3O_4 and $Fe(OH)O$. The $Zr_{55}V_{29}Fe_{16}$ nanopowder synthesized by the plasma arc discharge process showed a getter characteristic, even though it had a lower hydrogen sorption speed than the $Zr_{57}V_{36}Fe_7$ getter powder synthesized by the conventional hydride-dehydride method.

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