CONTROL OF VAPORIZATION AND CONDENSATION OF METAL MIXTURE FOR PRODUCTION OF SILICIDE NANO-PARTICLES BY THERMAL PLASMAS

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Abstract

Mechanism of vaporization enhancement of particular metals from metal mixture by hydrogen was investigated experimentally, and the condensation mechanism of metal mixture in thermal plasmas was investigated experimentally and numerically. For Si-M (Mo, Ti, Co, Fe, Cr, or Mn) system, composition of the prepared nano-particles can be controlled through the vaporization process by H_2 concentration in the arc, as well as the condensation process by adequate quenching.

1. Introduction

Attractive material processes with thermal plasmas have been proposed for production of nano-particles, however thermal plasmas have been simply used as high temperature source. Therefore thermal plasmas may have more capability for material process, if thermal plasmas are utilized effectively as chemically reactive gas.

Investigation of physical and chemical processes in thermal plasma processing is indispensable for production of nano-particles. Ohno and Uda [1, 2] investigated the vaporization phenomena of molten metals under "hydrogen plasma-metal" reaction, although they investigated only the reaction mechanism of pure metal. Yoshida, et al. investigated co-condensation process of metal vapors for Nb-Al and Nb-Si systems [3] and for Nb-Si and V-Si systems [4]. For preparation of intermetallic compounds with stoichiometric composition, the vaporization and condensation rates of the constituent metals should be controlled in the case of large difference in the vapor pressure.

The purpose of this paper is to investigate the mechanism of vaporization enhancement of particular metals from metal mixture by hydrogen in arc plasmas. Another purpose is to investigate the condensation mechanism of metal mixture vapor in thermal plasmas. These investigations are important for production of silicide nano-particles by thermal plasmas.

2. Experimental procedures

2.1 Experimental set-ups for vaporization investigation

Ar-H_2 DC arc was used for the investigation of vaporization enhancement of particular metals from metal mixture. A pellet, the diameter 20 mm and height 8 mm, of mixture of Si and M (M = Ti, Mo or V) used as raw material were placed on a water-cooled copper anode. Ar or Ar-H_2 arc was used for the vaporization of the raw material. Typical operating conditions are as follows; current: 200 A, voltage: 20–30 V, total pressure: 101 kPa, total gas flow rate: 25 Nl/min, H_2 concentration: 0, 20, 50 vol %, discharge time: 10–90 min. The metal fume was generated from the raw material surface on the anode soon after the raw material was arc-melted. The generated fume was transported by a gas circulation flow to the collection filter.

2.2 Experimental set-ups for condensation investigation

Induction thermal plasmas were used for the investigation of condensation mechanism of metal mixture vapor. Si powder premixed with metal powder (Mo, Ti, Co, Fe, Cr, or Mn) was introduced into the plasma. In the thermal plasma, the premixed powder was evaporated immediately and nano-particles were produced through the cooling process. The nano-particles were prepared on condition that metal vapor was quickly quenched by the water-cooled copper coil at different positions. Typical operating conditions are as follows; plate power: 20 kW, total pressure: 101 kPa, Ar flow rate: 34 Nl/min, discharge time: 10 min, powder feed rate: 0.1 g/min.

3. Results and discussion for vaporization process

3.1 Ti-Si system

The XRD pattern of the prepared particles represents that the preparation of $TiSi_2$ particles was most successful from the 47 at%-Ti raw material with the 50 %-H_2 arc. TEM photographs indicate that the all particles have spherical morphology with average particle diameter of 32.7 nm. The relatively large particles are attributed to the particle collection without quenching.

Relation between Ti fraction in the prepared particles and the initial composition is shown in **Fig. 1**. An increase in H_2 concentration in the arc leads to an increase in Ti fraction in the prepared particles. Hydrogen in arc plasmas enhances the vaporization of Ti element from the molten metals. Therefore, Ti fraction in the prepared particles can be controlled by H_2

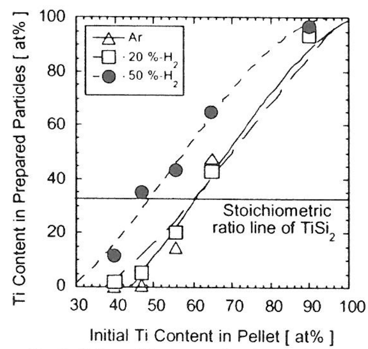

Fig. 1 Effect of hydrogen fraction in the arc on Ti content in the prepared particles.

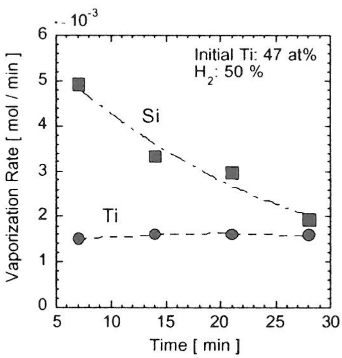

Fig. 2 Time dependence of vaporization rates of Si and Ti.

concentration in the arc. Nano-particles with the stoichiometric composition of $TiSi_2$ were prepared from the 47 at%-Ti raw material with the 50 %-H_2 arc. The similarity of vapor pressure of the constituent metals plays an important role in the preparation of silicide nano-particles. Therefore, single phase of intermetallic compound can be prepared with the properly controlled vapor composition in the case of Ti-Si system.

The vaporization rates of the constituent metals were estimated from the weight decease of the raw material together with the EDX results of the prepared particles. The vaporization rate of Si decreases with time, while that of Ti is almost constant during the arc treatment as shown in **Fig. 2**. The vapor composition is in Si-rich up to 15-min treatment compared with the stoichiometric composition of $TiSi_2$.

Figure 3 shows the spectroscopic measurements of the vaporized species during the treatment with the 20 %-H_2 arc and the Ar arc. The emission intensities of Si at 288.1 nm and Ti at 375.9 nm are normalized by the intensity of Ar at 430.1 nm. The Si intensities with the 20 %-H_2 arc and the Ar arc are almost the same. On the other hands, the Ti intensities with the 20 %-H_2 arc are much higher than those with the Ar arc. Higher intensity of Ti at higher H_2 concentration in the arc results from the vaporization enhancement of Ti element from the molten metals by hydrogen in arc plasmas.

3.2 Mo-Si system

Relation between Mo fraction in the prepared nano-particles and the initial composition is shown in **Fig. 4** for the Ar, 20 %-H_2 and 50 %-H_2 arc. An increase in H_2 concentration in the arc has little effect on Mo fraction in the prepared particles. The stoichiometric composition of $MoSi_2$ cannot be obtained even from the 85 at%-Mo raw material. Vaporization of Mo element should be more enhanced to obtain the stoichiometric composition of $MoSi_2$ in the prepared particles.

Coexistence of unreacted Si and Mo was found in the XRD results. These results indicate that each metal vapor is nucleated at different times and regions owing to the large difference in the vapor pressure. The vaporization and condensation of the constituent metals must be

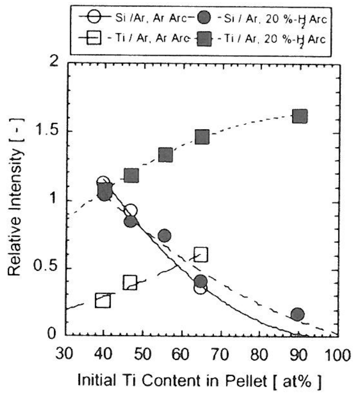

Fig. 3 Effect of hydrogen fraction in the arc on relative emission intensities of Si and Ti.

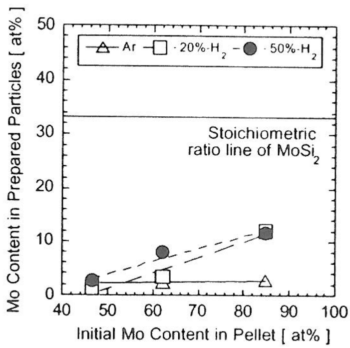

Fig. 4 Effect of hydrogen fraction in the arc on Mo content in the prepared particles.

controlled to overcome the large difference in the vapor pressure as in the case of Mo-Si system. TEM photographs indicate that the all particles have spherical morphology with average particle diameter of 20.9 nm.

3.3 Vaporization mechanism

Hydrogen in arc plasmas enhances the vaporization of particular metals on the anode. In Ti-Si system, the vaporization rate of Ti is enhanced by hydrogen in the arc. The reaction between molten metals and hydrogen arc is important for material processing such as production of nano-particles. Moreover, the selective vaporization would be applied for separation process of metal mixtures.

Vaporization rate of pure metal can be estimated by Hertz-Langmuir-Knudsen equation. From the experimental results, large difference is found among the separation factors obtained with the 50 %-H_2 arc, 20 %-H_2 arc and Ar arc. Therefore, Hertz-Langmuir-Knudsen equation can not be used for binary metal systems, because the chemical reactivity of hydrogen in arc plasmas is not considered in Hertz-Langmuir-Knudsen equation.

Ohno and Uda [1] proposed the reaction parameter, *Rp*, between molten pure metal and hydrogen in arc plasmas.

$$Rp = (- \Delta H / Ls) \{ n_{H2}(T) / n_{H2}(273\ \mathrm{K}) \} \qquad (1)$$

where ΔH is the reaction enthalpy of hydrogen recombination, Ls is the vaporization heat, and n_{H2} is the number density of H_2. If the vaporization enhancement is mainly attributed to the recombination of hydrogen atoms in molten metals, the ratio of the reaction parameters relates to the separation factor.

Relation between the separation factor and the ratio of reaction parameters estimated by Eq. (1) is presented in **Fig. 5**. Difference in separation factors between the 50 %-H_2 arc and the 20 %-H_2 reveals that the vaporization mechanism for pure metal proposed by Ohno and Uda [1] may not be applied for binary metal systems.

The vaporization enhancement is attributed to the following four factors; (1) recombination of hydrogen atoms in molten metals; (2) high thermal conductivity of hydrogen; (3) formation of intermediate products such as hydride; (4) activity modification by hydrogen in molten metals. From the above discussion, the first and second factors have small effect on the vaporization enhancement, therefore the third and/or fourth factors were considered to be the main factors. However hydride produced from molten metals with hydrogen arc has not been identified yet. Instability and unknown properties of hydride give rise to difficulty in the quantitative examination. Investigation of reaction mechanism of molten metals with chlorine or fluorine in arc plasmas would lead to the alternative solution [5], because chloride and fluoride are more stable and their properties have been known compared with hydride.

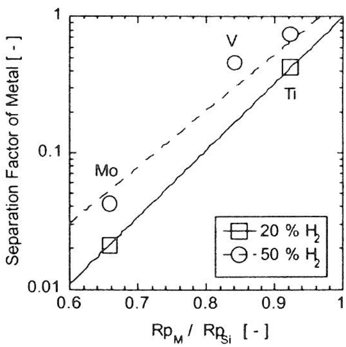

Fig. 5 Relation between separation factor and the ratio of reaction parameters.

4. Results and discussion for condensation mechanism

4.1 Ti-Si system

The XRD results indicate that Ti_5Si_3 can be prepared more easily than $TiSi_2$, because Ti_5Si_3 has wide composition range with 3 %, while $TiSi_2$ has the strict stoichiometric composition. TEM photographs show that the average particle diameter is 16.7 nm. Smaller diameter of the particles prepared with induction thermal plasmas is attributed to the rapid quenching. **Figure**

6 shows the relation between the relative intensity XRD spectrum of Ti_5Si_3 and the initial composition at different quenching positions. Larger amount of Ti_5Si_3 particles was prepared at larger Ti content in the feed powders. The quenching condition has little effect on the prepared nano-particle composition. Similar results were obtained in Cr-Si, Fe-Si, Mn-Si systems.

4.2 Mo-Si system

From the XRD results, induction thermal plasmas with rapid quenching provide larger amount of $MoSi_2$ particles than hydrogen arc without quenching. TEM photographs indicate the average particle diameter is 13.1 nm. **Figure 7** shows the relation between the relative intensity XRD spectrum of $MoSi_2$ and the initial composition at different quenching positions. The quenching condition has strong effect on the prepared silicide composition for Mo-Si system.

4.3 Numerical simulation for condensation process

Two-dimensional continuity, momentum and energy conservation equations with Maxwell's electromagnetic equation were solved to calculate plasma velocity and temperature field [6]. Trajectory and temperature history of single metal particle in thermal plasmas were calculated using the plasma field to estimate the vapor concentration. Temperature jump model and free molecular model were applied to the heat transfer estimation corresponding to the Knudsen number. Numerical results indicate that metal and silicon vapors coexist in the plasma torch, resulting in better preparation of the silicide.

The nucleation rate expression proposed by Girshick et al. [7] was used for the estimation of critical saturation ratio. Relationship between the nucleation rate and saturation ratio is

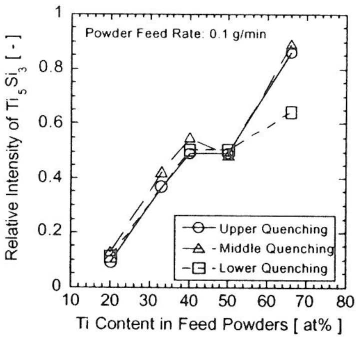

Fig. 6 Effect of quenching position on the prepared particle composition for Ti-Si system.

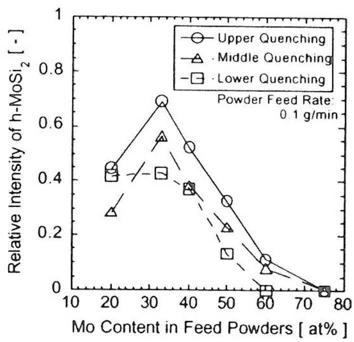

Fig. 7 Effect of quenching position on the prepared particle composition for Mo-Si system.

shown in **Fig. 8**. The nucleation rate is strongly dependent on the surface tension and the saturation ratio. When the nucleation rate is over 1.0 $cm^{-3}\ s^{-1}$, particle formation can be conveniently observed experimentally. Therefore the corresponding value of saturation ratio is defined as the critical saturation ratio [8]. The critical saturation ratio of Si was estimated to be 4, while the other metals have the critical saturation ratio from 40 to 130.

The nucleation temperature at the critical saturation ratio was shown in **Fig. 9** for constituent metals of silicide. The nucleation temperature of the metals except Si almost corresponds to the melting temperature, while Si has wide liquid range between the nucleation and melting temperature, resulting in better preparation of silicide. For Mo-Si system, nucleation position of Mo is different from that of Si. Therefore, quenching position has strong effect on the particle composition of molybdenum silicide nano-particles.

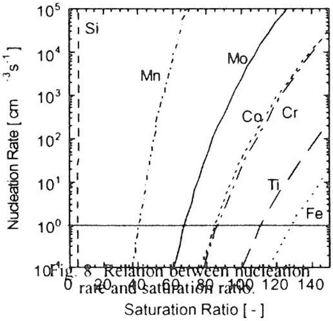

Fig. 8 Relation between nucleation rate and saturation ratio.

5. Conclusions

Experiments were carried out to investigate the vaporization enhancement of particular metals from metal mixture by H_2 arc. Experiments and numerical simulations were performed to investigate the condensation of metal mixture vapor in thermal plasmas. For Si-M (Mo, Ti, Co, Fe, Cr, or Mn) system, composition of the prepared silicide nano-particles can be controlled through the vaporization process by H_2 in the arc, as well as the condensation process by adequate quenching.

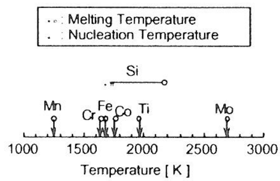

Fig. 9 Nucleation and melting temperature

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Acknowledgement

The financial support given by the Kanagawa Academy of Science and Technology Research Grant is gratefully acknowledged.