Formation of Zirconium Nitride by Means of Nitrogen Plasma Jet*

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Zirconium nitride was formed by a transferred plasma torch. The plasma jet was prepared by passing nitrogen gas rapidly under ordinary pressure through the electric discharged arc between copper crucible anode and a cooled tungsten cathode. When zirconium metal piece was set on the crucible, the nitrogen plasma jet reacted easily with the zirconium piece on the crucible. The nitrogen flow rate was 1.5~4 l/min at a power input of 4~8 kW. The weight of the metal reacted with nitrogen plasma jet increased with increasing reaction time. It was confirmed by means of X-ray diffraction method that the chemically reacted metal surface had been transformed to ZrN. The kinetics of the nitride formation obeys a parabolic relationship. Influences of the current intensity and the nitrogen flow rate on the reaction were also investigated.

1. Introduction

Zirconium nitride was found to be formed by the reaction between ZrO_2 and the nitrogen plasma jet.¹⁾ The authors have also studied on $\text{TaN}^{2)}$, $\text{Mo}_2\text{N}^{3)}$, $\text{W}_2\text{N}^{3)}$, $\text{TiN}^{4)}$, and $\text{AlN}^{5)}$, which are formed by the reaction between corresponding metal rods and the nitrogen plasma jet produced at a transferred plasma torch. In this report, results are presented on the formation of zirconium nitride by the reaction between zirconium button and the nitrogen plasma jet.

2. Experimental

Materials: Zirconium metal (99.7 % Zr + 0.3 % Hf) button of about 10 g which was obtained by melting zirconium sponge with argon plasma jet was used. Highly pure argon and nitrogen gas was applied.

Apparatus: The apparatus used for the nitride formation was described previously²⁾.

The nozzle diameter of the plasma torch was 7 mm.

Methods: The method of the zirconium nitride formation was carried out in the same way as that reported previously²⁾. The microstructure of the cross section of the chemically transformed zirconium piece was observed with a metallurgical microscope.

3. Results

3.1 Confirmation of the Product

As the nitrogen plasma jet reacted with the zirconium, the color of the surface of the metal changed to grey. Typical X-ray diffraction pattern is shown in Fig. 1. According to these diffraction patterns, it was confirmed that the product formed on the metal surface consists of almost pure ZrN. The lattice constant of the product was about 4.59 Å which is close to the literature value of 4.57 Å.

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Fig. 1 X-ray diffraction of Zirconium metal surface reacted with nitrogen plasma jet

3.2 Energy Consumed for Zirconium Nitride Formation

a) Characteristics of the plasma torch.

Potential – current curves on the plasma torch are shown in Fig. 2. The potential decreased with increasing current intensity at various nitrogen flow rates. The relation between power input and nitrogen flow rate at varied current intensities are shown in Fig. 3. The power input increased with increasing nitrogen flow rate.

Fig. 2 Current-potential curves

Fig. 3 Relation between power and N₂ flow rate

b) Energy input for nitrogen plasma jet.

From Fig. 3, the relations between nitrogen flow rate and the energy consumed per unit volume for the nitrogen plasma jet (kW·min/l) was obtained and are shown in Fig. 4. The energy decreased with increasing nitrogen flow rate. In the plasma jet, sufficient energy would be given to the nitrogen to form atomic nitrogen. From the consideration of excitation energy, ionization of nitrogen can be supposed to occur easily. Therefore, the nitrogen plasma jet is considered to be composed of N, N⁺, electron and a small amount of N₂.

All of the energy input for nitrogen plasma jet may not be consumed for zirconium nitride

Fig. 4 Relation between energy and N₂ flow rate

formation, of course. Examination of these cooling effects shows that the heat energy given to the cooling water amounts rather more than energy required to form nitrogen plasma jet. This indicates that the chemical reaction of ZrN formation is highly exothermic.

3.3 Temperature Measurement

A surface temperature of the zirconium metal reacting with the nitrogen plasma jet was measured with the micropyrometer. The relation between the temperature of the metal surface and the current intensity at various nitrogen flow rate is shown in Fig. 5. The measured values were corrected by use of Wien's equation in consideration of the emissivity of the metal.

The surface temperature of the zirconium metal was higher than the melting point of the zirconium at the current of 50A. The temperature increased with increasing current intensity and nitrogen flow rate. When the current intensity came up to higher than 60A, the surface temperature was higher than the melting point of ZrN.

Fig. 5 Surface temperature of zirconium reacted with the nitrogen plasma jet

3.4 Influences of Several Factors Affecting the Reaction of ZrN Formation

Influences of current intensity, nitrogen flow rate and the reaction time on the ZrN formation were studied.

The relations between the weight gain of the metal and the reaction time at various current intensities and nitrogen flow rates are shown in Fig. 6.

Fig. 6-1 Relation between W and reaction time (N₂ flow rate 2 l/min)

Fig. 6-2 Relation between W and reaction time (N₂ flow rate 3 l/min)

Fig. 6-3 Relation between W and reaction time (N_2 flow rate 4 l/min)

The weight gain (Δw) increased with reaction time. At the beginning of the reaction, the reaction kinetics of the nitrogen plasma jet and zirconium metal was represented by the parabolic relationship $(\Delta w)^2=kt+c$, as shown in Fig. 7, where $(\Delta w)^2$ is a square of the weight gain, k is a rate constant and c is a constant. The rate constant k is listed in Table 1. The values is very larger than that obtained in the reaction between zirconium metal and nitrogen gas at about 1000°C ^{6),7)}.

Arrhenius plots for the reaction kinetics are shown in Fig. 8. It may be seen that $\log k$ varies linearly with $1/T$ at definite flow rate of nitrogen gas. And as the flow rate of nitrogen gas

Fig. 7-1 Relation between $(W)^2$ and reaction time. (N_2 flow rate 2 l/min)

Fig. 7-2 Relation between $(W)^2$ and reaction time (N_2 flow rate 3 l/min)

Table 1 Nitriding Rate Constant of Zirconium ($\text{g}^2\text{cm}^{-4}\text{sec}^{-1}$)

Dravnieks ⁶⁾	Rosa, Smeltzer ⁷⁾	This work
2.2×10^{-13} (862°C, 80 mm)	1.39×10^{-12} (800°C, 400 mm)	1.63×10^{-5} (2850°C, N_2 3 l/min)
1.1×10^{-12} (920°C, 70 mm)	1.11×10^{-11} (900°C, 400 mm)	2.33×10^{-5} (3200°C, N_2 3 l/min)
6.8×10^{-12} (1430°C, 80 mm)	1.11×10^{-10} (1000°C, 400 mm)	2.60×10^{-5} (3560°C, N_2 3 l/min)

Fig. 7-3 Relation between $(W)^2$ and reaction time (N_2 flow rate 4 l/min)

Fig. 8 Arrhenius plot

increased log k increased and the gradient of the line decreased. Therefore, it is considered that the reaction of ZrN formation is affected by the nitrogen flow rate and the current intensity.

An example of the relations between the weight gain of the zirconium metal and the current intensity is given in Fig. 9, which shows the weight gain of the zirconium metal to

Fig. 9 Relation between W and current intensity (N_2 flow rate 3 l/min)

increase with increasing current intensity.

The weight gain of the zirconium metal is proportional to the square of the nitrogen flow rate at any definite current intensity as shown in Fig. 10. The number of species in the nitrogen plasma jet (N , N^+ , electron and N_2) may remarkably affects the reaction of ZrN formation.

Fig. 10 Relation between W and square of N_2 flow rate (Current intensity 100A)

4. Discussion

As mentioned above, it may be considered that the components of the nitrogen plasma jet are N , N^+ , electron and small amount of N_2 . Due to the heating by the plasma jet, the zirconium piece would melt to liquid state.

The chemical reaction between the nitrogen plasma jet and the molten zirconium take place at the metal surface to form ZrN at the place. The nitriding rate may be represented by the parabolic relationship at the beginning of the reaction. This indicates that, at the beginning of the reaction, the diffusion of the nitrogen ion in the metal controls the rate determining stage.

The weight gain of the zirconium metal, however, is much higher than that of nitriding the zirconium metal with the nitrogen gas at about $1000^\circ C$.

The cross section of the product was investigated metallographically. And the micrographs obtained are shown in Photos. 1 and 2. Photo. 1 is the micrograph of the cross section of the metal reacted with the argon plasma jet, while photo. 2, that of the metal reacted with the nitrogen plasma jet. The cross section of the metal reacted with the argon plasma jet seems to be of homogeneous metal phase, while the cross section of the metal reacted with the nitrogen

× 50

Photo. 1

× 50

Photo. 2

plasma jet to be of heterogeneous.

The relation between the nitrogen concentration and the distance from the surface of the metal reacted with nitrogen plasma jet was obtained by use of X-ray microanalyser and is shown in Fig. 11. At the surface region, the nitrogen concentration is nearly uniform. At the inner region, the nitrogen concentration decreases with increasing distance from the surface. The product in the surface region consists of almost ZrN as confirmed by X-ray diffraction. The inner region, the product may be ZrN_{1-x} .

Reaction conditions: 100 A, N_2 3 l/min, 5 min

Fig. 11 Relation between $NK\alpha$ intensity and distance from the surface

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