Influence of Hydrogen Induced Thermal Pinch on Nanoparticle Formation in Arc Plasma*

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Fe nanoparticles were prepared by DC arc plasma method under Ar, Ar-50%H₂ or H₂ flow. The arc plasma was well constricted due to thermal pinch effect when Ar-50%H₂ or H₂ was used, and the generation ration of the Fe nanoparticles was significantly enhanced with the pinched arc. Our numerical simulation indicated that the Fe anode can be efficiently heated (close to boiling point of Fe) due to the thermal pinch effect, and thereby the generation ratio can be increased. Since the thermal pinch effect enhanced the arc flow velocity as well, the size of the resulting Fe nanoparticles was also influenced.

Key Words: DC arc, Thermal pinch effect, Nanoparticles, Generation rate, Hydrogen, Input power

1. Introduction

DC arc plasma can result in a localized high energy density, giving a very high temperature with capable of melting and vaporizing metals, and simultaneously induced plasma jet can rapidly quench vaporized metals. Thus, the arc plasma can be act as self flow reactor for producing nanoparticles. Because it is a route to prepare high-purity nanoparticles with high productivity at low cost, the arc plasma technique has attracted great interest¹⁻³⁾.

Ohno and Uda developed an effective method for production of metallic nanoparticles by using hydrogen gas^{4,5)}. They showed that vaporization rate of metals were well enhanced with increasing hydrogen gas mixture ratio under atmospheric pressure. It was proposed “hydrogen plasma-metal reaction” model for the hydrogen assisted high vaporization effect, which is that dissociated hydrogen in the arc plasmas dissolves into molten metals of anode and enhances the vaporization of metal elements when hydrogen atoms are emitted from the molten metals.

The mechanism of the vaporization enhancement by hydrogen in arc plasmas has been still interesting topic. Watanabe et al. have prepared nanoparticles of Si-based inter metallic compounds, and observed the vaporization enhancement of particular metals from metal alloys by hydrogen in arc plasma⁶⁾. Similar tendency was observed in Sn-Ag mixture⁷⁾. It was shown that this phenomenon can not be explained by only “hydrogen plasma-metal reaction” model.

It is well known that heat flux to the anode is low in argon arcs, and mixtures of argon with helium, hydrogen and nitrogen are used for its enhancement. Thus, arc properties such as maximum

arc temperature, maximum flow velocity and heat flux density are strongly dependent on ambient gaseous conditions. Recently, Tanaka et al., have investigated the influence of shielding gas composition on arc properties in TIG welding^{8,9)}. It was found that the addition of hydrogen to argon increases the arc and anode temperature due to thermal pinch effect⁸⁾. The changes in arc plasma state may also influence formation of metal fumes or nanoparticles.

In the present study, Fe nanoparticles were prepared by DC arc plasma method. The specific features focused on were the arc constraint (thermal pinch effect) associated with hydrogen gas and its relevance to generation rate and size of the resulting Fe nanoparticles.

2. Experimental procedure

2.1 Experimental set up

Fig.1 shows a schematic illustration of experimental set-up. The apparatus mainly consists of the DC power supply, a water-cooled vacuum chamber, a particle collector, a gas

Fig. 1 A schematic illustration of experimental set-up for preparation of Fe nanoparticles by arc plasma method

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circulator and a vacuum pump. The diameter of tungsten cathode was 8.0mm with a 60° conical tip. The Fe pellet (99.8%) was placed on the water-cooled copper anode plate.

Subsequent to achieving a base vacuum of 200Pa, Ar, H₂ or Ar-50%H₂ was introduced. The arc plasma was generated under total pressure of 101kPa with gas flow rate of 100 l/min. Fe nanoparticles or the generated Fe fume was transported by the gas circulation flow to the collector chamber. In this study, arc current of 150A and arc gap of 10mm were carefully controlled to be constant during the nanoparticle preparation.

2.2 Analysis

The weight of the collected Fe nanoparticles was measured to estimate their generation ratio. The specific surface area of the Fe nanoparticles was measured using a nitrogen gas absorption instrument (micromeritics ASAP 2010, Shimadzu, Japan), based on the BET method, which was used for calculation of the particle size ($=6/\rho S$, ρ : density, S : specific surface area)¹⁰. The morphology and the structure were examined by scanning electron microscopy (ERA-8800FE, Elionix, Japan).

The numerical simulation was also conducted for the present plasmas. Using unified models of the arc and the arc electrodes which were developed recently ^{9,11)}, the maximum arc temperature, the maximum flux flow and the maximum concentration on Fe vapor on the anode were calculated. In all cases, the following parameters were used: an arc current of 150A, an arc length of 10mm, a 8.0mm diameter theoriated tungsten cathode, Fe pellet anode on a water cooled copper, a gas flow rate of 120L/min, atmospheric pressure. The details of the calculation are given in Ref.12-13.

Fig. 2 Photographs of 150A arcs in Ar, Ar-50% H_2 and H_2 .

Fig. 3 H₂ concentration dependence of generation ration of Fe nanoparticles.

3. Result and discussion

Figure 2 shows a set of photographs of 150A arcs in Ar, Ar-50%H₂ and H₂. As can be seen, the arc plasma was significantly constricted by addition of 50% H₂. This is due to the thermal pinch effect ⁸⁾. When only H₂ was used, the arc was mostly constricted. The blue colors observed in the Ar-50%H₂ and H₂ arcs were identified as the ionized Fe vapor. It is indicated that the hydrogen plays an important role on efficient vaporization of the Fe anode.

Figure 3 shows the H_2 concentration dependence of the generation rate of the Fe nanoparticles. The significant enhancement of the generation rate was observed for the Ar-50% H_2 arc, which was increased about two orders of magnitude compared with that of Ar arc. Although H_2 arc increased more, the rate of the increase was only slightly higher than that of Ar-50% H_2 arc. It is noted that the present dependence is similar to that reported by Uda ¹⁴⁾. The generation rate is directly correlated to concentration of Fe vapor from the anode, and therefore, the vaporization of Fe was well-enhanced in the Ar-50% H_2 arc, but more mixing of H_2 , 100% H_2 did not result in further enhancement. The non-linear relationship between Fe vaporization ratio and H_2 concentration in Ar can not be fully explained by the “hydrogen plasma-metal reaction” model ^{4,5)}.

The input power ($=I \times V$) is also shown in Fig.3. It increased with almost proportional to H_2 concentration. Since the arc current was fixed to be 150A, the observed increase of the input

power was due to the increase of the arc voltage. In arc plasma, input power is consumed mostly for Joule heating, and the heat is transported to anode electrode with very high efficiency. Therefore, in the present study, the increase of H_2 concentration must result in the increase of the heat flux density which strongly influences the surface temperature of the anode. The origin of arc properties changed with H_2 concentration is also due to the hydrogen induced thermal pinch effect⁸⁾.

H_2 can induce most effectively thermal pinching of the arc. In recent studies performed by Tanaka et al.^{8,9)}, the thermal pinch effect strongly depends on specific heat of gas (except for helium). The specific heat of H_2 is the most highest among conventionally used gaseous species⁸⁾, and thereby the arc plasma is mostly constricted under H_2 flow. The arc constriction leads to increase of arc voltage under the constant current flow, and the greater ohmic heating gives rise to increase arc temperature, which enhances the heat flux to anode, i.e., metal vaporization from anode. Another interest of the thermal pinch effect is the arc flow velocity, because it also influences formation behavior of Fe nanoparticles. Decreasing the arc cross-sectional area increases the current density J and the velocity of the arc via magnetic pinch effect, since the pressure gradient is proportional to JB , where B is the self-induced magnetic field strength. The enhanced arc flow velocity increases quenching rate of vaporized Fe.

Here, we discuss a possible mechanism of the hydrogen assisted high vaporization effect from point of the thermal pinch effect, with help of our numerical simulation. Table 1 summarizes the calculated maximum arc temperature, maximum arc flow velocity and maximum concentration of Fe vapor near Fe anode. As expected, these arc properties are significantly increased with H_2 concentration. It is noticeable that the maximum concentration of Fe vapor in Ar-50% H_2 arc is higher about two orders of magnitude compared with that of Ar arc, and is slightly lower than that in H_2 arc. These calculated mass ratios are good agreement to those shown in Fig.3.

The maximum concentration of Fe vapor was calculated by taking account of Fe vapor pressure which directly relates to the surface temperature of the Fe anode. In this calculation, the estimated surface temperature of the Fe anode was 2103K for Ar arc.

Table 1 Summary of the calculated arc properties for 150A arcs in Ar, Ar-50% H_2 , H_2

	Maximum arc temperature (K)	Maximum arc flow velocity (m/s)	Maximum conc. of Fe vapor near anode (mol%)
Ar	18080	184	0.02
Ar-50% H_2	25210	796	4.07
H_2	39800	4181	4.71

This temperature is higher than the melting point of Fe (1808K) and less than the boiling point (3160K). On the other hand, the estimated surface temperature was 3027K for Ar-50% H_2 arc. The surface temperature of the anode heated by Ar-50% H_2 arc is very close to the boiling point of Fe, and about 1000K larger than that by Ar arc. This is obviously resulted from increase of the heat flux density due to hydrogen induced thermal pinch effect. Therefore, according to the present numerical simulation, vaporization from the Fe anode could be enhanced by efficiently heated surface of the anode. In case of 100% H_2 , since the surface temperature could not be increased more than boiling temperature, it would rather widen the boiled region on the anode, and increase vaporization with depending on the size of boiled region. Thus, the generation ratio of Fe nanoparticles may be increased slightly than that of Ar-50% H_2 arc. The more detail and systematic discussion about the hydrogen assisted high vaporization will be described in a near future, in terms of the thermal pinch effect.

a) Ar – 50% H_2

b) 100% H_2

Fig.4 SEM image of Fe nanoparticles produced from a) Ar-50% H_2 arc and H_2 arc.

There was no significant difference in the generation ratio for Ar-50% H_2 and H_2 arcs. However, there is a quite difference between them for the arc flow velocity, which would influence the particle size and structures. Figure 4 shows the SEM images of Fe nanoparticles produced from Ar-50% H_2 and only H_2 arcs. As can be seen, the particles produced from Ar-50% H_2 arc is a slightly larger than that of H_2 arcs. The particles sizes estimated from average specific surface area for Ar-50% H_2 and only H_2 arcs are 41nm and 33nm, respectively. It can be considered that the higher arc flow velocity in H_2 arc would lead to the more nucleation density. On the other hand, the particle size of Fe nanoparticles produced in Ar arc was 9nm, which was mainly due to the low vaporization of Fe from the anode. The more detail of nucleation and condensation, i.e., formation behavior of Fe nanoparticles will be treated in a separate paper.

4. Conclusions

Fe nanoparticles were prepared by DC arc plasma method under Ar, Ar-50% H_2 or H_2 . The thermal pinch effect was induced for Ar-50% H_2 or H_2 arcs, and Fe ionized vapor was observed for their arcs. The generation ratio of Fe nanoparticles was significantly enhanced for Ar-50% H_2 or H_2 arcs. The numerical simulation of the present arcs revealed that the arc properties of the maximum arc temperature, the maximum arc flow velocity and the maximum arc are significantly increased with H_2 concentration. It is noticeable that the maximum concentration of Fe vapor in Ar-50% H_2 arc is higher about two orders of magnitude compared with that of Ar arc, which are good agreement to the experimental mass ratio of the Fe generation for their arcs. According to our numerical calculations, the enhanced vaporization from the Fe anode may be due to efficiently heated surface of the anode which relates to hydrogen induced thermal pinch effect. Since the thermal pinch effect also enhanced the arc flow velocity, the particles size of the resulting Fe nanoparticles was influenced even under the similar concentration of Fe vaporization of Ar-50% H_2 and H_2 arcs. The present study indicates that control of the thermal pinch effect may be the important factor for producing metallic nanoparticles by arc plasma method.

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