HYDROGEN EFFECTS IN INTERACTION BETWEEN THERMAL Ar-H₂ PLASMA AND METAL

M. Suzuki, M. Hirayama, M. Nishikubo and H. Akatsuka

Research Laboratory for Nuclear Reactors
Tokyo Institute of Technology
2-12-1 O-okayama, Meguro-ku, Tokyo 152, Japan

Abstrract

In order to examine effects of hydrogen atoms on pure metals irradiated by argon-hydrogen plasma, some experiments are carried out. A large amount of hydrogen atoms can dissolve in a metal sample by argon-hydrogen plasma irradiation and consequently the lowering of the solidifing temperature is observed. Experimental results and their physics are discussed thermodynamically.

1. INTRODUCTION

Hydrogen is one of the gases most widely used in plasma processes[e.g.(1)(2)(3)]. At the normal atmospheric pressure around 10^5 Pa, the dissociation reaction of hydrogen supplied in the molecular state, commences at temperature around 2000K. Therefore, it confirms that at the common operating temperatures of most plasma process, a large proportion of the hydrogen is in the atomic state, so that any metallurgical processes conducted in those vessel will need involve the participation of dissociated hydrogen atoms. It is readily available and, apart from its usual reducing or deoxidizing role, is also useful as a heat transfer medium on account of its high heat content and thermal conductivity in the plasma state. Hydrogen mixing effects on the increase of energy transport not only due to its light mass but also due to dissociation reaction.

We have observed that the metal sample, which is heated by pure argon plasma jet and kept below melting temperature, melts immediately after adding hydrogen as the plasma gas. Of cource, this is caused by increasing of the heat flux, maily. In this observation, however, it seemed to have another effect due to hydrogen. The objectives of this study are to investigate basic behaviors of hydrogen atoms in plasma and metals irradiated by reactive plasma in order to contribute to more understand of the hydrogen effects. In this study the lowering of the melting point

of metal by hydrogen dissolution into metals are measured experimentally and discussed thermodynamically.

2. EXPERIMENTAL

Experiments have been carried out in a water-cooled plasma chamber where an arc plasma jet generator and a hearth are set inside. Plasma is generated by an arc discharge between a 5mm-diam. tungsten cathode tip and a 4mm-i.d. copper-nozzle. Working gas with argon/hydrogen ratio prepared properly is fed at the constant flow rate. Experimental conditions are arc current 100A, operation pressure 760Torr and hydrogen concentration 5%. For the solidifying temperature measuremens, the copper or silver sample filled up in the crucible with having a supplementary heater as shown in Fig.1. The samples are heated by

5(Ar+H_2(5%)) [l/min]
DC 100 [A]

Z = 4 [cm]

Crucible

Thermocouple
(ϕ1.2)

20

20

Heater

Fig.1 Schematic of experimantal set–up.

both of the plasma irradiation and the heater, because heat flux and hydrogen atom flux from the plasma jet increase as getting away from the cathode and they are not controllable independently. So, the sample is placed with keeping the proper distance from the nozzle to avoid the excess heating up. In this situation we measured the Hα line to confirm the existence of enough amount of hydrogen atom. Thermocouples measuring sample temperature are covered with the 1.2mm-o.d. ceramic tube to prevent from contacting with the plasma flow and the sample metals directly and temperature change is recorded continuously and it is confirmed that they can follow sufficiently such a temperature change as appeared in our experimental conditions.

Before starting experiments, the plasma chamber is evacuated and filled up with argon gas at atmospheric pressuure. A metal sample is heated and melted by heater only and the covered thermocouple is inserted into melted metal to measure temperature. Figure 2 shows the schematic example of the recorded temperature time history. The melting or solidifying point of the sample is judged by the plateau of temperature history resulting from releasing or absorbing latent heat. At first, by the
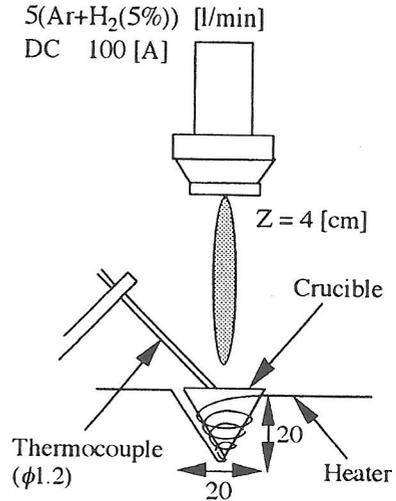
heater on/off operation it is confirmed that thermocouple indication agrees with the reference values within an error at melting point and solidifying point of the sample. Secondly, the sample is heated up and melted by both of the heater and the plasma irradiation and its temperature is kept at a ceartain temperature above
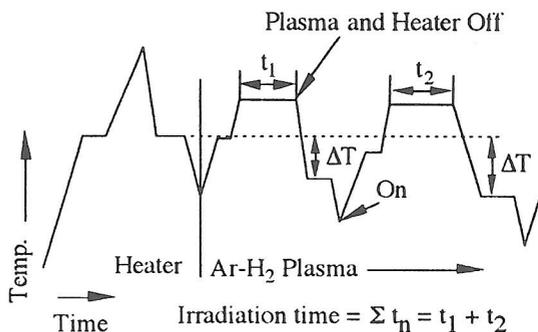

Fig.2 Example of the recorded temperature history of a sample.

the melting point during some minutes by adjusting the heater power. And both of the heater and the plasma irradiation is shut off and the solidifying temperature is measured. After that, this operation is continued several times. In this experiment the plasma irradiation time is defined as the sum of time kept at the constant temperature. Although measurements of the melting point are desired, the error is to large to get the accurate temperature in heating up by plasma irradiation. Because the upper part of thermocouple above the sample surface is exposed in the plasma flow and heating up of that part due to its convection heat fux produces some error. Measurements of the solidifying point were carried out in both cases of pure argon plasma and argon/hydrogen plasma.

3. RESULTS AND DISCUSSIONS

The solidifying temperature of samples of pure copper and pure silver were measured by above mentioned procedure. Although our plasma irradiated is not in equilibrium and it is impossible to discuss about the phenomena quantitatively, we ascertained qualitatively by some experiments that the hydrogen atom plays the leading role in this phenomena. Figure 3 shows that the solidifying temperature lowers depending on the irradiation time argon-hydrogen plasma and the copper sample has larger lowering than the silver. In the same experiments of pure argon plasma irradiation it has been made sure that no lowering phenomena takes place in both samples. Figure 4 shows that the the larger sample needs the more time to approach the steady state. Furthermore, In order to make it sure that hydrogen atoms play the leading role in this phenomena, we changed the discharge current to increase the number density of hydrogen atom during irradiation. In Fig.5 it is observed that
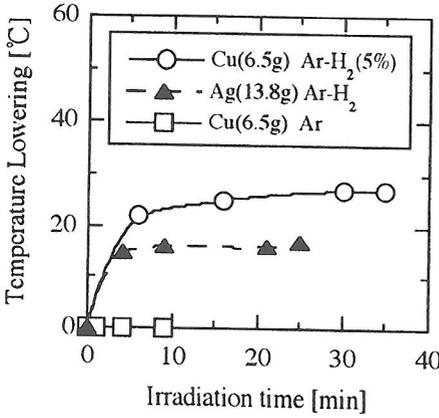
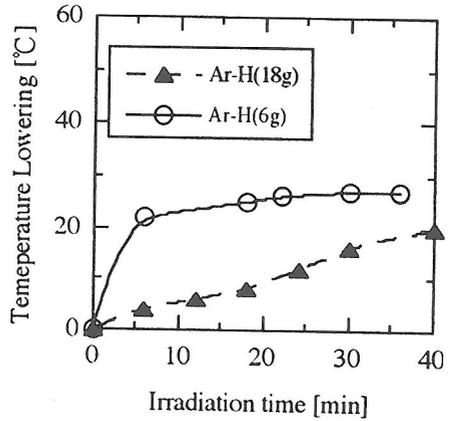Fig.3 Lowering of the solidifying temperature of copper and silver sample.

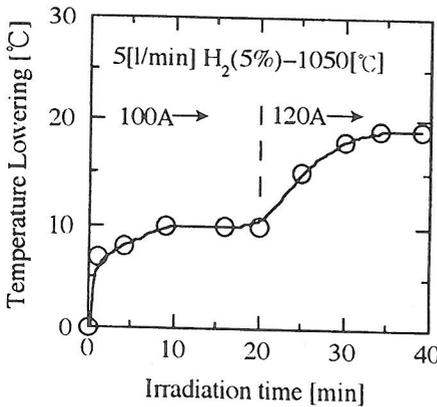Fig.4 Mass dependence of lowering of the solidifying temperature of silver.

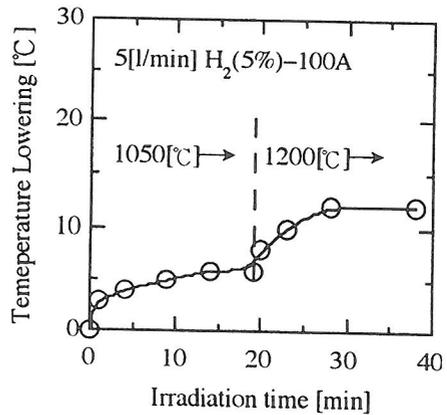Fig.5 Influence of discharge current to the solidifying temperature of silver sample.

Fig.6 Influence of temperature under irradiation to the solidifying temperature of silver sample.

the temperature lowering increases responding to this operation. During irradiation we changed the temperature kept constant before shutting off the heater and irradiation from 1050℃ to 1200℃. The increase by this operation is shown in Fig.6.

From these results it is clear that the lowering of the solidifying temperature exists in atomosphere of argon-hydrogen plasma and hydrogen atoms play a leading role in this phenomenon. Although such a phenomenon in a plasma has not been

reported, the lowering of the melting point has been investigated theoretically and observed qualitatively in high pressure experiments using iron and vanadium by Fukai[4]. He explaines this phenomena in terms of the model of interstitail solution for solid and liquid states and by using the extended Gibbs free energy to the liquid state. Using the condition of equilibrium coexistence of solid and liquid phases the following equation[5] is obtained,

$$\left(\frac{T_m}{T} - 1\right)\frac{\Delta Q_m}{N_o k T_m} = -\left(r_L - r_S\right)\ln\left(1 - \frac{x_S}{r_S}\right)$$

where, T_m and T are the melting points in normal state and hydrogen existance state respectively, ΔQ_m is the heat of fusion, x is the hydrogen-to-metal ratio n/N_o, r is the number of interstitial sites per metal atom N/N_o, n, N and N/N_o, are the number of hydrogen atom in a specimen, the number of interstitial sites in a specimen and the number of metal specimen respectively, k is the Boltzmann constant and subscripts S and L mean the solid state and the liquid state respectively. The ratio $\Delta Q_m/N_o k T_m$ is known to be assumed constant 1.15 in a large number of metals. Furthermore, assuming that in the solid state the local configuration of interstitial sites is conserved and in the liquid state geometrical and elastic constraints of the lattice are removed. Thus in the liquid state for fcc metals like copper and silver $r_L = 3$ (O and T sites) can be obtained. In the solid state $r_S = 1$ for fcc and r_S decreases from 4 depending on hydrogen concentration. The calculated solidus and liquidus lines for fcc structure metals are shown in Fig. 7 as the temperature dependence of the atomic ratio of hydrogen. For copper, calculating the atomic ratio of hydrogen by using the the measured lowering of the melting temperature, $x' = 0.012$ can be obtained. Similarly, the atomic ratio of hydrogen can be obtained 0.006 for silver.

Thus, such high concentration of hydrogen atoms in the metals as solid solution is quantitatively calculated through the observed solidifying temperature and conversely dissolution of such a large amount of hydrogen is needed to
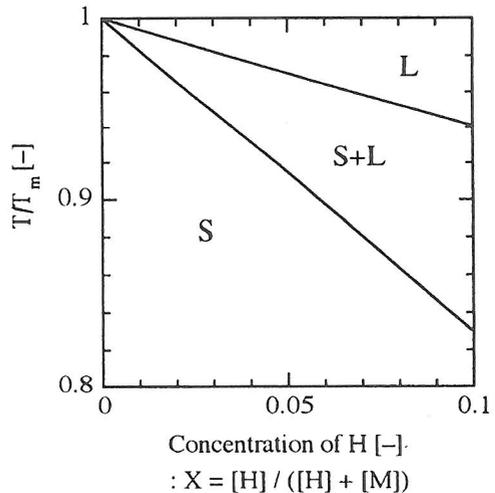

Fig.7 Theoretical lowering of the solidifying temperature due to hydrog dissolution

induce the lowering. Generally, in the thermodynamic of a solid solution[5], considering of the thermal equilibrium between a solid solution and H_2, the condition is given by the equality of the chemical potential in the gas phase and the solid phase. In our situation, although the value of chemical potential hydrogen atom in the solid phase can be estimated theoretically assuming the thermal equilibrium, the chemical potential oh hydrogen atom in the gas phase can not be obtained because of the non-equilibrium of the gas phase. It can be expected that the temperature of the gas phase is much higher than that of the solid phase and there exist a proper amount of the non-equilibrium hydrogen atom with having the larger potential enough than that in the solid phase. The existence of hydrogen atoms by spectroscopy can convince us of its possibilities.

4. CONCLUSIONS

From these experimental results and discussions, the following conclusions were obtained. It was observed that dissolution of hydrogen into metals induces the lowering the solidifying temperaturte of the metals. The concentration of hydrogen atoms in the metals as solid solution was quantitatively calculated through the observed solidifying temperature by Fukai's theory. It was shown thermodynamically that a large number of hydrogen atoms can dissolve in the metal samples by using argon-hydrogen plasma jet.

REFERENCES
(1) D. R. Mac Rae : Proc. ISPC-8, DII-01 (1987) 1850
(2) P.Humbert, R.Combes et.al. : ISPC-10, 1.5-5 (1991)
(3) M. Suzuki, T. Yano, E. Tojima and A. Kitamoto : Proc. ISPC-10,1.4-21 (1991)
(4) Y. Fukai : J. Less-Common Met. 8, (1991) 172
(5) Y. Fukai : The Metal Hydrogen System, Springer-Verlag (1993)