Formation of Aluminum Silicate Film on Ni alloy Surface in the System of Granite-Cu under Low Pressure-Hydrothermal Conditions

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In granite-Cu-dry steam system, aluminum silicate film was found to form on Ni alloy(SUS-304), and Cu was observed on granite surface. In these experiments, the autoclave used was only filled with vapor phase. This means the dissolution and transportation of metals occurred in the vapor phase. Therefore, as the mechanism of the film formation, it can be suggested that Cu first transported to dry steam and then deposited on granite surface as a granular metal Cu, and that Cu affected on dissolution of aluminum and silicon oxide and their transportation to Ni alloy surface, thus forming the aluminum silicate film. The conditions for aluminum silicate film formation were hydrothermal temperature 340℃, for several hundreds hours, pressure 9 MPa, and degree of filling 4%. In this system, Cu was assumed as Cu oxide or Cu(0) aquo complex to be transported. In order to examine this process further, Au was used as transportation element due to the fact that its ionization tendency is lower than that of Cu. Experimental results showed that Au was neither dissolved in vapor, nor transported in vapor. Therefore, it is suggested that Cu was transported only as Cu oxide, not as Cu(0) aquo complex.

1. Introduction

1.1. Dry Steam

Pressure-temperature diagram of water is shown in Fig.1. The critical temperature of water is about 374℃ and critical pressure is about 21 MPa. Water at the above temperature and pressure of critical point, is called supercritical water. In these conditions, many researches have been done. However, the application is generally difficult for these vigorous conditions due to its high cost, strong corrosion, and difficulty in operation. Below the saturated vapor pressure, the steam can be named dry steam. Dry steam has low ionic product and low dielectric constant, so, the organic reaction occurs easily in this area. And application is easy for these mild conditions[1,2].

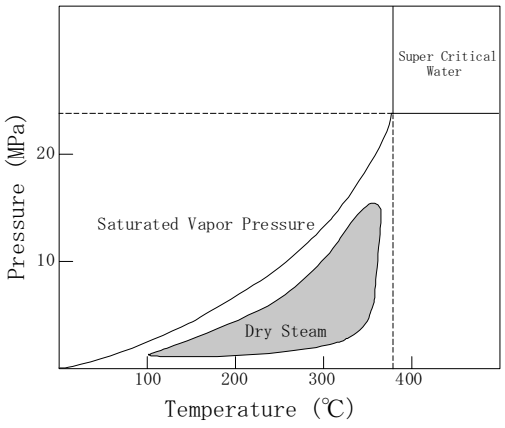

Fig.1. Saturated vapor pressure of water and dry steam.

1.2. Aluminum Silicate Film Formation

The study of granite-water system has been conducted[3-8].Some of them have dealt with film formation in dry steam[8]. We have studied aluminum silicate film formation in granite-Cu-dry steam system. Aluminum silicate film on metal plate will exhibits a high corrosion resistance, and is also expected to enhance the toughness.

The conditions of aluminum silicate film formation were 340 ℃, 9 MPa and 4% degree of filling. Under theses conditions, the water becomes vapor perfectly. It is generally regarded that metals

are not dissolved in vapor, however our experiments showed that metal Cu was dissolved and deposited on the granite surface. And the surface of granite was partly dissolved, and aluminum oxide was found on the surface of Ni alloy. Therefore it means that aluminum oxide was also dissolved in vapor, and transported from the granite to the Ni alloy surface. The objective of this study is to examine why Cu can be transported in vapor, and how the aluminum silicate film forms. In order to understand Cu transportation property, i. e. as Cu oxide or Cu(0) aquo complex, Au has been used as transportation element due to its lower ionization tendency than that of Cu.

2. Experimental Methods

A schematic illustration of the sample-autoclave system, used is shown in Fig. 2. Hastelloy-C autoclave was used. The type 304 stainless steel pipe(Ni alloy) had a height of 85 mm, outer diameter 20 mm, and wall thickness of 2.2 mm. Before the experiment, Ni alloy was cut to 80 mm and 5mm in height. The granite (sample) was a cube (8 x 8 x 8 mm). Au was a rectangular solid (10 x 10 x 0.3 mm). The autoclave was filled to 4% with distilled water and heated at 340℃ for 170 h. After autoclaving, Au, granite and Ni alloy were observed by scanning electron microscopy (SEM) with energy dispersive X-ray spectroscopy (EDX), and the change of chemical composition were examined. About stainless steel pipe, the 5mm cut part of Ni alloy was used to analyze easily.

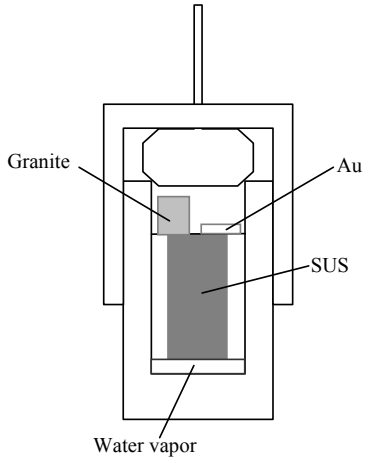

Fig.2. Schematic representation of autoclave and sample location inside an autoclave.

3. Results and Discussion

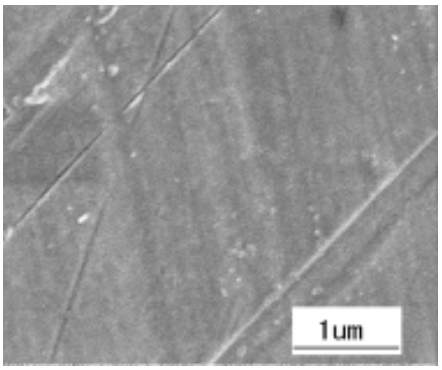

Fig.3. Before the treatment SEM image of Au surface.

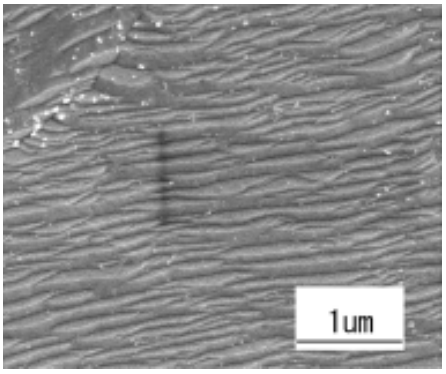

Fig.4. After the experiment SEM image of Au surface in granite-Au-dry steam system (pressure:9 MPa, temperature:340 ℃ degree of filling:4 %).

Table.1. The weight change(g/m^2) of Cu(Au) , granite and Ni alloy in granite-Cu-dry steam system and in granite-Au-dry steam system (pressure: 9 MPa, temperature:340 ℃ reaction time: 200 h)

	Cu system	Au system
Cu or Au	−54.7	0
Granite	−81.8	−1.36
Ni alloy	0.616	0.136

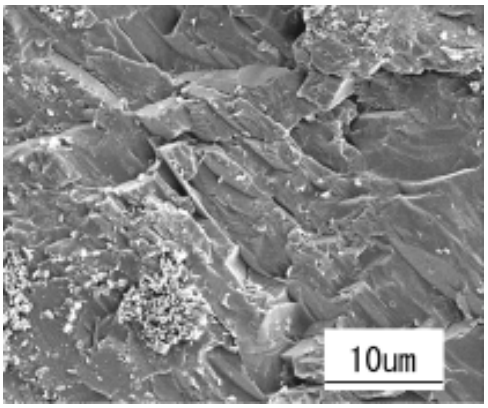

Fig.5. SEM image of granite surface in granite-Au-dry steam system (Pressure:9 MPa, temperature:340 ℃, reaction time: 200 h).

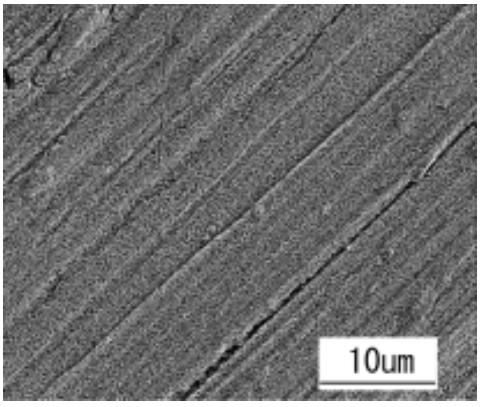

Fig.7. SEM image of Ni alloy surface in granite-Au-dry steam system (pressure:9 MPa, temperature:340 ℃, reaction time: 200 h).

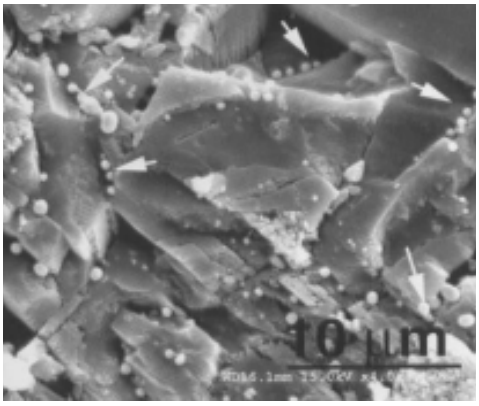

Fig.6. SEM image of granite surface in granite-Cu-dry steam system(pressure:9 MPa, temperature:340 ℃, reaction time: 200 h).

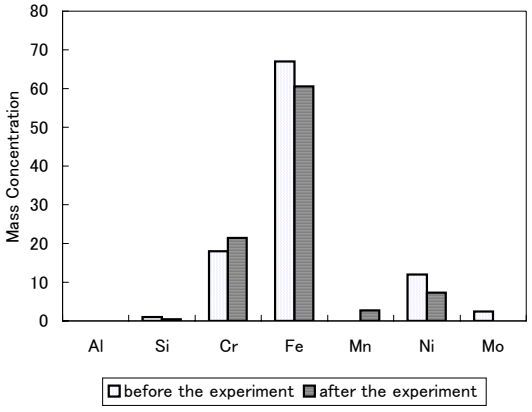

Fig.8. Comparison of chemical composition between before the experiment and after the experiment.

Figures 3 and 4 show SEM images of Au before the treatment and after the treatment respectively. The change was not observed on Au surface, and the weight of Au was not changed (Table.1). However, in granite-Cu dry steam system, the weight of Cu decreased after the experiment. These results show that Au was not dissolved. Therefore, this behavior suggests that Au didn't form the Au(0) aquo complex under these conditions. This also results that Cu didn't form the Cu(0) aquo complex under these conditions in the same way, but that Cu was transported as Cu oxide.

SEM image of the granite surface is shown in Figures 5 and 6 shows SEM image of the granite surface in granite-Cu-dry steam system. In granite-Cu-dry steam system, many copper metal particles were observed on the granite surface. But in granite-Au-dry steam system, there were no such particles of Au on the granite surface. These results suggest that Au was not dissolved in vapor. On the other hand, granite surface was found to be dissolved. However, in granite-Au-dry steam system, the degree of reaction was much smaller than that in case of granite-Cu-dry steam system. In

case of using Cu, it is considered that granite was dissolved quickly. These results suggest metal Cu have promoted the dissolution of the granite.

SEM image of Ni alloy surface is shown in Fig.7, and chemical composition of Ni alloy surface is shown in Fig.8. Aluminum was not observed on the Ni alloy and no increasing of the chemical composition of silicon was observed. These results show that the aluminum silicate film didn't formed on Ni alloy surface.

4. Conclusions

Because no aluminum silicate film formed in granite-Au-dry steam system, we suggest that Au was not changed into Au(0) aquo complex. From those results, it would be concluded that in granite-Cu-dry steam, Cu was not transported as Cu(0) aquo complex, but as Cu oxide, and that Cu had capability of promoting the dissolution of granite surface.

Reference and Notes

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