# Technical development for the liquid diffusion experiments on Ag-Cu alloys in the TR-1A No.7 rocket


**Misako Uchida*[1], Minoru Kaneko*[2], Tomoharu Fukazawa*[2], Akira Tanji*[3], Tadahiko Masaki*[1], Satoshi Matsumoto*[4] and Toshio Itami*[4]**

*1 Space Utilization Research Center, National Space Development Agency of Japan

*2 Space Department, Ishikawajima Jet Service Co., Ltd.

*3 Space Experiment System Department, Ishikawajima-Harima Heavy Industries Co., Ltd.

*4 Space Utilization Research Program, National Space Development Agency of Japan



**Abstract**

In order to investigate the relationship between the self- and mutual diffusion coefficients, diffusion experiments on liquid Ag-Cu alloys were planned in the flight chance of TR-1A No.7 rocket in 1999. Experimental procedures, reactivity of liquid Ag-Cu with a crucible material, vaporization process of liquid Ag-Cu, sample preparation procedure etc. were investigated for the rocket experiments.


**Introduction**

Darken's relation is known as the relationship between the self- and mutual diffusion coefficients, in which the mutual diffusion coefficient, $D_{12}$ under the constant volume condition is written in terms of the self-diffusion coefficients of each component, $D_1$ and $D_2$, the activity coefficient, $f_1$, and the atomic fraction of each component, $x_1$ and $x_2$.

$$D_{12} = (x_2 D_1 + x_1 D_2)\left(1 + \frac{\partial \ln f_1}{\partial \ln x_1}\right)$$

In order to verify this relation, the self- and mutual diffusion experiments were planned in the flight of TR-1A No.7 rocket. The Ag-Cu alloys are suitable for the investigation because it is easy to handle the samples due to the low chemical reactivity. However, since the Ag-Cu system is a eutectic alloy as shown in Figure 1, the solidification problem, such as the segregation should be serious and the shear cell technique is needed to avoid this problem. Here, the experimental preparations,

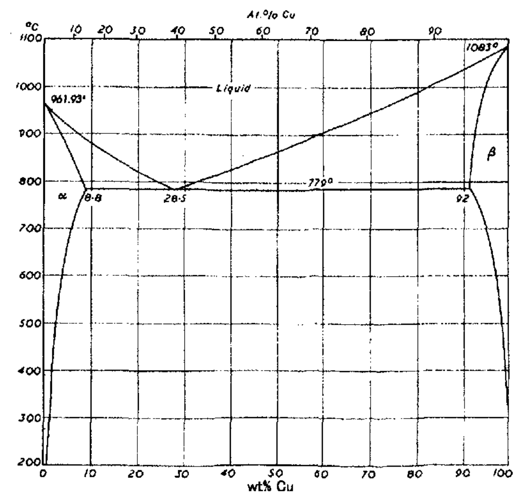



**Figure 1 Phase diagram of Ag-Cu system (Smithells Metals Reference Book 7[th] ed.)**

which are a reactivity test with a crucible material, the vaporization characteristics of liquid Ag-Cu samples and sample preparation process, were examined. Also, the numerical simulations were performed to search the suitable experimental condition.

**Shear cell samples**

In order to measure the self- and mutual diffusion coefficients of the Ag-Cu system in the rocket experiment, we developed a shear cell, which contains 10 diffusion couples in one cartridge, as shown in Figure 2. Half of the diffusion couples (5 couples) were put in the carbon spring side and the other half were in the other side. A sample of 1.5 mm diameter was designed to be pushed by a tungsten spring to follow the volume change of the sample during the course of the experiment and to avoid the formation of the free surface, which generates the Marangoni convection. The crucible material was chosen to be a boron nitride. Figure 3 shows the contact angle between $Ag_{50}Cu_{50}$ and boron nitride measured by the sessile drop method. The contact angle was about 158 degree even at 1300 degree C, and no reaction occurred. The crucible material should have a high contact angle to the sample material because the sample would be spilt out from the crucible in the present spring mechanism if the contact angle is low. Therefore it was confirmed that boron nitride was suitable for the crucible material in the present microgravity experiments.

Table 1 shows the combination of the diffusion couple samples to measure the self- and mutual diffusion coefficients. The self-diffusion coefficients were planned to be measured at 4 concentrations ($Ag_{25}Cu_{75}$, $Ag_{50}Cu_{50}$, $Ag_{40}Cu_{60}$ and $Ag_{75}Cu_{25}$) and with pure samples (Ag and Cu), and the mutual diffusion coefficients were planned to be measured with 4 combinations ($Ag_{30}Cu_{70}$-$Ag_{20}Cu_{80}$, $Ag_{45}Cu_{55}$-$Ag_{55}Cu_{45}$, $Ag_{30}Cu_{70}$-$Ag_{80}Cu_{20}$ and Ag-Cu). The star (*) in the table 1 represents the enriched stable isotope, which is $^{65}Cu$ and $^{107}Ag$, respectively.

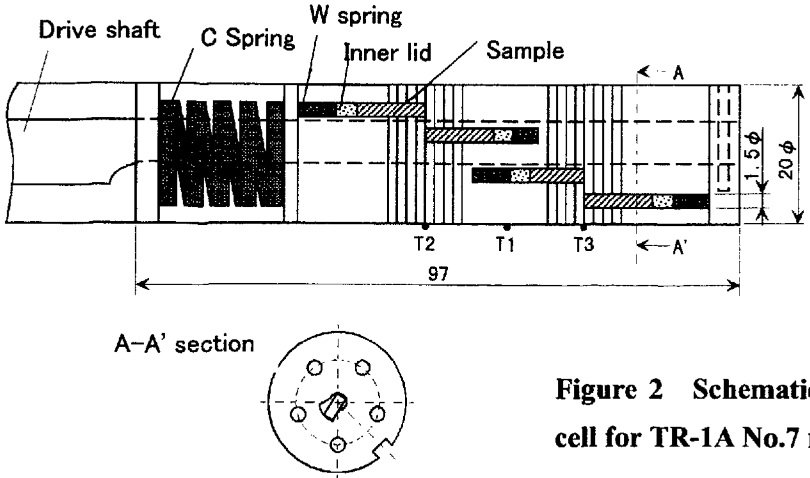



**Figure 2 Schematic drawing of the shear cell for TR-1A No.7 rocket experiments**

**Table 1 Combination of the diffusion couples**

| Experiments | Samples |
|---|---|
| Self-diffusion measurements | Ag - Ag* |
| | Cu - Cu* |
| | $Ag_{25}Cu_{75}$ – $Ag^{*}_{25}Cu^{*}_{75}$ |
| | $Ag_{50}Cu_{50}$ – $Ag^{*}_{50}Cu^{*}_{50}$ |
| | $Ag_{40}Cu_{60}$ – $Ag^{*}_{40}Cu^{*}_{60}$ |
| | $Ag_{75}Cu_{25}$ – $Ag^{*}_{75}Cu^{*}_{25}$ |
| Mutual diffusion measurements | $Ag_{30}Cu_{70}$ – $Ag_{20}Cu_{80}$ |
| | $Ag_{45}Cu_{55}$ – $Ag_{55}Cu_{45}$ |
| | $Ag_{30}Cu_{70}$ – $Ag_{80}Cu_{20}$ |
| | Ag – Cu |

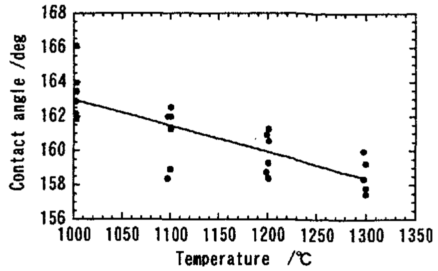



**Figure 3 Contact angle between boron nitride and $Ag_{0.5}Cu_{0.5}$**

**Vaporization test for Ag-Cu samples**

Since the shear cell consists of a pile of thin disks as shown in Figure 2, the sample can vaporize through the slight gap of these disks. The vaporization test should be performed to prevent the sample vaporization during the experiments.

The thermogravimetric and the differential thermal analysis (TG-DTA) was carried out for Ag, Cu, $Ag_{75}Cu_{25}$, $Ag_{50}Cu_{50}$ and $Ag_{25}Cu_{75}$. Figure 4 shows the TG-DTA data for Ag. The absorption and the emission of the latent heat at melting and at solidifying, respectively, were confirmed from the DTA data. It was found that the weight of Ag sample reduced around 1260 degree C from the TG data. The reduction of the sample weight for the Cu and Ag-Cu alloys were smaller than that of Ag. Therefore, the maximum experimental temperature was determined to be 1260 degree C from these results. Figure 5 shows the vaporization ratio for the diffusion experiments calculated from the TG data. The calculation was performed under the conditions as follows: the sample size was 1.5 mm diameter and 7.5

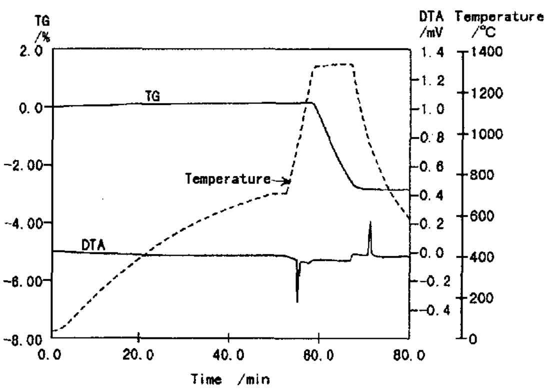



**Figure 4 Thermogravimetric and differential thermal analysis data for Ag**

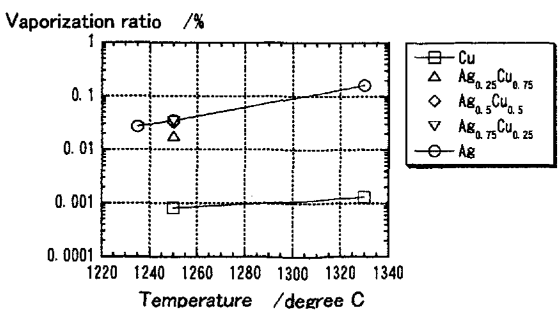
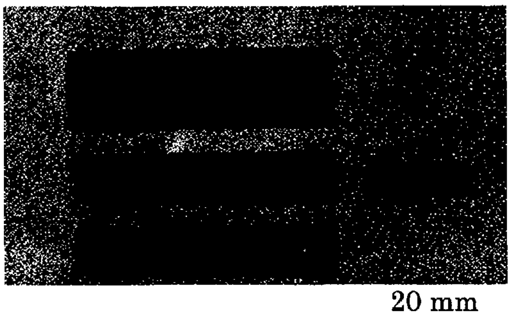



**Figure 5 Calculated vaporization ratio for the diffusion experiments**

mm length; the 5 μm gap of the disks and the sample end of 1.77 $mm^2$ were open to the atmosphere; the sample is kept for 6 minutes. The vaporization ratio increased with the contents of the Ag. It was confirmed that the vaporization ratio was less than 0.05 % at 1260 degree C for all samples.

**How to make a sample**

The sample preparation procedure is as follows: 1. samples of pure Ag and Cu are deoxidized; 2. the required amounts for diffusion samples are weighed, melted and mixed together; 3. the mixed sample is cast into a rod with 1.65 mm diameter; 4. the sample is ground into a capillary with 1.47 mm diameter.




**Photograph 1 Mold for making thin Ag-Cu samples**

Prior to determining the sample preparation of Ag-Cu alloys, some tests were performed to obtain the optimum condition for it. Since the surfaces of the mother metals, Ag and Cu, were oxidized, the deoxidization procedure was examined. The $Ag_{25}Cu_{75}$ sample was prepared from these Ag and Cu with and without deoxidization process under hydrogen atmosphere at 500 degree C for 1 hour. The $Ag_{25}Cu_{75}$ sample made of deoxidized material had better surface than that made without deoxidation. The deoxidization process was concluded to be required in the sample preparation procedure.

The deoxidized Ag and Cu was mixed together and cast into a rod of 1.65 mm diameter using a graphite mold, which can be split into two parts to prepare a thin sample to be taken out easily, as shown in Photograph 1. The diffusion sample should have a uniform concentration profile, and should not have a long shrinkage in it. An $Ag_{50}Cu_{50}$ sample was cast with various conditions to find a suitable way for preparing a sample. Table 2 shows the casting conditions and the results. It was found that the middle cooling rate, which was realized by air cooling with glass wool wrapping around the quartz ampoule, was the best to make a sample without a long shrinkage. The sample of 30 mm long was analyzed by EPMA (Electron Probe Microanalyzer). The concentration of Ag was 44, 47 and 44 atomic % at the top, at the middle

**Table 2 Casting condition and sample shape (WC: water cooling, AC : Air cooling)**

| Keeping temperature /degree C | Keeping time / min. | Atmosphere | Cooling | Glass wool | Results (shrinkage) |
|---|---|---|---|---|---|
| 950 | 30 | Ar | WC | Without | Long |
| 950 | 30 | vacuum | 95 C water | Without | Long |
| 950 | 30 | vacuum | WC | Without | Long |
| 1000 | 30 | vacuum | WC | Without | Long |
| 1000 | 30 | vacuum | AC | With | small at the top |
| 880 | 30 | vacuum | AC | With | small at the top |

and at the bottom, respectively. The concentration in the sample was confirmed to be almost homogeneous.

**Numerical analysis for the shear cell experiments under microgravity**

Some numerical analyses were performed to determine the experimental conditions. First, the change of the concentration profile during a diffusion experiment was calculated. From the results of this calculation, the length of a diffusion sample was decided to be 10 mm, and the thickness of the disks in the shear cell was modified from 2 mm to 1.5 mm for more precise diffusion measurements.

In addition, the effect of the cell misalignment was calculated. Diffusion couple samples are joined in the shear cell method after the temperature becomes steady at an experimental temperature. If the diffusion couple samples are misaligned, the measured diffusion coefficient becomes smaller than the true value. The numerical analysis was performed to calculate the error by the misalignment. The results are shown in Table 3. The possible machining accuracy of the shear cell is considered to be a few tens μm, and the effect of this misalignment of a few tens μm is about 0.3 % from Table 3. It was confirmed that the misalignment effect was small enough for the experiments.

**Table 3 Effect of the misalignment of the shear cell on the diffusion measurements**

| Ratio of the misalignment ( ): Length of the misalignment | Diffusion coefficient without misalignment (True value) | Diffusion coefficient with misalignment | Error / % |
|---|---|---|---|
| 0 % (0 mm) | $1.15 \times 10^{-8}$ m$^2$ s$^{-1}$ | $1.150 \times 10^{-8}$ m$^2$ s$^{-1}$ | 0 |
| 2.5 % (0.038 mm) | $1.15 \times 10^{-8}$ m$^2$ s$^{-1}$ | $1.147 \times 10^{-8}$ m$^2$ s$^{-1}$ | -0.26 |
| 5 % (0.075 mm) | $1.15 \times 10^{-8}$ m$^2$ s$^{-1}$ | $1.140 \times 10^{-8}$ m$^2$ s$^{-1}$ | -0.90 |
| 10 % (0.15 mm) | $1.15 \times 10^{-8}$ m$^2$ s$^{-1}$ | D can't be obtained. | - |

**Conclusions**

The self- and mutual diffusion coefficients of Ag-Cu alloys were planned to be measured in TR-1A No.7 rocket. The experimental procedure including the sample preparation process, the shear cell design, the experimental conditions, etc. were determined.