EXPERIMENTS WITH LIQUID DIFFUSION IN REDUCED GRAVITY

X. Zhu, M. Kaya and R.W. Smith
Queen's University at Kingston
Canada, K7L 3N6

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ABSTRACT

It is found that the reproducibility of liquid diffusion coefficients measured at 1g is poor due to the intrinsic diffusive transport being enhanced by uncontrolled buoyancy convection. However, it has been reported that if the diffusion capillary is less than about 1 mm diameter, then the rate of diffusion is reduced. Thus it is conventional to write:

$$D_{Measured} = D_{intrinsic} + D_{buoyancy} + D_{Wall\ effect} + D_{thermal}.$$

If a diffusion couple is isothermally processed in microgravity $D_{buoyancy}$ and $D_{thermal}$ will be absent and so only $D_{intrinsic}$ and $D_{Wall\ effect}$ should be present. Choosing capillaries of different diameters should provide an estimate of $D_{Wall\ effect}$ and hence permit a accurate value of $D_{intrinsic}$ to be obtained. If diffusion couples are processed at a number of temperatures, then the temperature dependence of the transport process may be obtained. This can provide clues to the mechanism(s) by which diffusion occurs.

Such experiments are being carried out by the authors for a number of alloys. The most complete data set is available for the Au in Pb and will be described. These results fit best an Arrhenius - type relationship.

INTRODUCTION

Diffusion in liquid metals is of fundamental importance in studying and modelling metallurgical processes. For example, all solidification of an alloy from the melt involves the redistribution of alloying elements. However, it is well known that gravity-driven convection provides a great contribution to the transport of mass in liquid metals. Even though great efforts have been made in past decades, it is still difficult to produce accurate experimental data in the terrestrial laboratory. This problem hinders the development and application of our knowledge to practical liquid metal systems. An example of this situation is the temperature dependence of the diffusion coefficient. This relation is of practical and theoretical importance. There are many theories, each giving a different equation, to describe this relation; these equations cannot be distinguished by terrestrial experimental results because of the poor reproducibility. Fortunately, the space environment offers a solution to this problem. A few space experiments have already shown good prospects of this[1]. The most successful and systematic study of self- and inter-diffusion in liquid metals in the 1980's is Frohberg's work in the Sn system. One conclusion obtained was that the temperature dependence of the diffusion coefficient obeys the predictions of the fluctuation theory more closely than an Arrhenius-type relationship for both self and inter-diffusion in liquid Sn-In[2]. However, such high quality results are still scarce. More accurate results are needed before a general conclusion can be reached.

The present work was motivated by the need for more and accurate experimental data for the study of metallurgical processes. This work will also help us to obtain a better understanding of the mechanism(s) of diffusion and the structure of liquid metals. A series of diffusion experiments in liquid metal systems were carried out both in the terrestrial and micro-gravity conditions. Experiments in the micro-gravity condition were performed in the U.S. Space Shuttle under the two projects: QUESTS (Queen's University Experiments in Space Transportation Systems) and QUELD (Queen's University Experiments in Liquid Diffusion), sponsored by the Canadian Space Agency.

Interdiffusion in a molten binary alloy has been studied. The initial composition was 1 wt.% gold in lead. The alloy can be considered as a dilute solution and the interdiffusion coefficient can be considered independent of the concentration. The melting point of this alloy is close to the melting point of pure lead. The long capillary specimen assembly technique and semi-infinite diffusion couple were selected as a suitable experimental method. Fick's second law can be applied, namely,

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} \text{............} (1)$$

where C is the composition at distance x, D is interdiffusion coefficient, and t is diffusion time. With initial and boundary conditions,

$t=0$: $0<x<d$, $C=C_o$; $x>d$, $C=0$; (2)

$t=t$: $x=$infinite, $C=0$, (3)

equation (1) has the solution,

$$C(x,t) = \frac{C_o d}{\sqrt{\pi D t}} \exp(-\frac{x^2}{4Dt}) \text{......} (4)$$

where C_o and d are the initial composition and length of the alloy part of the diffusion couple. d has to be very small compared to the whole diffusion length.

Gravity-driven convection was expected to be detected by the comparison of results coming from different environments. The temperature dependence of the diffusion coefficient was to be determined and examined in connection with the predictions of the various theories.

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EXPERIMENTAL TECHNIQUES

A Pb - 1 wt%Au alloy has a simple eutectic structure when solid; when liquid it can be considered as a dilute solution. High purity lead (99.999%) was used. The alloy was prepared in a sealed quartz tube under the protection of argon and the melt temperature was held at 950°C for one day.

The diffusion couples were manufactured by a cast coating technique developed during this study. This sample preparation method gives a diffusion couple of sharp and oxide-free interface[3]. The diffusion couple was 1.5 mm in diameter and 25 mm in length. The length of alloy section was controlled to be less than 1.5 mm. The diffusion couple was placed in a graphite crucible and sealed by a graphite end cap. This capsule was enclosed in a stainless steel sheath by two laser welded end caps. In order to avoid surface tension driven convection (Marangoni convection) any free surface between the diffusion couple and the crucible had to be eliminated. This was done by applying a external spring to the graphite cap to eliminate free space and permit the volume change during the melting and freezing processes.

Two series of micro-gravity experiments were performed, namely automatically in the Space Shuttle Endeavour mission STS-47 and manually by a Canadian astronaut in the Space Shuttle Columbia mission STS-52. The devices used were composed of a furnace, a quench block and temperature control system. Diffusion processing was performed for a series of designed temperatures and times. In order to heat the specimen quickly to the diffusion temperature, the furnace was calibrated and pre-heated to a temperature above the dwell temperature. Then the insertion of the specimen quenched the furnace to the desired diffusion temperature.

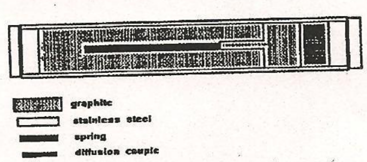

Figure 1. Specimen assembly.

The terrestrial experiments were performed with the same devices used in space. However, the specimen was placed in vertical position with the alloy section of the diffusion couple at the bottom.

After return to the ground, the space-processed samples were analyzed. Since the lead-gold alloy gives a two phase (eutectic) micro-structure, there may be segregation problems with those spot analysis methods such as the electron micro-probe technique. In view of this, the atomic absorption spectrophotometry technique was used for concentration analysis. The elemental sensitivity of this technique is about 0.002 weight percent and the accuracy of measurement is generally about <0.5%. Each sample was sectioned by cutting perpendicular to the diffusion direction and the resulting pieces were dissolved into sample solutions. The concentration distribution profile was generated by plotting the composition of successive points along the specimen axis. Each point on the composition/distance curve corresponds to a cross section of the sample. An example of these profiles is shown in figure 2.

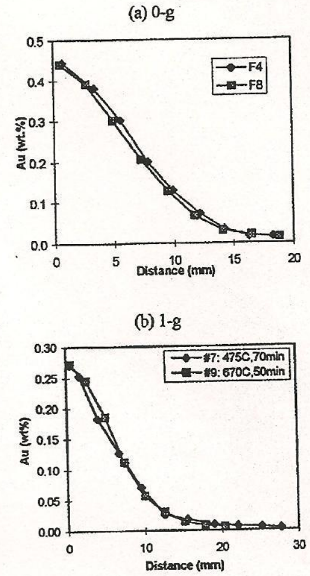

Figure 2. Concentration profile for Pb-Au diffusion,

RESULTS

Taking the logarithm of each side of equation (4) gives,

$$lnC = -\frac{x^2}{4Dt} + \ln(\frac{C_o d}{\sqrt{\pi Dt}}) ......(5)$$

The second term in the right-hand side of equation (5) is constant. By making a semilog plot of ln(C) versus the distance squared, a straight-line plot is obtained. The slope of the resulting concentration plot is -1/4Dt. The original concentration profiles were transferred into the above coordinates, as shown in figure 3.

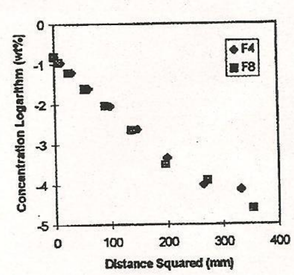

Figure 3. Concentration profile for a Pb-Au diffusion.

The diffusion coefficient was then calculated from the value of the slope. Space results as well as terrestrial results are shown in Table 1.

Table 1. Diffusion Coefficients of Au in lead.

Temperature (°C)	D x10^{-5}(cm^2/sec) micro-gravity	D x10^{-5}(cm^2/sec) terrestrial
363	2.27	3.81
400	-	3.53
437	3.03	3.35
450	3.40	3.79
475	-	4.19
500	-	4.89
538	4.23	5.19
550	4.40	-
615	-	5.96
670	-	6.39
700	5.80	-
850	7.95	9.10

DISCUSSION

From the above results, the temperature dependence of the diffusion coefficient may be determined. This relationship has been examined with respect to the predictions of various liquid diffusion theories. Of these theories[1,4], the temperature dependence relationships obtained from the Arrhenius law and the fluctuation model get most experimental proof. The Arrhenius law gives an exponential relation of the diffusion coefficient with temperature, i.e.

$$D = D_o \exp(-\frac{Q}{RT}) ......(6)$$

where Q is the activity energy. In contrast, the fluctuation model proposed that the diffusion coefficient should be proportional to the temperature squared, i.e.

$$D = AT^2, \qquad (7)$$

where A is a constant. The present analysis concentrates on these two theories. The results are expressed as the accuracy of experimental data fitting to the predicted temperature dependence relationships, Table 2.

Table 2. Examination of the temperature dependence of the diffusion coefficient.

Accuracy	Arrhenius law		fluctuation model	
	0-g	1-g	0-g	1-g
average relative error, %	2.39	6.72	6.3	6.0
maximum relative error, %	5.14	21.9	23.2	20.7
maximum absolute error (cm^2/sec)x10^{-5}	0.28	0.68	0.63	0.65

The above results show that the temperature dependence of the diffusion coefficient in the Pb-Au system under micro-gravity conditions may be distinguished with the different theories. This relationship prediction in Pb-Au system fits the Arrhenius law more closely than it does the fluctuation theory, a fact somewhat surprising in view of the earlier work with Sn-In[2]. This fact demonstrates again that space experiments offer better data for the critical examination of different liquid diffusion theories. With the Arrhenius relation, the difference in the accuracy between space and terrestrial results is evident. Better accuracy is achieved with space results. Self-diffusion and interdiffusion experiments in Sn-In system in micro-gravity condition also showed this result[2]. However, there is no significant difference between space and terrestrial results with the fluctuation model.

The temperature dependence of the diffusion coefficient in accordance with the Arrhenius law is shown in Figure 4 for both space and terrestrial results.

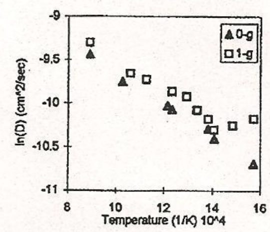

Figure 4. Temperature dependence of the diffusion coefficient.

The above figure shows clearly that the diffusion coefficient under micro-gravity conditions is lower than that under terrestrial condition. This indicates the absence of gravity-driven convection.

CONCLUSION

1. Gravity-driven convection has been successfully distinguished by space experiments. Compared with the terrestrial results, the space environment gives lower diffusion coefficients. This indicates that gravity-driven convection enhances the mass transport process.

2. The temperature dependence of the diffusion coefficient in molten dilute lead-gold alloys is best fitted to the Arrhenius relation, which implies that liquid diffusion in this system is a thermally activation process.

3. The temperature dependence of the diffusion coefficient has been more accurately determined in micro-gravity.

4. The concentration distribution has been successfully analyzed with the Atomic Absorption Spectrophotometry technique. Most of the concentration profiles are smooth. However, diffusion in a liquid metal is sensitive to the surrounding conditions. Any vibration during the experiment operation may have influence on the concentration distribution. This is presumed to be the main reason for the deviation in some of the concentration profiles obtained in STS-52.

ACKNOWLEDGEMENTS

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