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INTERFACE SCIENCE

High magnetic field controlled interdiffusion behavior at Bi-$Bi_{0.4}Sb_{0.6}$ liquid/solid interface

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Abstract The effects of a high magnetic field on the interdiffusion behavior at liquid Bi/solid $Bi_{0.4}Sb_{0.6}$ interface have been experimentally investigated. It was found that the migration of the interface due to interdiffusion decreased markedly with the increasing strength of magnetic field. This was relevant to the increasing of the viscosity in the liquid metal under a high magnetic field, which in turn caused diffusion activation energy to increase. As a consequence, in the presence of a high magnetic field, a considerable decrease in the effective diffusion coefficient occurred. Moreover, the retarding effect of magnetic field gradient on diffusion was found to be more significant than that of a uniform magnetic field.

Introduction

During the processing of many materials, such as hot dipping, soldering and brazing, unidirectional solidification, etc., a diffusion couple develops at the solid/liquid interface due to the metallurgically dissimilarity between the solid and liquid phases. It is widely recognized that the microstructure and the final products formed at the interface are governed by the mass transfer happening in such a diffusion couple. With a liquid phase, the interface under consideration is not stable. Therefore, it must simultaneously consider the mass transfer caused by both convection and diffusion.

With the recent developments in high magnetic field technology, their application for the mass transfer control has attracted attention of researchers [1–3]. Although the magnetic field effects on convection control [4–8] during mass transfer process have been studied extensively, sufficient information is not available with regard to the role of a magnetic field on the diffusion behavior. Youdelis et al. [9] found that a significant decrease in the diffusivity in the Al/Al–3%Cu diffusion couples annealed under a 3 T field condition. Zhao et al. [10] reported that during thermal aging treatments the interdiffusion coefficient of the Sn–3Ag–0.5Cu/Cu solder joints increased with the increasing intensity of high magnetic field. Wang et al. [11] discussed that high magnetic fields exerted a non-monotonic influence on the diffusion of liquid aluminum in solid copper. However, Nakajima et al. [12] observed no noticeable effect of a 4 T magnetic field on the diffusion of nickel in titanium. These different reported results on the mechanism of diffusion behavior under a high magnetic field have motivated our interest in the kinetics of diffusion in the presence of a high magnetic field. Considering that the reaction diffusion in the previous study [10, 11] make it difficult to differentiate the magnetic field effects on diffusion from its effects on reaction, in this work a Bi-$Bi_{0.4}Sb_{0.6}$ diffusion couple was selected as a candidate to investigate the atomic interdiffusion occurring at the solid/liquid interface with and without a high magnetic field. The parabolic relationship between the diffusion migration of the interface and the annealing time may be believed to hold well in such a solid-solution diffusion couple, in which only atomic interdiffusion occurs and no phase transformation is involved. On the basis of the experimental observation, the kinetic features for the

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diffusion behavior under various magnetic field conditions are discussed briefly.

Experimental procedure

The solid solution alloys with a composition of Bi–60wt.%Sb were prepared with 99.99% pure Bi and Sb by induction melting in alumina crucibles under vacuum environment. The ingot was turned over and re-melted three times and then homogenized at 573 K for 10 h. Disks with the dimension of Φ9.9 × 10 mm were cut from the ingots, grinded and polished their surfaces to 3 μm metallographical finish, then ultrasonically cleaned with acetone. The diffusion couples were produced by placing the disk and 3.3 g pure Bi (*on the top of the disk*) in Φ10 alumina crucible. Previous to this step, the Mo wire used as an inert marker of the original interface was adhered to the surfaces of the disks.

The crucible set with Bi-$Bi_{0.4}Sb_{0.6}$ couple was kept into a vertical resistance furnace, which is located inside the bore of 12 T superconducting magnet as shown in Fig. 1. The crucibles, which were always in the isothermal area of the furnace, were fixed in the uniform and gradient sections of the magnetic field, respectively. The magnetic field was kept on during the entire experimental process. Interdiffusion experiments were carried out at various ranges of temperature such as 623, 633, and 643 K for 1200, 3600, and 6000 s under a protective atmosphere of high-purity argon. The chosen temperature was suitable to keep pure Bi in liquid phase and the alloy disk in solid phase.

After the interdiffusion process, the temperature was decreased to room temperature and the magnetic field was reduced to zero. The polished longitudinal section of the samples was analyzed by an optical microscope and an electron probe. The distance from the original marker to the final interface was measured in five regions using electron probe analysis (EPMA) to obtain the mean migration distance of the interface, ΔX, by the least-squares method.

Results and discussion

Under the experimental conditions, surface wetting of the solid alloy by the melting pure Bi resulted in the creation of a solid/liquid interface. Following the wetting, atoms from the liquid Bi diffused into the solid $Bi_{0.4}Sb_{0.6}$ alloy through grain-boundary paths due to the existence of concentration gradient. In the meantime, the active Sb atoms from the alloy diffused into the liquid metal region. With the diffusional mix, the increase of Bi element at the surface of the alloy would lead to the alloy melting point depression, since the melting point of Bi is lower than that of the matrix. Thus, the alloy melted partially to form a fusion zone at the interface under the experimental temperature ranging from 623 to 643 K. After cooling, as a consequence of solidification and recrystallization, the interface migrated from the original location (*Mo inert marker*) to the inner side of the disk. The backscattered electron image in Fig. 2 revealed the basic feature of the final interface (*the green layer in the figure*), which migrated into the inner side of the basal alloy due to diffusion.

Figure 3 shows the typical optical micrographs of the Bi/$Bi_{0.4}Sb_{0.6}$ diffusion couple after annealing at 633 K for 3600 s without and with a high magnetic field. In the figure, three zones, shown as amplified graphs (d–f), with different grain size were easily differentiated. Considering that there was a discontinuity of grain size at the location of (e) in the figure, we drew a black line, which distinguishes different grain zones, as the final interface. The position of

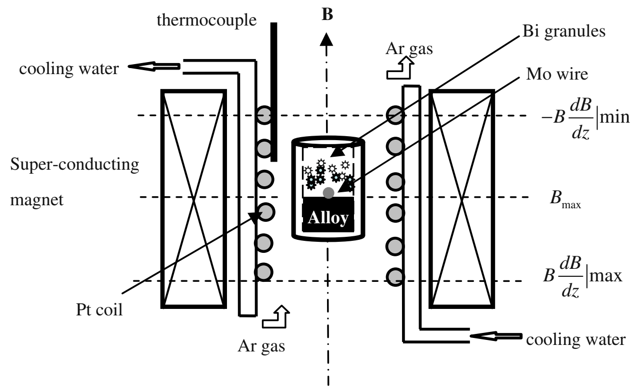

Fig. 1 Schematic view of a superconducting magnet with heat treatment furnace

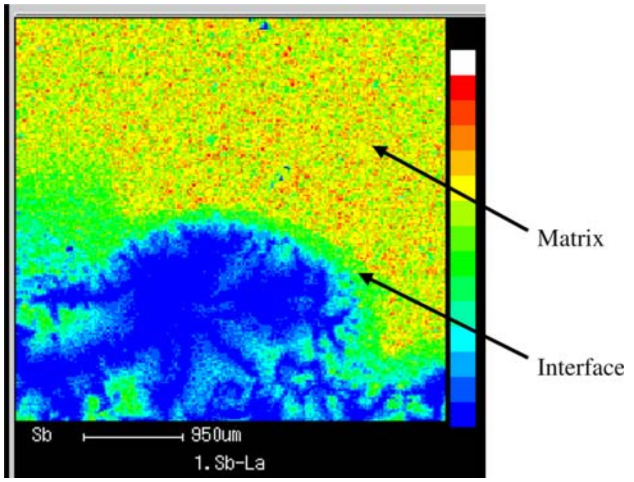

Fig. 2 Backscattered electron image of the interface migrated into the mother alloy due to diffusion

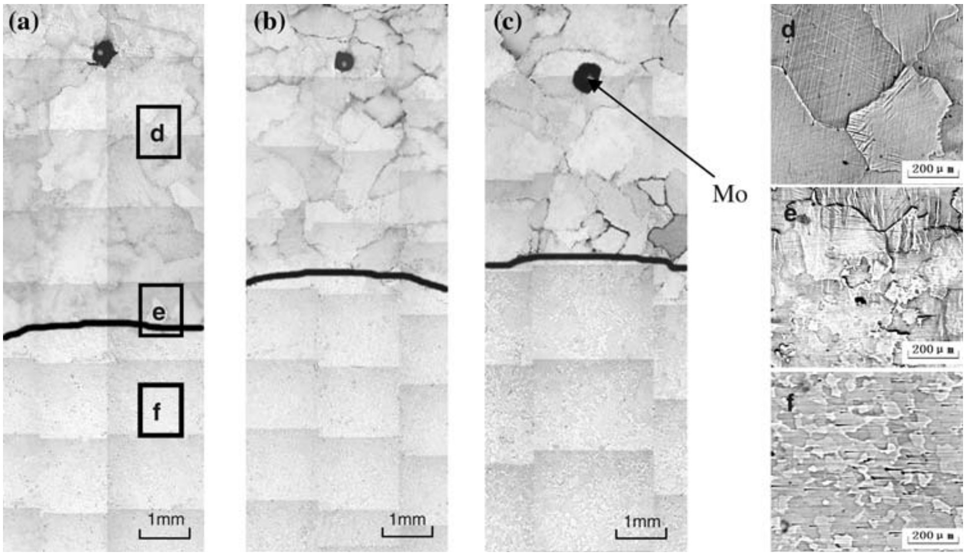

Fig. 3 Microstructure of Bi and $Bi_{0.4}Sb_{0.6}$ diffusion couple heated at 633 K for 1 h under different magnetic field conditions: **a** 0 T, **b** 8.8 T, and **c** 11.5 T. The cross section of the Mo wire can be seen as a white dot in the black hole

original interface was marked by Mo wire that could be seen as a white spot in the figure. Attempts were made to determine the migration of the interface based on the distance, ΔX, from the Mo wire to the final interface.

From Fig. 3 it could be seen that the distance decreased as the magnetic field strength increased. A similar tendency was found when the samples were annealed at 623 or 643 K for 1 h under the same magnetic field conditions. According to EPMA, the composition of Bi in the three zones was higher than 50% as shown in Fig. 3d, 40–50% in Fig. 3e, and nearly 40% in Fig. 3f, respectively. The element depth profiles and ΔX were measured along the dotted line marked on the micrograph (Fig. 3a) by EPMA, which is shown as Fig. 4, where the zero on the abscissa indicated the position of Mo, and the positions (marked as the dot lines) with the concentration equal to that of $Bi_{0.4}Sb_{0.6}$ indicated the final interfaces.

Close examination of ΔX formed at each temperature for holding time from 1200 to 6000 s revealed that the kinetic of interface migration appeared to follow a parabolic relationship, $(\Delta X)^2 = Dt$, where D is the effective diffusion coefficient and t is the annealing time in seconds. The parabolic rate law was still fulfilled with and without a high magnetic field. From the slope of plots of $(\Delta X)^2$ versus t, D under various magnetic flux densities was evaluated at each temperature. Figure 5 shows a considerable decrease in the effective diffusion coefficient with an increase in magnetic flux density.

In view of the fact that the diffusion coefficient expressed by an Arrhenius equation [13], $D = D_0 e^{-Q/RT}$, it can be written in natural logarithmic form, $\ln D = \ln D_0 - \frac{Q}{RT}$, we could obtain the diffusion constant (D_0) and the activation energy (Q) for diffusion from the intercept and the slope of the lines in Fig. 6, respectively.

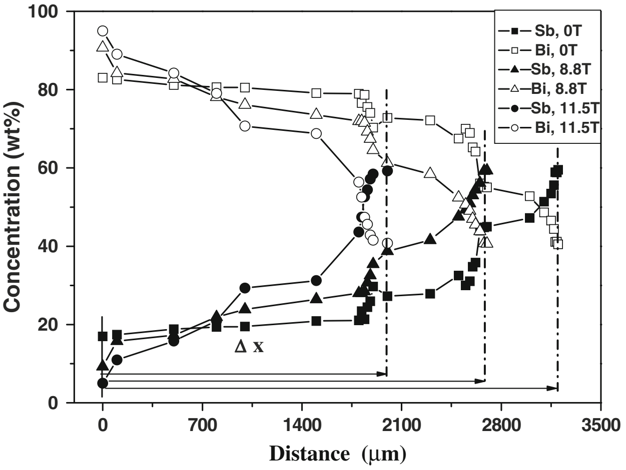

Fig. 4 Effects of magnetic fields on Bi (Sb) depth profile in the diffusion zone formed at 633 K for 3600 s

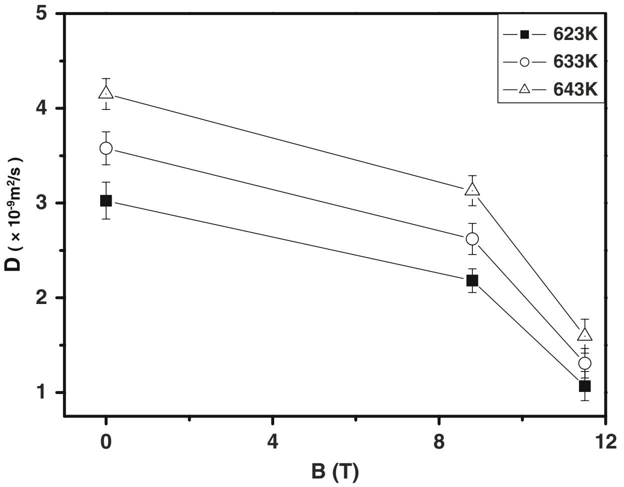

Fig. 5 The dependence of the effective diffusion coefficient with magnetic flux density at different temperatures

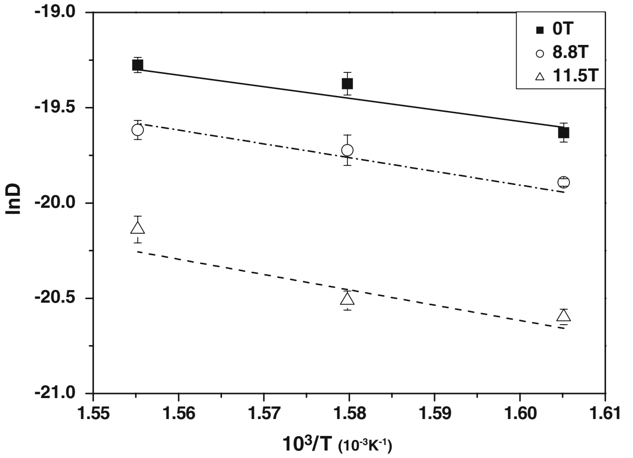

Fig. 6 Temperature dependence of the effective diffusion coefficient for samples annealed with magnetic flux density of 0, 8.8, and 11.5 T

Table 1 The diffusion constant and the diffusion activation energy under high magnetic fields

Magnetic flux density B (T)	Diffusion constant D_0 ($\times 10^{-4}$ m^2/s)	Diffusion activation energy Q ($\times 10^4$ J/mol)
0	0.50601	5.0371
8.8	2.3348	5.9985
11.5	4.0810	6.6578

Data in Table 1 indicate that the high magnetic field increases the diffusion activation energy and the diffusion constant simultaneously. With regard to the experimental results, the decrease of D induced by the high magnetic field could be attributed to the enhancement of activation energy, which has a decisive effect on D when compared with that of diffusion constant.

The observed retarding effect of a magnetic field on diffusion with a liquid phase existence can be attributed to the change of apparent viscosity of melts under magnetic field conditions, since there is a direct relation between viscosity and diffusion in liquids. According to the earlier report [14], the diffusion coefficient is given by $D = kT/6\pi\eta r$, where η is the viscosity, k is the Boltzmann's constant, and r is the radius of a spherical particle moving in a continuous liquid. If we consider the diffusional atoms in $\mathrm{Bi/Bi_{0.4}Sb_{0.6}}$ couple as spherical particles, an inverse relation can be established between D and η. On the other hand, Sun et al. [15] fitted the viscosity values of Sb–Bi alloy under different magnetic field and found that these corresponded well with the following relationship, $\eta_B = \eta_0 + AB^2$, where η_B is the viscosity under magnetic field, η_0 is the viscosity in the absence of magnetic field, A is a positive constant, and B is the magnetic flux density. That is, the viscosity increases with the enhancement of magnetic intensity. In this work, the imposition of a high magnetic field increases the viscosity of the liquid metal, thereby decreasing the diffusion coefficient.

Besides diffusion coefficient changes due to viscosity, the influence of convections in the liquid metal on diffusion must be considered, because the enhancement of mass transport caused by convection can lead to systematic overestimation of the effective diffusion coefficient. In other words, if the convections are minimized, a decrease of the measured diffusivities can be expected. Many researchers have applied magnetic fields to suppress the convection in liquid metals due to their large electrical conductivities [16, 17]. Armour and Dost [18] demonstrated that the application of a static magnetic field prohibits the formation of large convection cells in the Ge (Si) melt. Miyake et al. [19] discussed that under high magnetic fields, the obtained Sn–In diffusion coefficient data were of the same order of magnitude with the data measured under purely diffusive conditions, almost without any convection, in outer space. We believe that in the result presented here the retarding effect of high magnetic fields on natural convection is one possible reason for the decrease of the diffusion coefficient. If the convective contamination effect of magnetic field dominates the diffusion in this work, the diffusion coefficient measured under fields of both 8.8 and 11.5 T should be identical, since a static magnetic field of 4 T was considered to be sufficient for damping convection [4, 19]. However, there was a significant decrease in D when the magnetic flux density increased from 8.8 to 11.5 T. Therefore, the experimental results cannot be fully attributed to the effect of magnetic field on convection.

In addition, we repeated the experimental process using field gradients of $BdB/dZ = \pm 166$ T^2/m ($B = 8.8$ T) and $BdB/dZ = \pm 282$ T^2/m ($B = 11.5$ T) to investigate the influence of the value of the field gradient on the kinetics of

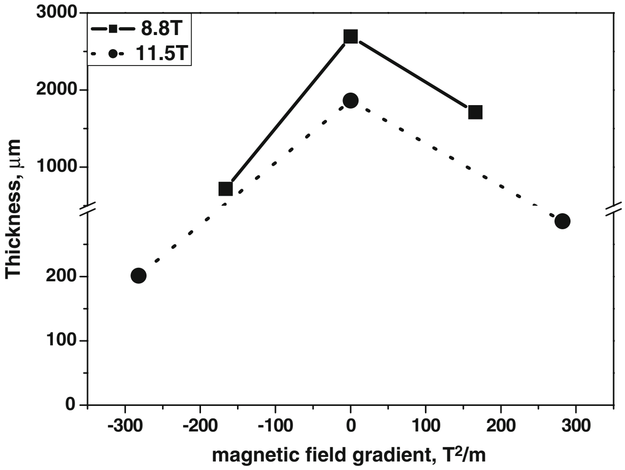

Fig. 7 The migration distance of the interface under different the magnetic field gradients

interdiffusion at liquid/solid interface. Figure 7 shows the migration distance of the interface after annealing at 633 K for 1 h under different magnetic field gradients. For comparison, the data obtained from the samples with 8.8 and 11.5 T uniform magnetic fields are also shown in the figure. It was found that the migration distance was decreased by the application of magnetic field gradients in contrast to that of a uniform magnetic field. Moreover, the retarding effect of a "negative" magnetic field gradient on diffusion seemed more significant than that of a "positive" one. Previous work [20] has also shown that the diffusion of Zn in Cu could be retarded by a magnetic field gradient, whether the magnetic field gradient was negative (−) or positive (+). The detailed discussion of the results obtained is possible only in a complicated pattern, taking into consideration the dependence of many factors on a magnetic field gradient, such as vacancy formation energy of the base alloy, transition activation energy of the active atoms, magnetic free energy, susceptibility for Bi and Sb, etc. Further attempts to investigate the possible mechanisms of the magnetic field gradient's influence on the interdiffusion process are under progress.

Conclusion

The diffusion experiments of liquid Bi in solid $Bi_{0.4}Sb_{0.6}$ alloy were performed under various high magnetic field conditions. The effective diffusion coefficients were calculated based upon the fact that a parabolic relationship holds well between the migration distance and the diffusion time whether with or without a magnetic field. The decrease of the effective diffusion coefficient, in the presence of a magnetic field, could be a consequence of the enhancement of diffusion activation energy. Given that the magnetic field caused the viscosity to increase in the liquid metal could lead to this result. Under gradient magnetic fields, in spite of the direction of the gradients, the interdiffusion process was retarded more significantly when compared with the case of uniform magnetic field.

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