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The Kinetic Theory of Growth of Zr-Sn Diffusion Layers on $Zr_{55}Cu_{30}Al_{10}Ni_5$ Metallic Glass *

CHAI Kan(柴戡)[1], LIN Tie-Song(林铁松)[1], HE Peng(何鹏)[1**], SUN Jian-Fei(孙剑飞)[2]

[1]*State Key Laboratory of Advanced Welding and Joining, Harbin Institute of Technology, Harbin 150001*
[2]*School of Materials Science and Engineering, Harbin Institute of Technology, Harbin 150001*

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The growth kinetics of the intermetallic compound layer between molten pure Sn and $Zr_{55}Cu_{30}Al_{10}Ni_5$ bulk metallic glass (BMG) is mainly controlled by the diffusion mechanism at stage I at which the value of the time exponent is approximately 1/2, also there is unusual or unique stage Ⅱ whose time exponent of the growth is suppressed to 1/3. It is deduced that phase transition such as nucleation, coalescence occurring in the vicinity of the interface of the diffusion layer within the BMG and the average size growing as one-third power of time, called the Lifshitz–Slezov law. A more elegant means of attack is based upon the Fokker–Planck approach, which permits us to calculate directly the probability of the distribution of steady-state thickness fluctuations. Physical implications of the analytical results also give the one-third power of time of distance scale. The transmission of Sn particles through a disorder system of the BMG, scattered by the local fluctuation levels, is the source of the time exponent from 1/2 to 1/3 as a macroscopic cumulative effect.

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$Zr_{55}Cu_{30}Al_{10}Ni_5$ bulk metallic glass (BMG) called Inoue alloy is characterized by high strength, large elastic strain, and a low Young's modulus.[1] These alloys have already found some important applications in industry.[2] Up to date, from the viewpoint of practical applications of BMGs, the maximum dimensions of the BMGs that can be directly prepared are still limited, typically no more than several centimeters, constraining their applications as structural and functional parts. Thus joining might be necessary in some situations. Among many bonding techniques, soldering has become an important joining technology and has been used widely in electronic packaging processes.[3] The liquid alloy melt can react with substrates, resulting in the formation of intermetallics at the interface during soldering.[4] It is desirable to achieve a good metallurgical bond while forming a thin intermetallic layer. However, excessive intermetallics growth may have a deleterious effect since the intermetallics are brittle in nature.[5] It is found that the intermetallics exist at the interface between the molten In-Sn alloy and $Cu_{40}Zr_{44}Al_8Ag_8$ BMG.[6] Therefore, the information of the interfacial growth kinetics between molten alloys and BMGs is fundamentally important for the reliability evaluation of BMG joints. Few works have been carried out on the growth kinetics of the intermetallic layers between molten Sn-based solders and Zr-based BMGs. In this Letter, the growth of the intermetallic layer between molten pure Sn and $Zr_{55}Cu_{30}Al_{10}Ni_5$ BMG was studied during isothermal aging. Some special laws of growth phenomenon of the layer will be the inductive and deductive inference qualitatively.

The ingots of $Zr_{55}Cu_{30}Al_{10}Ni_5$ (at.%) were prepared by arc melting the pure elements with a purity of 99.5% or better under a Ti-gettered argon atmosphere. All BMG specimens were immersed in the molten Sn (99.99 wt.%) in a solder pot by isothermal aging at the temperature range between 513 and 633 K with 30 K temperature interval. Each hour the specimens were taken out, cooled down in acetone, sectioned and polished, and then etched using the 5% HNO_3 alcohol solution to examine the possible interfacial reactions by using scanning electron microscopy (SEM). Thickness measurement of the intermetallic layer was performed by using image analysis software. Figure 1 presents the typical SEM micrograph of the molten $Sn/Zr_{55}Cu_{30}Al_{10}Ni_5$ BMG reaction coupling after aging for 36 h at 573 K.

It is found that the intermetallic compound exists at the interface between Sn and $Zr_{55}Cu_{30}Al_{10}Ni_5$ BMG, marked by the arrow. The thickness of the intermetallic layer increases with the increase of aging temperature and aging time. Figure 2(a) shows the curves of mean thickness of the intermetallic layers with time and temperature. Generally, the thickness of a reaction layer in the diffusion couples is expressed by the simple parabolic equation

$$h(t) = kt^n, \tag{1}$$

where $h(t)$ is the thickness of the reaction-layer; k is the growth rate constant; n is the time exponent; and t is the reaction time. If the growth process is controlled by the diffusion mechanism, the thickness of the intermetallic compound layer increasing after aging should follow the square root time law, $h(t) = kt^{1/2}$. It is empirically found that n takes the value of 1/2

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**Corresponding author. Email: hithepeng@hit.edu.cn
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when the reaction is mainly controlled by the diffusion mechanism.[7,8]

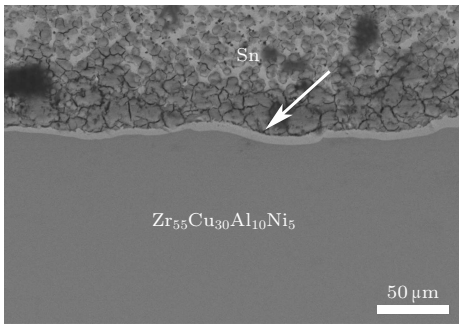

Fig. 1. Backscattered electron micrograph of the cross section of $Sn/Zr_{55}Cu_{30}Al_{10}Ni_5$ BMG reaction couple after aging for 36 h at 573 K.

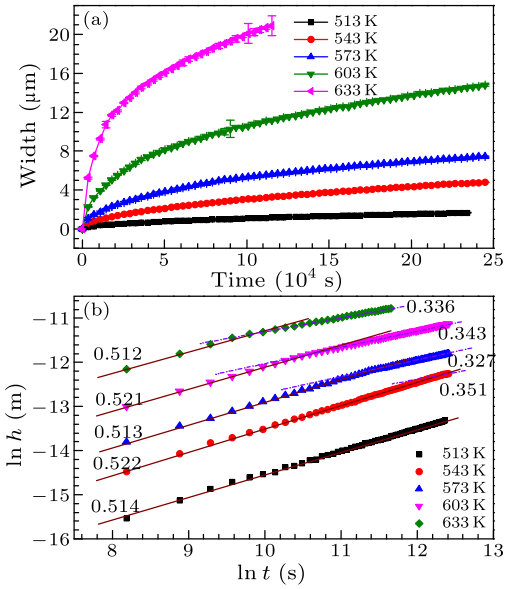

Fig. 2. (a) Mean thickness of the intermetallic layers with time and temperature; (b) bilogarithmic diagram of linear fitting the thickness data in two segments.

It is found that the growth of the intermetallic layer is mainly controlled by atomic (Sn and Zr) diffusion. The time exponent n can be obtained from the slope of the $\ln h$ versus $\ln t$. By means of linear fitting the data segmentation, we found that there are two values of the time exponent corresponding to two stages. As shown in Fig. 2(b) and for the exponents listed in Table 1, the time exponent n_1 of stage I is approximately 1/2 and the time exponent n_2 of stage II is approximately 1/3. The apparent activation energy calculated for the growth of the diffusion layer in stage I is 142.23 kJ/mol, and 155.94 kJ/mol in stage II.

Table 1. Time exponents of two stages of growth of the layer at different temperatures.

	Temperature (K)				
Exponent	513	543	573	603	633
n_1	0.514	0.522	0.513	0.521	0.512
n_2	-	0.351	0.327	0.343	0.336

Then the empirical equation of the thickness can be deduced as

$$h(t) = k_1 t^{1/2} + k_2 t'^{1/3} + A, \tag{2}$$

or piecewise equation as

$$h(t) = \begin{cases} k_1 t^{1/2} + A, & t \in [0, t_c) \\ k_2 t'^{1/3} + B, & t' \in [t_c, t_{\max}), \end{cases} \tag{3}$$

where $B = A + k_1 t_c^{1/2}$ is the layer thickness at t=0; $k_{1,2}$ is the growth rate constant corresponding to the stage of growth; t_c is the critical time when the diffusive growth changes from stage I to stage II. Critical time t_c could not be determined precisely by our experiment. Based on the dimensional analysis, we list the data of growth constant rate $k_{1,2}$ in Table 2.

Table 2. Growth rate $k_{1,2}$ at different temperatures by fitting the experimental data.

	Temperature (K)				
Growth rate	513	543	573	603	633
k_1 ($m/s^{1/2}$)	3.0×10^{-9}	7.6×10^{-9}	1.8×10^{-8}	3.7×10^{-8}	7.4×10^{-8}
k_2 ($m/s^{1/3}$)		7.4×10^{-8}	1.4×10^{-7}	2.4×10^{-7}	3.8×10^{-7}

It is concluded that there are two stages of the kinetic process of the growth of the layer. Stage I is a free diffusion controlled process, in which $h \sim t^{1/2}$. It is deduced that phase transition such as nucleation, coalescence causes the stage II of the growth of the layer. New-phase aggregates arising in a stochastic manner via thermal fluctuations, such as homogeneous nucleation in the BMG, has proceeded to the extent that domains of one phase have begun to form, and subsequently grow. The driving force for growth is the reduction in interfacial energy that occurs as the domain becomes larger and growth has no appreciable effect on the degree of metastability of the BMG. When there are a small number of minority phase clusters, with a distribution of cluster sizes, the effect of curvature that is the local solubility of the minority component is higher near the smaller cluster than that near the larger ones; the smaller clusters dissolve and the new phase is absorbed by the larger ones. This process, by which larger clusters grow at the expense of the smaller ones, can show that the average size grows as one-third power of time called the Lifshitz–Slezov law, and the average domain size $R(t)$ is[9,10]

$$R(t) = \left(\frac{4}{9} D\gamma t\right)^{1/3}, \tag{4}$$

where D is the diffusion coefficient, and γ is the effective interfacial tension. This relation of macroscopic cumulative effect corresponding to the second item of the thickness of Eq. (2), which means that diffusion coefficient D is cubic of k_2 at stage Ⅱ, and square of k_1 at stage I of course.

An interface becomes rough increasingly as random elements, such as local inhomogeneities, begins to have a large scale cumulative effect and the morphology behind the front has become extraordinarily complex. The details of the physical processes discussed above could not be confirmed by our experiment. We need a more general description for the kinetic process. For such slow processes,[9] the simplest and the most elegant means is based upon the Fokker–Plank approach, which permits us to calculate directly the probability distribution of steady-state thickness fluctuations. From a standard textbook,[11] denoted by $P[h(\boldsymbol{x});t)]$, here $h(\boldsymbol{x})$ is the distribution functional of the surface position. We regard the stochastic growth Kadar–Parisi–Zhang (KPZ) equation[12,13]

$$\dot{h}(\boldsymbol{x},t) = v\nabla^2 h + \frac{\lambda}{2}(\nabla h)^2 + \eta(\boldsymbol{x},t), \tag{5}$$

where $\eta(\boldsymbol{x},t)$ is the Gaussian noise with correlator $\langle\eta(\boldsymbol{x},t)\eta(\boldsymbol{x}',t')\rangle = D\delta(t-t')\delta(\boldsymbol{x}-\boldsymbol{x}')$. The noise term, being non-negative while random, mimics the probabilistic nature of growth, which is present everywhere at any time. Thus the initial seed evolves into a growing cluster, expanding into unoccupied space, since the bulk phases are essentially homogeneous. The corresponding Fokker–Plank equation is

$$\frac{\partial P[h;t]}{\partial t} = -\int d\boldsymbol{x}\frac{\delta}{\delta h}\left\{\left[\nabla^2 h + \frac{\lambda}{2}(\nabla h)^2\right]P\right\} + \int d\boldsymbol{x}\frac{\delta}{\delta h^2}P. \tag{6}$$

It is possible to show that if we start from a flat configuration, denoted by $\bar{h}$, the mean position of the surface at time t, then the probability of finding the surface at h is[14]

$$P(h) \sim \exp\{-[(h-\bar{h})/t^{1/3}]^{\eta_+}\}, \tag{7}$$

where η_+=3/2. Equation (7) is only valid for $h > \bar{h}$, which can be traced to the fact that thickness fluctuations of the interface correspond to free energy fluctuations in the disorder medium,[14] where we need to calculate quenched disorder averages of arbitrary positive moments. Systems with quenched disorder such as BMGs is notoriously hard to study analytically. We arrive at the problem via an attractive delta function potential, with many-body Hamiltonian in one direction

$$H_n = -D\sum_{\alpha}\frac{\partial^2}{\partial x_\alpha^2} - V^2\sum_{\beta>\alpha}\delta(x_\alpha - x_\beta). \tag{8}$$

The n-body Schrödinger equation reads

$$\{-\sum_{\alpha}\partial_\alpha^2 - \sum_{\beta>\alpha}\delta(x_\alpha - x_\beta)\}\psi(x_1,\ldots,x_n) = E\psi(x_1,\ldots,x_n). \tag{9}$$

Consider the modified wave function of ground state[15]

$$\psi \sim \exp\left\{-\sum_{\alpha>\beta}|x_\alpha - x_\beta| - \frac{1}{4Dt}\Big(\sum_{\alpha=1}^{n}x_\alpha\Big)^2\right\}, \tag{10}$$

where we recognize the last term is diffusive motion, while the second term is just the kinetic energy. We know that transverse deviation must scale as $x \sim t^{2/3}$, and both the terms in Eq. (10) should be of the same order of magnitude.[14] We obtain

$$\Big(\sum_{\alpha=1}^{n}x_\alpha\Big)^2\frac{1}{4Dt} \sim t^{1/3}, \tag{11}$$

which in turn implies that the relative distance must also scale as

$$|x_\alpha - x_\beta| \sim t^{1/3}. \tag{12}$$

The fundamental problem is the transmission of particles through a disordered medium, the tunneling of a quantum particle through a macroscopically smooth potential barrier of finite thickness in which the particle undergoes elastic sub-barrier scattering from random scatterers.[16] The first question to be considered is the energy spectrum of a particle in the field of a disordered system of scattering centers. For the concentration fluctuation, at an early stage, the mentioned energy spectrum $\nu(E,c)$ is[16]

$$\nu(E,c) \sim \exp\left\{-\frac{8}{3\sqrt{3}}\lambda\frac{\Delta E^{1/2}}{c}\right\},\ \lambda = \frac{\pi^4\sqrt{2}}{3\mu^{3/2}}, \tag{13}$$

where c is the impurity concentration due to quantum fluctuation;[16] ΔE is the shift energy; μ is the reduced mass. The energy spectrum for the high-concentration local fluctuations due to the structure relaxation of the late stage is

$$\nu(E,c) \sim \exp\{\lambda\Delta E^{-3/2}c\}. \tag{14}$$

Based on a macroscopic cumulative effect of the mechanical similarity and unified dimension in the disorder average medium, the time dimension of the Sn transmission behavior at stage I is $\sim t^{1/2}$, and at stage Ⅱ is $\sim t^{1/3}$.

In summary, the unique phenomena of growth of the diffusion intermetallic layer is divided into two stages, where the time exponent of kinetics is 1/2 at stage I and 1/3 at stage Ⅱ. The propagating edge of the layer growth becomes increasingly rough due to local variations in the scattering center concentration. As Sn displaces atoms in the closed-packed cluster of the BMG, easily seen from above, pushes ahead of atoms

getting kinetically roughened, due to local inhomogeneities in the random disorder medium. Incorporating effects of structure relaxation in the BMG, locally normal growth of the diffusion interface (i.e., parallel propagation of the front directed to the BMG), and the incessant peppering of stochastic noise, have come to represent a crucial step in eliciting kinetic roughening phenomena. The phenomena are patently governed in some measure by the essential nonlinear mechanism of parallel transport of the interface. In retrospect, it is hardly thinkable so that the explication of such physical processes would necessitate the layer growth on BMG touched upon here. Nonetheless, our research endeavors diffused far beyond the original intension; e.g., suggestions concerning interfacial growth with the structure details of the BMG. Admittedly, such matters are more important for scientific curiosity than for practical applications.

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