

Effect of plastic deformation on the kinetics of the solid state reaction between Cu and Zn

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The kinetics of the solid-state reaction at the interface of a Cu-Zn bulk diffusion couple subjected to compressive plastic deformation has been studied as a function of plastic strain, strain rate, and temperature. The experimental data have been interpreted on the basis of classical atomic transport theory, considering also the effect of plastic deformation on the growth rate of the reaction product. The diffusion coefficient at 150 °C (larger than the purely thermal value at the same temperature by about four orders of magnitude) is almost independent of temperature and is linearly dependent on the strain rate at which the deformation occurs. The only parameter controlling the thickness of the reacted layer appears to be the total strain experienced by the diffusion couple. These features of plastically enhanced diffusivity are coherent with a simple model of the behavior of the excess point defects created by plastic deformation, similar to that developed in order to describe radiation-enhanced diffusion. [S0163-1829(99)04417-3]

INTRODUCTION

The effect of plastic deformation on the kinetics of solid-state reactions is one of the most important issues in the study of mechanical alloying induced by high-energy ball milling¹ or by extensive cold rolling of thin metal foils.² The investigation of this subject is complicated by the stochastic nature of the ball-milling process, so that detailed microstructural characterization by microscopical methods suffers from the lack of knowledge of the thermomechanical history of the small piece of matter under investigation. On the contrary, those methods which analyze large enough samples, like x-ray diffraction and differential scanning calorimetry, are able to provide only average information, which, generally, does not allow a detailed description of the interdiffusion mechanism. In fact, it has been ascertained that during the first stages of the milling process a convoluted multilayered structure is formed, at least when ductile metals are processed. The solid-state reaction is then assumed to proceed because of the high density of heterogeneous interfaces under the effect of the plastic shear induced by the deformation process.³ At the same time an extensive research effort has been devoted to the study of the reaction kinetics during milling.^{4,5} In these studies it has been found that the reacted fraction and the atomic level strain accumulated by the reactants increase exponentially with milling time, at least in the early stages of the process. In addition, the effect of the excess point defects created by the plastic deformation on the kinetics of the solid-state reaction has been studied in a careful experiment where ball milling of Ag-Cu powders has been carried out at several temperatures.⁶

We proposed, a few years ago, to investigate the effect of plastic deformation on the atomic transport properties, by studying with transmission electron microscopy the reaction at the interface of a bulk diffusion couple during a plastic deformation experiment carried out under controlled conditions.^{7,8} This method was applied to the Ni-Zr system which is known to yield an amorphous reaction product when alloyed by ball milling, and was able to give quantitative information on the kinetics of the amorphous phase

growth at the interface between the two metals.

When applied to systems which yield crystalline reaction products this approach presents several experimental problems. In fact, most of the intermetallic compounds which are the possible products of a mechanical alloying experiment have a very limited ductility; as a consequence when a diffusion couple is subjected to plastic deformation and begins to react so that a thin layer of intermetallic compound grows at the interface, the diffusion couple fractures at the interface itself, as the intermetallic layer is often not sufficiently ductile to support further plastic deformation. On the other hand, when the reaction product is a ductile solid solution, the kinetics of the solid-state reaction can only be derived from a chemical profile at the interface, which, considering the limited thickness of the reacted layer, has to be performed by x-ray microanalysis in the transmission-electron microscope. It is reasonable to expect that for most systems this method does not have sufficient spatial resolution; in fact, in the case of Ni-Zr, the amorphous layer was found to have a thickness ranging from a few to a maximum of about 20 nm.⁷ The choice of the diffusion couple plays then a key role in the success of this kind of experiment.

In this paper we report about the kinetics of solid-state reactions at the interface of plastically deformed Cu-Zn bulk diffusion couples. This system was selected since previous studies² have shown that the reaction proceeds through the diffusion of Cu into the Zn matrix so that the first phase appearing as a result of mechanical alloying is the Zn-rich epsilon phase, which has a chemically disordered hexagonal close-packed structure expected to show ductile behavior. Moreover, owing probably to the low melting point of Zn, the reaction kinetics is particularly fast, so that we expect a thickness of the reacted layer large enough for a reliable characterization. The purpose of this experiment is to ascertain the role of the excess point defects, created by the plastic deformation, on the kinetics of the reaction, and to study the interdiffusion behavior as a function of the parameters of the plastic deformation, mainly total strain, strain rate, and temperature.

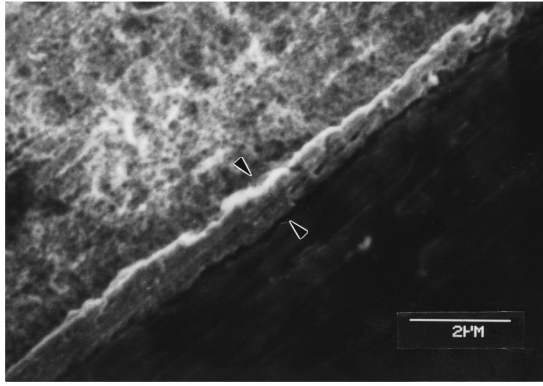


FIG. 1. SEM image of the Cu-Zn interface where the etching procedure has evidenced the reacted layer, between arrows, made of the epsilon phase.

EXPERIMENTAL

The reaction kinetics at the interface between Cu and Zn was studied with a method similar to that used previously for a Ni-Zr diffusion couple. Bulk trilayers comprising a 1 mm thick Zn foil between two Cu sheets with the same thickness, were pressed together between the pistons of a hydraulic press. The sample surface before deformation was about 0.25 cm², and the maximum load supplied by the machine was 250 kN. The load applied to the sample increased linearly with time and the time for full loading was larger than 1 s in most cases; the deformation temperature was in the range from room temperature to 200 °C and was controlled by heating with a suitable rf coil both the specimen and the machine pistons. The sample surface, much smaller than the piston area during the whole deformation process, increased to about 1 cm² at the maximum load, so that the maximum applied stress was of the order of a few GPa.

The details of the procedure concerning the sample surface preparation and the measurement of the temperature increase due to the plastic deformation have already been reported.⁹ In the present experiment the temperature increase during the deformation was limited to a few °C owing to the good thermal contact between the sample and the machine pistons acting as a large heat sink.

When the experiment was able to bond together the two metals the deformed sample was cut in a cross section by a diamond slitting wheel; after conventional metallographic grinding and polishing the sample was etched in a solution of 20 g CrO₃ in 100 cm³ water with an applied voltage of 8 V, in order to evidence the reaction products, and then examined with a Cambridge 250 MKIII scanning electron microscope equipped with both backscattered electron and x-ray detectors.

Morphological observations of the etched surface were carried out at 10 keV with the secondary electron signal, while x-ray spectroscopy at 20 keV and backscattered electron images were used to identify the nature of the reacted layer evidenced by the etching procedure. A typical result is shown in Fig. 1, where it is possible to observe a layer of the epsilon phase at the interface between the two metals. Quantitative x-ray microanalysis confirmed that the chemical composition was within the stability range of this phase. In order to correlate the thickness of the epsilon phase with the

TABLE I. Deformation parameters of the samples examined in the present study.

Load (kN)	Time (s)	Temp (°C)	<i>d</i> (nm)	ϵ	$\dot{\epsilon}$ (s ⁻¹)
55	0.25	150	300	1.2	4.8
55	0.25	150	400	1.38	5.5
110	0.5	150	450	1.58	3.16
165	0.75	150	710	2.8	3.73
220	1	150	800	3.5	3.5
220	0.1	150	640	2.43	24.3
220	10	150	1160	3.04	0.304
220	50	150	600	3.2	0.064
220	100	150	800	3.64	0.0036
220	100	150	600	3.3	0.0033
55	0.25	200	500	1.95	7.8
55	0.25	200	500	2.3	9.2
110	0.5	200	700	2.92	5.8
220	1	200	1000	2.64	2.64
220	1	200	1050	3.5	3.5
110	0.5	120	700	2.04	4.08
110	0.5	120	650	2.43	5.86
220	1	120	700	2.26	2.26
220	1	120	800	2.7	2.7

parameters of the plastic deformation, the local thickness of the Zn layer was measured on low magnification scanning electron microscope (SEM) pictures. As it will be shown later, the plastic deformation of the epsilon phase is an important parameter in the description of the interdiffusion process. Being impossible to measure directly the strain of the reaction product, we have assumed that the epsilon phase and the Zn matrix have the same tensile properties, owing to their structural and chemical similarity.

In order to compare the growth kinetics induced by plastic deformation with the purely thermal behavior, samples previously deformed with a load able to induce the growth of a thin epsilon phase layer at the interface between Cu and Zn have been heat treated at 150 °C for different times before the SEM observation. The accuracy of this kind of analysis is limited by the critical thickness of the ϵ phase layer, at which the γ phase, which is the next appearing in the phase formation sequence of this diffusion couple, is first detected.

RESULTS AND DISCUSSION

A. The diffusion coefficient

The deformation parameters of the samples examined in this experiment are reported in Table I which lists also the thickness *d* of the ϵ phase, the absolute value of the strain $\epsilon = \ln(a_0/a)$, where *a*₀ and *a* are the thickness of the Zn layer before and after the experiment, respectively, and the average strain rate $\dot{\epsilon} = \epsilon/t$, where *t* is the deformation time. The strain and the strain rate of the Zn foil are both assumed to be equal to the same deformation parameters of the ϵ phase.

According to Gösele and Tu,¹⁰ when a phase of thickness *x* grows at the interface between the parent phases, the growth rate can be expressed as

$$dx/dt = G\Delta cK/(1 + xK/D), \quad (1)$$

where G is a parameter whose value depends on the atomic volume and on the chemical composition of both the parent phases and the reaction product, Δc is the range of stability of the growing phase, K is the interface reaction constant, and D is the apparent diffusivity. Considering only the two limiting cases corresponding to diffusion control ($xK \gg D$) and to interface control ($xK \ll D$) of the reaction rate it is possible to make the following approximations:

$$dx/dt = G\Delta c D/x \quad \text{if } xK \gg D, \quad (2)$$

$$dx/dt = G\Delta c K \quad \text{if } xK \ll D. \quad (3)$$

In order to account for the reduction in thickness of the reacted layer induced by the plastic deformation, which is supposed to occur at a constant strain rate $\dot{\varepsilon}$, a further term $-\dot{\varepsilon}x$ has to be added to the right-hand side (rhs) of both Eqs. (2) and (3) which then become

$$dx/dt = (G\Delta c D/x) - \dot{\varepsilon}x \quad \text{if } xK \gg D, \quad (4)$$

$$dx/dt = (G\Delta c K) - \dot{\varepsilon}x \quad \text{if } xK \ll D. \quad (5)$$

Equations (4) and (5) can be integrated, and the thickness of the reacted layer as a function of time can be written as

$$x = (G\Delta c D/\dot{\varepsilon})^{1/2} [1 - \exp(-2\dot{\varepsilon}t)]^{1/2} \\ = (G\Delta c D/\dot{\varepsilon})^{1/2} [1 - \exp(-2\varepsilon)]^{1/2} \quad \text{if } xK \gg D, \quad (6)$$

$$x = (G\Delta c K/\dot{\varepsilon}) [1 - \exp(-\dot{\varepsilon}t)] \\ = (G\Delta c K/\dot{\varepsilon}) [1 - \exp(-\varepsilon)] \quad \text{if } xK \ll D, \quad (7)$$

where we have used the definition of strain rate $\dot{\varepsilon} = d\varepsilon/dt$ to eliminate the explicit dependence on time. Equations (6) and (7) describe diffusion control and interface control of the reaction, respectively. Both equations describe a situation where the thickness of the reacted layer saturates to limiting values given by $(G\Delta c D/\dot{\varepsilon})^{1/2}$ and $(G\Delta c K/\dot{\varepsilon})$, respectively, in contrast with the situation of thermally activated growth. This fact can be explained considering the structure of Eqs. (4) and (5). The first term on the rhs describes the growth rate without plastic deformation; this term is always positive and it has a constant value in the case of the interface controlled reaction [Eq. (4)], while decreasing with the square root of time in the case of diffusion control [Eq. (5)]; the second term, which takes into account the shrinkage of the reacted layer due to the plastic deformation, is always negative and its absolute value increases linearly with the reacted layer thickness. It is then evident that, once the reacted layer reaches a thickness at which the shrinkage rate induced by the plastic deformation is equal to the rate of growth due to the atomic transport, the thickness of the reacted layer remains constant with time. This fact does not mean that the reaction stops at this limiting thickness, since the surface area of the diffusion couple increases with time owing to the plastic strain. This result is particularly important when the fraction of reacted material is experimentally measured from the thickness of the interface layer.

The attainment of a limiting thickness of the reacted layer allows a fairly simple description of the reaction kinetics at a single interface having a time-dependent area $S(t)$. If ϕ_A and ϕ_B are the atomic fluxes of A and B across the bound-

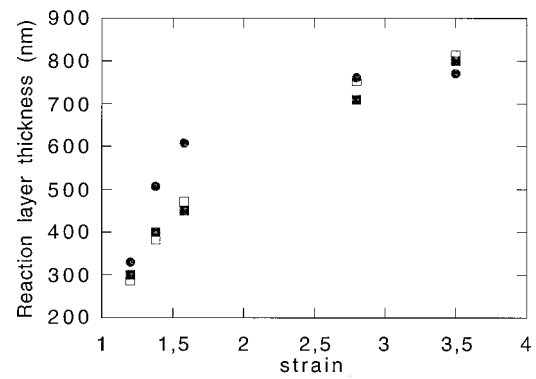


FIG. 2. Thickness of the epsilon phase as a function of strain. Full squares and dots refer to the computed thickness in the hypothesis of interface control and diffusion control, respectively, while open squares represent experimental data.

aries of the growing layer and K_A and K_B are two constants related to the atomic volumes of A and B and to the composition of the reacted layer, the reaction rate dV/dt during the compressive plastic deformation can be written as

$$dV/dt = [K_A \phi_A + K_B \phi_B] S(t). \quad (8)$$

According to Ref. 10 one has

$$\phi(t) = K_D/x(t) \quad (\text{diffusion control}), \quad (9a)$$

$$\phi(t) = K_I \quad (\text{interface control}), \quad (9b)$$

so that, after a time t_0 corresponding to the attainment of the limiting thickness x_0 and to a reacted volume V_0 , one has in either condition:

$$dV/dt = K_s S(t) = K_s V(t)/x_0 = K_v V(t), \quad (10)$$

where K_s and K_v are two constants. Integration of Eq. (10) gives finally

$$V(t) = V_0 \exp(K_v(t - t_0)) \quad (t \geq t_0), \quad (11)$$

thus showing that once a limiting thickness has been attained, the reacted volume at a single interface increases exponentially with deformation time until the moment when the reactants are exhausted and the reaction stops. It is important to notice that the reaction time has been eliminated from Eqs. (6) and (7), and that only the plastic deformation parameters, namely the total strain ε and the strain rate $\dot{\varepsilon}$, are the external variables controlling the thickness of the reacted layer, besides the thermodynamic features of the system. If one makes the hypothesis, whose validity will be confirmed later, of assuming a constant strain rate in our experiments performed at constant loading rate, we can derive the values of K or D by plotting the experimental thickness of the reacted layer versus the total strain of the diffusion couple. The relative strain rate is then evaluated as its average value measured from the thickness reduction of the Zn foil and from the reaction time.

The experimental data collected at 150 °C at constant loading rate are shown as a function of ε in Fig. 2, together with the best fits according to Eqs. (6) and (7). In both cases, in order to fit the data it is necessary, as in the previous case of Ni-Zr,⁸ to introduce a fraction of the total strain ε which

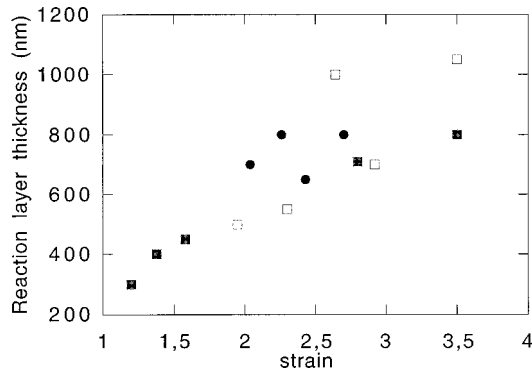


FIG. 3. Thickness of the epsilon phase as a function of strain. Experimental points are relative to deformation at 200 °C (open squares), 150 °C (full squares), and 120 °C (full dots).

appears to be ineffective for the solid-state reaction, so that in the relative equations ε has to be substituted by $(\varepsilon - \varepsilon_0)$. The presence of ε_0 can explain the experimental observation that some minimum strain is necessary for bonding together the two metals and it can be related to the requirement of creating fresh surfaces for the onset of the reaction. From Fig. 2, it is possible to notice a good agreement between the experimental data and the theoretical calculations. In particular the experimental data show clearly the saturation of the thickness of the reacted layer, indicative of the presence of the limiting thickness described above.

The experimental errors, mainly due to the difficulty of measuring accurately the actual strain, coupled with the small differences induced by either reaction mechanism on the growth kinetics, do not allow one to discriminate clearly between diffusion controlled and interface controlled kinetics. The values of both K and D can be derived from the fits of Eqs. (6) and (7) to the experimental points, and from the value of the limiting thickness. Considering a diffusion controlled mechanism, the fitting procedure gives $D = 4.2 \times 10^{-8} \text{ cm}^2/\text{s}$, while in the case of interface control one has that $K = 1 \times 10^{-4} \text{ cm/s}$. For the range of thicknesses observed in our experiments ($\leq 800 \text{ nm}$), the condition $xK \ll D$ which has to be satisfied in order to have an interface-controlled reaction leads to a value of the diffusion coefficient much larger than $8 \times 10^{-9} \text{ cm}^2/\text{s}$.

From the value of the limiting thickness, estimated to be $\approx 900 \text{ nm}$, one deduces a value of $D \approx 5.7 \times 10^{-8} \text{ cm}^2/\text{s}$, or a value of $K \approx 6.3 \times 10^{-4} \text{ cm/s}$. Considering the scattering of the experimental data we conclude that both analyses give consistent results. In summary, from the experimental data, we estimate an effective diffusion coefficient larger than $10^{-8} \text{ cm}^2/\text{s}$. In Fig. 3, all data collected with the same loading rate at the temperature of 120, 150, and 200 °C are reported. Even if the accuracy of the data does not allow a reliable estimate of the interdiffusion coefficient at each temperature, it is possible to notice that all the data can be approximately fitted by the same curve independent of the deformation temperature, showing the essentially athermal nature of the interdiffusion process induced by plastic deformation. It is interesting to notice that also the mechanical alloying process shows a nearly athermal nature, at least in the case of the Cu-Ag system.⁶

The thickness of the reacted layer as a function of time during thermally stimulated growth at 150 °C is shown in

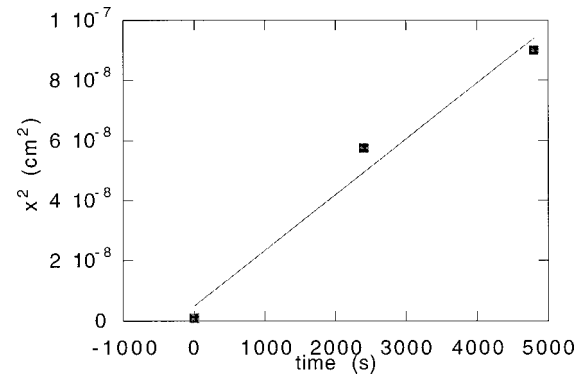


FIG. 4. Square of the reacted layer thickness versus time at 150 °C.

Fig. 4. The experimental data allow a fairly accurate measurement of the thermal diffusion coefficient, whose value of $4.6 \times 10^{-12} \text{ cm}^2/\text{s}$ is smaller by almost four orders of magnitude compared with the diffusivity measured during plastic deformation. Under the hypothesis that the jump frequency is not significantly affected by plastic shear, this difference can be ascribed to the relative concentration of the defects controlling the atomic flow, as detailed in the next section.

B. The diffusion mechanism

The features of the interdiffusion process during plastic deformation can be analyzed considering the behavior of the excess point defects created by the plastic shear. Actually, the creation of excess point defects, in particular vacancies, during plastic deformation has already been ascertained,^{11,12} and we have to consider their influence on the atomic transport properties. The interdiffusion process can be easily modeled if we make the hypothesis that the deformation micromechanisms, in particular the dislocation dynamics, are independent of the external parameters like temperature and strain rate. Under this hypothesis, the number of point defects created per unit shear is expected to be constant, so that the creation rate depends linearly on the strain rate, which plays therefore a role similar to the particle flux in an irradiation experiment. In analogy with radiation-enhanced diffusion (RED), the expected behavior will strongly depend on the mechanism through which the excess defects annihilate.^{13,14} Under fast particle irradiation the RED coefficient is athermal and depends linearly on the dose rate when the excess point defects annihilate at fixed sinks, like dislocations or grain boundaries. On the contrary it is thermally activated and increases with the square root of the dose rate when mutual interstitial-vacancy recombination is predominant.¹³ Probably because of the large difference between the energy of formation of vacancies and interstitials, it has been ascertained¹¹ that, contrary to what happens during fast particle irradiation, where the majority of defects are Frenkel pairs, mainly vacancies are created in the case of plastic deformation. This fact rules out the mechanism of mutual defect annihilation, so that the excess vacancies are forced to annihilate at fixed sinks independently of their supersaturation. Using the same formalism of RED (Ref. 13) and neglecting the equilibrium concentration of vacancies C_{v0} relative to the excess concentration C_v , it is possible to write the plastically enhanced diffusion coefficient D_p during

a plastic deformation experiment carried out at constant strain rate, under the hypothesis, discussed in what follows, that both the generation rate and the sink concentration are constant:

$$D_p = D_v C_v, \quad (12)$$

where D_v is the jump probability of the single vacancy and has the usual dependence on the temperature T :

$$D_v = D_0 \exp(-\Delta H/KT), \quad (13)$$

where ΔH is the height of the diffusion barrier.

On the basis of the above argument we can write the generation rate of excess vacancies as

$$dC^+/dt = K_c \dot{\epsilon}, \quad (14)$$

where K_c is supposed to be a constant. Considering that only annihilation at fixed sinks is operative, the rate of vacancy removal is given by¹¹

$$dC^-/dt = K_{vs} C_v C_s, \quad (15)$$

where C_s is the constant sink concentration and K_{vs} is the rate constant given by¹⁴

$$K_{vs} = (4\pi r_{vs}/\Omega) D_v, \quad (16)$$

where r_{vs} and Ω are the relevant reaction radius and atomic volume, respectively. The time variation of vacancy concentration in the structure is then given by

$$dC_v/dt = K_c \dot{\epsilon} - (4\pi r_{vs}/\Omega) D_v C_v C_s. \quad (17)$$

If a steady-state situation is reached, from Eq. (13) we obtain for the vacancy concentration:

$$C_v = K_c \dot{\epsilon} / (4\pi r_{vs}/\Omega) D_v C_s. \quad (18)$$

Finally, D_p can be written at steady state as

$$D_p = D_v C_v = K_c \dot{\epsilon} / (4\pi r_{vs}/\Omega) C_s. \quad (19)$$

Equation (19) shows that the diffusivity during plastic deformation is expected to depend linearly on the applied strain rate and to be independent of temperature. As stated above, this situation is the equivalent of what is observed during RED when excess point defects annihilate at fixed sinks.¹³ In order to verify the dependence of the apparent diffusivity on the applied strain rate we have performed deformation experiments at different loading rates. From Eq. (6) D_p can be expressed as

$$D_p = x^2 \dot{\epsilon} / [G \Delta c (1 - \exp(-2\epsilon))]. \quad (20)$$

The D_p values computed with Eq. (20) are shown as a function of the average strain rate in the log-log plot of Fig. 5. It is possible to notice how the slope of the linear interpolation is quite close to unity, confirming that, as predicted by Eq. (19), the diffusivity during plastic deformation increases linearly with the applied strain rate. Similar results are obtained considering that the reaction is interface controlled. In fact, in this approximation, the reaction constant K depends linearly on the strain rate.

We want to stress that our analysis cannot rule out some contribution of the interstitial point defects to the transport

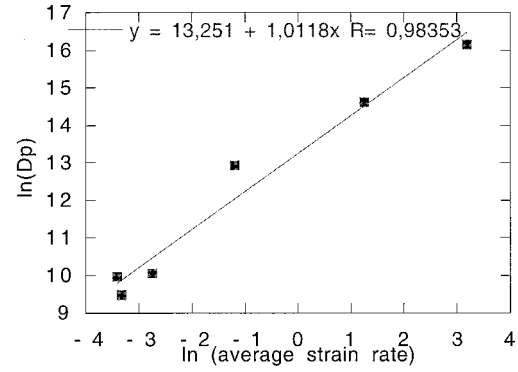


FIG. 5. Log-log plot of the diffusion coefficient versus the strain rate.

process during plastic deformation; in agreement with previous analyses of RED, the linear dependence of the actual diffusion coefficient on the generation rate of points defects and its athermal nature are only indicative of predominant annihilation of excess defects at fixed sinks. Considering the extremely high supersaturation observed in the present experiments, the absence of a detectable contribution of mutual vacancy-interstitial recombination appears to confirm that mainly a single kind of point defect is created by the plastic deformation in agreement with previous considerations and measurements.^{11,12}

According to this analysis, the ratios $D_p/\dot{\epsilon}$ and $K/\dot{\epsilon}$ have a constant value during the deformation, so that Eqs. (6) and (7) show that the only external parameter which controls the thickness of the reacted layer is the total strain of the diffusion couple. In fact, experimentally, both the temperature and the strain rate do not affect significantly the thickness of the reacted layer.

This feature of the interdiffusion process confirms the soundness of our hypothesis concerning the evaluation of the actual strain rate of the epsilon phase during the plastic deformation from the thickness reduction of the Zn layer and from the deformation time. The departure from linearity of the stress-strain curve, which is expected during the actual plastic deformation, appears therefore to have a negligible effect on the interdiffusion process, in the light of the above results. In fact even if the instantaneous strain rate deviates from its average value, the ratio $D_p/\dot{\epsilon}$ appearing in Eq. (6), which describes the growth of the ϵ phase, remains constant. The measured diffusion coefficient is therefore the average value during the deformation experiment.

The good agreement between the experimental results and the theoretical analysis based on the hypothesis of constant vacancy generation rate and constant sink density, with physically plausible values of the fitting parameters is quite surprising in the light of the typical features of the plastic deformation process. In fact, during a plastic deformation experiment we expect substantial microstructural changes and in particular dislocation multiplication and consequent work hardening. The dislocation density plays a double role in Eq. (19). In fact, dislocation glide is considered to be the main mechanism of excess vacancy generation, and the dislocations are probably the most important vacancy sink in a coarse-grained material as in the present case where the contribution of grain boundary to the annihilation of excess defects can be neglected.

Without entering into the details of the plastic deformation mechanisms, whose study under the present conditions is beyond the purpose of this paper, we suggest two possible explanations for the surprising fact that D remains constant during the experiments, despite all changes of the microstructure.

The first is related to dynamic recovery of dislocations occurring under the nonequilibrium condition, owing to the high vacancy supersaturation. In this case, a steady-state concentration of dislocations is reached,¹⁵ so that the deformation proceeds at a constant value of the dislocation density.

As an alternative explanation we have to consider the dependence of both the generation and the annihilation rate of excess point defects on the dislocation density, in particular for what concerns the constant K_c which describes the generation rate and the quantity C_s which is the density of sinks where the vacancies disappear.

If the dislocation density is not too large so that overlapping among the annihilation reaction radii is prevented, C_s is expected to grow linearly with the dislocation density. As far as the generation rate is concerned, we have to make some hypothesis on the mechanism through which the dislocation glide generates the point defects. In the classical approach,¹⁶ point defects are generated by the nonconservative glide of dislocation jogs created by intersection of dislocation gliding on different slip planes. In fact, when two screw dislocations cross under such a geometrical situation, a short segment of edge dislocation is created, which is forced by the applied stress to move nonconservatively by emission or absorption of vacancies. In the first case excess vacancies are created, while in the second interstitial atoms are generated.

The density of dislocation jogs, being related to the interaction between dislocations gliding on different slip planes, is expected to depend, at a first approximation, on the square of the dislocation density. On the other hand, the average slip distance of each dislocation jog per unit shear (or per unit time, once the strain rate is fixed) is expected to depend inversely on the dislocation density considering the linear contribution of the gliding of each dislocation to the macroscopic deformation.

In conclusion, the generation rate depends linearly on the dislocation density, being related both to the jog density, which increases with the square of the dislocation density, and to the average shear of the single jog in unit time which decreases linearly with the same parameter. Therefore, according to this approximate analysis both K_c and C_s depend linearly on the dislocation density.

As a result, D_p is independent of the dislocation density since in Eq. (19) only the ratio K_c/C_s appears. These considerations suggest, therefore, that, once a steady-state situation is reached, the vacancy concentration and the diffusion coefficient no longer depend on the dislocation density owing to a possible compensation between the generation and the annihilation rates.

CONCLUSIONS

With a simple experiment, based on the compressive plastic deformation of bulk diffusion couples, we have shown that the interdiffusion reaction at the interface between Cu and Zn is strongly enhanced by the plastic deformation, relative to the thermal situation. The apparent diffusion coefficient can be derived from the analysis of the experimental data on the basis of the classical model of the interdiffusion at the interface between two metals, taking into account the effect of plastic deformation on the growth rate of the reacted layer. At 150 °C, the measured diffusion coefficient is about four orders of magnitude larger than the thermal one. The diffusion coefficient during plastic deformation appears to be essentially athermal and to depend linearly on the strain rate at which the plastic deformation occurs. Owing to these features the thickness of the reacted layer at the interface depends only the total strain of the diffusion couple with a very good agreement between theory and experiment. The thickness of the reacted layer shows a saturation value, which, in the present case is of the order of 1 μm ; once this thickness has been reached the reaction proceeds only through the increase of the interface area. These features can be justified considering the kinetic features of the excess point defects created by the plastic deformation, which can be modeled on the basis of the approach currently used in the analysis of RED.

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¹R. Bormann, in *Materials by Powder Technology*, edited by F. Aldinger (DGM, Informationgesellschaft, Oberusel, 1993), p. 247.

²S. Martelli, G. Mazzone, S. Scaglione, and M. Vittori Antisari, *J. Less-Common Met.* **145**, 261 (1988).

³C. C. Koch, in *Materials Science and Technology. A Comprehensive Treatment*, edited by R. W. Cahn (VCH, Weinheim, Germany, 1991), Vol. 15, p. 193.

⁴G. B. Schaffer and P. G. McCormick, *Metall. Mater. Trans. A* **23A**, 1285 (1992).

⁵G. B. Schaffer and J. S. Forrester, *J. Mater. Sci.* **32**, 3175 (1997).

⁶T. Klassen, U. Herr, and R. S. Averback, *Acta Mater.* **45**, 2921 (1996).

⁷G. Mazzone, A. Montone, and M. Vittori Antisari, *Phys. Rev. Lett.* **65**, 2019 (1990).

⁸G. Mazzone, A. Montone, and M. Vittori Antisari, *Scr. Metall. Mater.* **28**, 281 (1993).

⁹S. Martelli, G. Mazzone, A. Montone, and M. Vittori Antisari, *J. Phys. (Paris), Colloq.* **51**, C4-241 (1990).

¹⁰U. Gösele and K. N. Tu, *J. Appl. Phys.* **53**, 3252 (1982).

¹¹J. F. Nicholas, *Acta Metall.* **7**, 544 (1959).

¹²R. W. Baluffi and A. L. Ruoff, *J. Appl. Phys.* **1**, 59 (1962).

¹³Fu Rong Ding, R. S. Averback, and H. Hahn, *J. Appl. Phys.* **64**, 1785 (1988).

¹⁴R. Sizmann, *J. Nucl. Mater.* **69&70**, 386 (1968).

¹⁵U. Essman and H. Mughrabi, *Philos. Mag. A* **40**, 731 (1979).

¹⁶R. W. K. Honeycombe, *The Plastic Deformation of Metals* (Edward Arnold, London, 1977), p. 271.