Effect of Plastic Flow on the Kinetics of Amorphous Phase Growth by Solid-State Reaction in the Ni-Zr System

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We propose a method of deforming a bulk diffusion couple which allows separate control of the effects on the kinetics of glass formation due to plastic flow and temperature increase. It is found that plastic flow enhances, by several orders of magnitude, the interdiffusion coefficient (whose temperature dependence is described by a dual-regime Arrhenius behavior) and that increasing the rate at which the load is applied results in a considerable enhancement of the process of diffusion. All these observations are tentatively ascribed to the creation of excess free volume by plastic flow.

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Solid-state reactions (SSR) induced by mechanical deformation (cold rolling or ball milling) may produce amorphous phases if one makes a suitable choice of sample composition and processing conditions. While the thermodynamic requirements dealing with the first point are reasonably well understood,[1] there is an active debate concerning, on one hand, the mechanisms controlling the reaction kinetics[2] and, on the other hand, the effect of the process parameters on the diffusion rate and the reaction path.[3] This is largely due to an intrinsic difficulty in the characterization of the deformation process and, in particular, of the successive steps which lead to the SSR. It has been shown that, in the early stages of mechanically alloying elemental powders, the metal particles are converted to elemental multilayers with a structure similar to that obtained by alternate vacuum deposition.[4] These composites can be transformed to a homogeneous glassy phase either by heat treatment[5,6] or by further ball milling.[7,8] In the first case similar results are obtained from both types of samples; for instance, in the Ni-Zr system the rate-limiting step is the diffusion of Ni through the already formed Ni-Zr glass with an apparent activation energy of about 1.2 eV for temperatures higher than 500 K.[5,9]

Recently, vacuum-deposited specimens have shown a second regime of diffusion characterized by a smaller apparent activation energy and occurring in a low-temperature region not yet explored with mechanically prepared multilayers.[10] For the concerns of amorphization by further milling, this phenomenon is influenced by several process parameters whose effects are difficult to evaluate both theoretically and experimentally.[11,12] In fact, both the sample temperature and the amount of plastic deformation are determined, among other factors, by the velocity of the colliding balls which, in turn, depends on the milling strength. As a result it is difficult to separate the effect of temperature from the effect of plastic flow which, in amorphous materials, has been suggested to produce a considerable amount of excess free volume[13-15] whose influence on the interdiffusion coefficient has been pointed out by Turnbull and Cohen.[16]

In order to gain a better understanding of the variables which influence SSR induced by mechanical deformation and with the aim to separate thermal effects from those related to plastic flow, we propose a novel method based on the compressive plastic deformation of a bulk diffusion couple, such that the macroscopic mechanical parameters as well as the reacting interface temperature can be controlled and changed independently. Macroscopic trilayers prepared placing a 0.5-mm-thick 99.9% Ni electropolished foil between two 1.6-mm-thick 99.7% Zr lapped sheets (both metals being recrystallized commercial products) were deformed in compression with a load normal to the Ni-Zr interface in a fatigue machine operated in the single-cycle mode. The experiments were carried out at several temperatures, heating with an rf coil both the specimen and the machine pistons, whose size was in all cases much larger than the sample area after deformation. All samples used in this study had a square shape with a 5-mm side. The true temperature of the interface during plastic deformation was measured with a thermoelectric method. To this purpose two of the three foils were used as a thermocouple during the deformation process itself, the hot junction being the reacting interface. In order to ensure that the cold contact was not heated by conduction from the hot junction, the sheets used for this set of experiments were machined to a shape such that a square of the usual size was connected to a 3-cm-long strip. The thermocouple output was recorded with a digital oscilloscope as a function of load with all loads applied in a time of 50 ms. The corresponding temperature increase varied linearly from 60 K at 50 kN, which turned out to be the minimum load required for strong adhesion between Ni and Zr and marked the onset of macroscopic deformation of both metals, to 85 K at the maximum load allowed by the machine (220 kN).

Considering that this procedure measures the average interface temperature, a check was performed by inserting a thin NiCr-NiAl thermocouple between the reacting sheets in a small groove machined on the Zr side. This thermocouple, spot welded on the Zr surface in order to make a local measurement of the interface temperature, was used to detect the presence of hot spots due to inhomogeneities in the process of deformation. The two sets of measurements were in agreement within about 10 K. The small temperature increase, notwithstanding an energy input of about 30 J at the maximum load, was due to the good thermal contact between the specimen surfaces and the machine pistons. The thickness and the nature of the interface layers were studied by TEM examination of cross sections prepared with the usual method of slicing, grinding, and dimpling; final thinning was performed by Ar-ion-beam milling in a liquid-N_2-cooled stage. Further details about the experimental procedure can be found in Ref. 17.

The thickness of the interface layer was measured as a function of load, keeping the deformation time constant, and as a function of external temperature and strain rate at constant load. A typical structure of the Ni-Zr interface after deformation is shown in the TEM micrograph of Fig. 1. Between crystalline Ni and Zr one observes a thin (~8 nm) featureless layer whose amorphous structure is evidenced by the microdiffraction pattern shown in the inset of Fig. 1, which, because of beam broadening, also shows some Bragg spots due to crystalline Ni and Zr. Despite considerable plastic deformation of the sample, the interfaces appear quite regular with a smooth surface and a nearly constant thickness. All these features of the reacted layer were confirmed by the observation of several samples. At 50 kN the sample area after deformation increased by a factor of 2 so that the stress at the end of the compression cycle was about 1 GPa. Similar interfaces were obtained deforming the composite with loads higher than 50 kN.

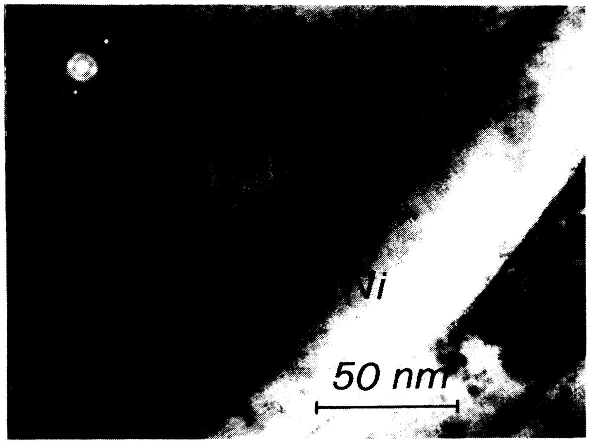

FIG. 1. TEM bright-field image of the Ni-Zr interface in the trilayer deformed with 200 kN at room temperature. The two arrows mark the thickness of the amorphous layer. Inset: Microdiffraction pattern of the glassy layer.

The thickness of the amorphous layer as a function of load is shown in Fig. 2. Even considering the increase of sample temperature with applied load, a purely thermal effect cannot account for the thickness of the glassy layer. Under the hypothesis that the rate-limiting step is the diffusion of Ni through the glass, as observed for thermal diffusion, it is possible to estimate the effective interdiffusion coefficient D from the amorphous layer width X by means of the relation

$$4Dt = X^2, \tag{1}$$

where t is the interdiffusion time for which, as suggested by our experiments at different temperatures, an upper bound is given by the deformation time. The D values range from 5×10^{-18} to 3×10^{-16} m^2/s at temperatures around 340 K, to be compared with a D value of the order of 10^{-22} m^2/s characterizing thermal diffusion at 380 K.[10] Notice that, in order to explain our results by means of thermal diffusion, the reaction temperature should be well above the Ni-Zr crystallization temperature which has been measured to be not higher than about 850 K.[18] We are therefore led to conclude that plastic deformation of the growing Ni-Zr glass enhances considerably the diffusion process.

The suggestion that plastic flow in a glassy phase creates a large amount of excess free volume has already been reported.[13,14] This experimentally observed dilatation of glassy samples subjected to plastic flow[15] can be coupled with the Turnbull and Cohen model[16] which predicts an exponential variation of the interdiffusion coefficient as a function of the free volume fraction in the atomic cage. In our case the experimental situation is quite complicated since the glass is deformed while growing from the crystalline parent phases, so that the present setup is not suitable to test the connection between the above model and our experimental findings. Additional information about the diffusion process dur-

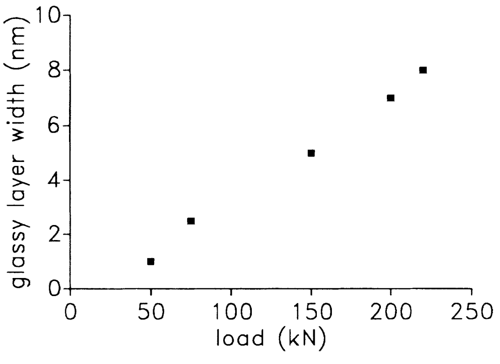

FIG. 2. Width of the interface layer vs applied load.

ing plastic deformation has been obtained from the other sets of experiments mentioned above.

The square of the amorphous layer thickness measured on samples deformed with 75 kN in 50 ms, in the temperature range between 330 and 730 K, is shown in the usual Arrhenius representation in Fig. 3. The point corresponding to the temperature of 730 K is not considered in the calculation of the activation energies since at this temperature one observes the presence of intermetallic compounds. The reaction temperatures in Fig. 3 have been approximately corrected for the small effect due to plastic deformation adding to the constant piston temperature the measured peak value of the temperature increase. The diffusion data shown in Fig. 3 reveal two distinct Arrhenius regimes with different apparent activation energies. Fitting the experimental data with two independent diffusion mechanisms one deduces that a regime with an activation energy of 0.18 eV is dominant up to about 570 K, while at higher temperatures the activation energy changes to 1.3 eV. A similar behavior has been observed also in samples obtained by thermal annealing[10] and ion-beam mixing.[19] In the first case the measured activation energies were 0.2 and 3.5 eV, while in the second case the observed reduction by a factor of 3–4 of these values has been interpreted as being due to the migration of radiation-created point defects. These facts suggest the existence of similarities in the mechanism of diffusion in ion-beam-mixed and plastically deformed samples, which can be tentatively related to the presence in both cases of excess-free-volume–enhancing atomic mobility in the glassy phase.

Finally, we notice that the temperature variation of D is described by an Arrhenius plot if all experimental points are referred to the same duration of the diffusion process. Considering that the removal of the samples from the machine after the deformation occurs with an unavoidable delay, ranging at random from a few seconds to one minute, and that the results do not reflect this unsystematic stay of the sample at the piston temperature for a time which is orders of magnitude longer than 50 ms, we deduce that the deformation time, or a nearly constant fraction of it, is the relevant physical time involved in the diffusion process.

The amount of flow dilatation of a glassy phase depends on the balance between two processes:[13,14] First, as mentioned above, we have the creation of free volume by plastic flow; second, we have its annihilation by thermally activated atomic jumps. Consequently, the instantaneous amount of free volume depends not only on the stress but also on the rate at which the load is applied since, by lowering this rate, more time to relax is given to the structure. In order to search for this effect, if one accepts the connection between diffusion and free volume, a load of 150 kN was applied at room temperature in times ranging from 50 ms to 50 s. While the macroscopic deformation of the samples was practically the same for all times, a considerable variation of the thickness of the amorphous phase has been observed. Notice that at the highest strain rate the temperature increase enhances the interdiffusion coefficient by a factor of 4 so that the product Dt increases by a factor of 250 going from the shortest to the longest time.

The thickness of the amorphous layer reported in Fig. 4 as a function of deformation time shows that the effect associated with the strain rate reverses completely the combined effect of time and temperature. As a consequence, the data of Fig. 2 contain also a small contribution due to the variation of the strain rate which does not significantly affect the conclusions concerning the marked influence of applied load on the thickness of the reacted layer.

In summary, a simple method based on the controlled deformation of a bulk diffusion couple has allowed us to examine separately the effect of temperature and mechanical stress on the kinetics of solid-state amorphization in the Ni-Zr system. Plastic flow has been found to play an extremely significant role enhancing the effective interdiffusion coefficient by several orders of

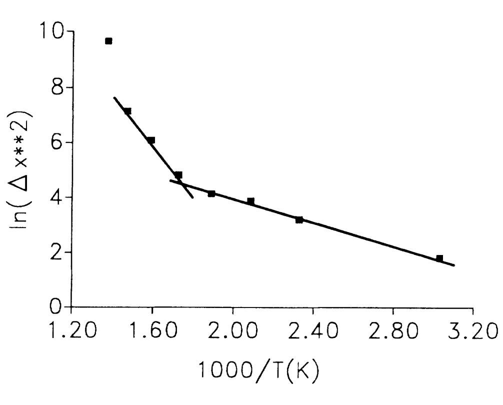

FIG. 3. Arrhenius plot of the square of the glassy layer thickness X vs reciprocal temperature for samples deformed with 75 kN in 50 ms.

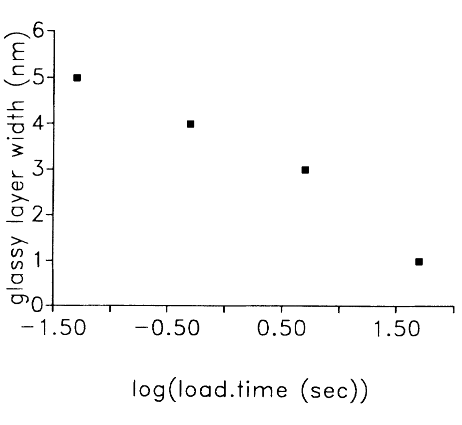

FIG. 4. Width of glassy layer vs loading time for samples deformed with 150 kN at room temperature.

magnitude, so that this effect has to be taken into account when studying SSR induced by mechanical deformation. The temperature dependence of the glassy phase growth rate can be described by an Arrhenius behavior with two distinct regimes, in a way similar to thermally activated and radiation enhanced diffusion. Finally, the reaction kinetics increases considerably with the strain rate. All these effects seem related to the creation by plastic flow of excess free volume in the glass.

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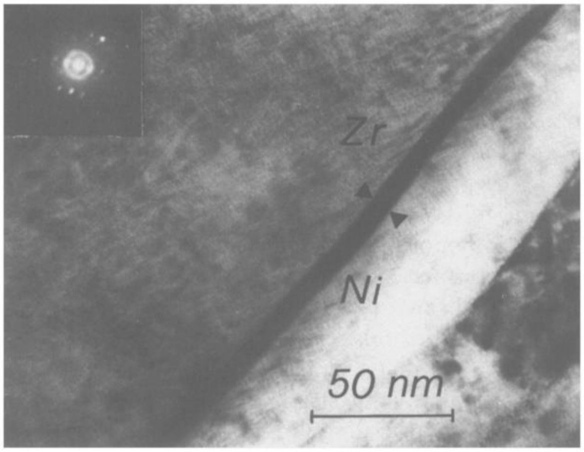

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