Structural relaxation induced by passing electric current in amorphous $Cu_{50}Ti_{50}$ at low temperatures

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The effects of passing current i on the structural relaxation in amorphous $Cu_{50}Ti_{50}$ annealed at 423 K were investigated at and below 413 K. On the scale of the electric field ϵ corresponding with i, for ϵ above the threshold ϵ_T (0.5 V/cm at 413 K and 0.7 V/cm at 373 K), the electrical resistance R of the specimens showed a dramatic decrease against elapsed time t, but for ϵ below ϵ_T, R remained unchanged. After completion of the decrease in R, the specimens became brittle. These results suggest that a strong increase in topological short-range order (TSRO) which can be expected to occur for thermal annealings above 600 K was induced even below 413 K under $\epsilon > \epsilon_T$. An effect of hydrogen possibly contained in the specimens was found to be negligible for the present results. It was further found that the TSRO process under ϵ could be explained by the Johnson-Mehl-Avrami model and the application of ϵ caused, surprisingly, a strong decrease in the effective activation energy, 0.8 eV/(V/cm), for the TSRO process. This effect of ϵ cannot be explained by the usual electromigration mechanism.

Amorphous alloys obtained by melt quenching reveal the structural relaxation during the subsequent heat treatments due to their metastability. For convenience the corresponding atomic rearrangements are subdivided into a change in chemical short-range order (CSRO) and a change in topological short-range order (TSRO) or crystallization, while these SRO's may not be totally independent. With respect to changes in the physical properties due to the structural relaxation, a faster and reversible component is associated with CSRO and a slower and irreversible one with TSRO, respectively.[1] For the electrical resistance R measurements for amorphous $Cu_{50}Ti_{50}$ (hereafter, a-CuTi),[2,3] it has been reported that with elevating temperature T, R of an as-quenched specimen increased by about 1% between 400 and 550 K, mainly around 500 K, due to an increase in CSRO, and then decreased strongly above 600 K due to an increase in TSRO. For CSRO, the representative value of the activation energy E was reported to be 1.86 eV.[2] To the strong decrease in R corresponding with TSRO, the Johnson-Mehl-Avrami (JMA) analysis[4] was applied for $Y(t)$ $= [R_a - R(t)]/(R_a - R_c)$ using

$$Y(t) = 1 - \exp[-(Kt)^n], \qquad (1)$$

where K is the rate constant $K_0 \exp(-E/kT)$, t is the elapsed time, and k the Boltzmann constant. R_a and R_c denote R at T for the amorphous state and that for the crystallized state, respectively. For a-CuTi, the JMA exponent n and E were reported to be 3.0 and 2.1 eV, respectively.[3] Further, it was reported that after annealing just below the crystallization temperature a-$Cu_{59}Zr_{41}$ specimens became very brittle but showed no x-ray-diffraction peak from crystalline phase.[5] In the present work, we found that passing low current i to a-CuTi specimens at and below 413 K induced a strong decrease in R and an embrittlement, i.e., an intensive increase in TSRO was induced by i. This paper is the first report on this surprising

effect of i.

Specimens were cut from a-$Cu_{50}Ti_{50}$ ribbons prepared by the melt spinning method, and mechanically polished in water to remove the surface layer by a few μm avoiding heatup during polishing. During this polishing, a pickup of hydrogen into the specimen, in general far below 0.1 at.%, may be expected.[6] Therefore the effect of hydrogen was separately investigated, and hydrogen possibly picked up into the specimen was found to have a negligible effect on the present data. For R measurements, four thin copper wires were attached onto the specimen surface. The specimen size was 20–30 μm thick, 1–2 mm wide, and the gage length between potential leads was about 10 mm. The specimen with lead wires was set into an electric furnace and annealed at 423 K for 3 h for controlling the initial condition. During this annealing R was monitored with $i = 0.01$ A, and it increased by about 1%, due to an increase in CSRO.[3] Starting from this initial state, R measurements against time t were made for various i's with i kept constant and with the same polarity of i. These measurements were made at 413, 373, and 293 K, where the specimen temperatures were controlled within the accuracy of ± 0.03 K. The i's used here were mostly around $i = 0.5$ A, where immediately after i was increased, the specimen temperature showed a transient increase by about 5 K due to the Joule heat. However, by adjusting the furnace temperature, the specimen temperature decreased to the controlled temperature in a few minutes. It is noted that the specimen temperature during this transient increase has never exceeded 423 K. These annealing and R measurements were carried out in the air. It is noted that both specimens annealed in the air and those in vacuum of 10^{-4} Pa showed the same results for subsequent R measurements, indicating no effect of surface oxidation on the present results.

At and below 413 K, R of the specimens previously annealed at 423 K remained constant against t when i stayed at 0.01 A. In contrast, when i was increased beyond a

threshold value mentioned later, R showed a dramatic decrease (the R decrease). Figure 1 shows an example for the R decrease observed at 413 K with $i = 0.5$ A, where i was kept constant during measurements. $i = 0.5$ A corresponded with the current density i_d of roughly 1600 A/cm^2 and ϵ_0 of 0.60 V/cm. ϵ_0 denotes the electric field ϵ observed just after i was increased to 0.5 A, where ϵ is the potential difference $V_s = iR$ divided by the gauge length. Since the measuring accuracy of the gauge length between potential leads was much better than that of the cross-sectional area of the specimen, ϵ_0 will be used in preference of i_d in the following. Immediately after i was increased, R showed a small and transient increase of the order of 0.1% (not shown here, but see Fig. 3) at first. As already mentioned, just after i was increased, the specimen temperature showed a transient increase for a few minutes. A change in R due to this transient temperature increase was estimated to be about -0.03% reflecting the negative temperature coefficient of R in the present temperature range. Therefore, this small and transient increase in R was surmised to correspond with an increase in CSRO. In Fig. 1, R_0 is a maximum value of R attained during this small increase. After this increase, R decreased following a curve typical for isothermal transformation as shown in the figure. This R decrease will be discussed in Fig. 4. The saturation value R_∞ was estimated to be $R_\infty/R_0 = 0.58$ for Fig. 1. All these features mentioned above were commonly observed for various specimens except that the value of R_∞/R_0 varied in the range between about 0.6 and 0.8. Furthermore, after the R decrease was completed the specimen became very brittle but the x-ray diffraction indicated no spot from crystalline phase. To compare with embrittlement due to thermal annealings, as-prepared specimens were separately annealed in vacuum of 10^{-4} Pa at elevated temperatures. After annealing at about 630 K for 3 h where a strong decrease in R was expected,[3] the specimen became very brittle, but the specimens annealed at lower temperatures
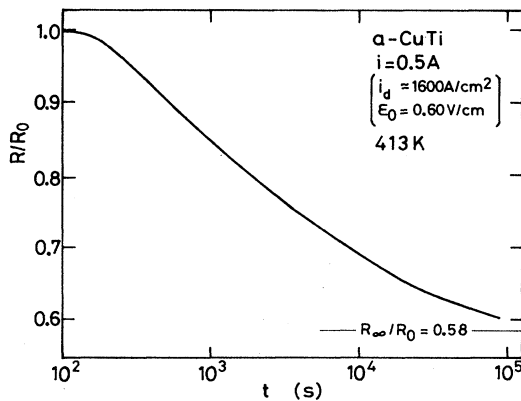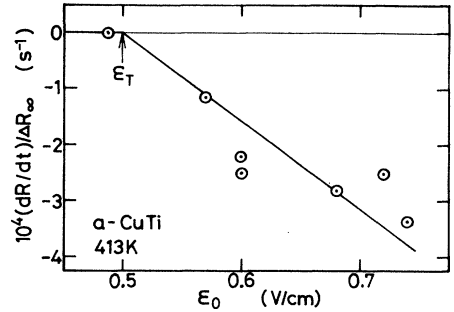

FIG. 2. The electric field (ϵ_0) dependence of the rate of change in electrical resistance $(dR/dt)/\Delta R_\infty$ at 413 K observed on seven a-Cu$_{50}$Ti$_{50}$ specimens. Here, dR/dt was evaluated at $t = (2-3) \times 10^2$ s. ΔR_∞ denotes the saturation value of the change in R.

were less brittle. These results suggest that the R decrease and embrittlement induced by ϵ at 413 K are associated with an increase in TSRO.

This surprising effect of ϵ was, however, observed only when ϵ was increased beyond the threshold ϵ_T. However, once ϵ was increased beyond ϵ_T, R continued to decrease even when ϵ became smaller than ϵ_T (note that the measurements were made at constant i). In Fig. 2, the normalized rate of change in R, $(dR/dt)/\Delta R_\infty$, was plotted against ϵ_0 where dR/dT was evaluated at $t = (2-3) \times 10^2$ s. It can be seen that the threshold ϵ_T is 0.5 V/cm at 413 K which corresponds with the threshold $(i_d)_T \doteq 1500$ A/cm^2, and with increasing ϵ_0 above ϵ_T, the decreasing rate of R at early time increases but R_∞ remains unchanged (which is not shown here). In Fig. 3, dR/dt vs ϵ_0 measured during stepwise increase in ϵ_0 are shown for two specimens at 413 K and one specimen at 373 K. Here, i was kept constant for several hundred seconds at each step of ϵ_0 and $(dR/dt)/R$ was evaluated just after i was increased for increasing $R(\epsilon_0 < \epsilon_T)$ and at $(2-3) \times 10^2$ s after i was increased for decreasing $R(\epsilon_0 > \epsilon_T)$. It can be seen that ϵ_T is about 0.5 V/cm at 413 K and about 0.7
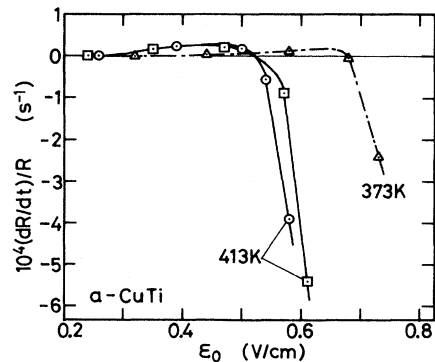

FIG. 1. An example of the observed result of a decrease in the electrical resistance R of an a-Cu$_{50}$Ti$_{50}$ specimen induced by passing dc current i at 413 K. i was kept constant at 0.5 A, which correspond with the current density i_d of about 1600 A/cm^2 and the electric field (ϵ_0) of 0.60 V/cm at $t = 0$. t denotes the elapsed time after the application of $i = 0.5$ A.

FIG. 3. Similar to Fig. 2, here we plot $(dR/dt)/R$ measured during stepwise increase in ϵ_0 for two a-Cu$_{50}$Ti$_{50}$ specimens at 413 K and one specimen at 373 K. i was kept constant for several 10^2 s at each step of ϵ_0 and dR/dt was evaluated just after i was increased for increasing R and at $(2-3) \times 10^2$ s after i was increased for decreasing R.

V/cm at 373 K, respectively. At 293 K, no change in R was observed in the present range of ϵ_0 (not shown here). These results suggest that ϵ_T increases with decreasing temperature. Further, the change in R observed with increasing ϵ_0 appears similar to that observed with elevating temperature,[2,3] so that it can be suggested that the increase in ϵ_0 decreases E in K in Eq. (1).

The stronger ϵ_0 dependence of dR/dt in Fig. 3 compared with that in Fig. 2 seen at ϵ_0 above ϵ_T for 413 K is due to the following fact: At ϵ_0 above ϵ_T, R decreases during measurements at each step in Fig. 3, therefore i_d used in Fig. 3 is larger than that in Fig. 2, if it is compared at the same ϵ_0.

TSRO in a-CuTi due to thermal annealing is known to proceed mainly above 600 K with $E = 2.1$ eV.[3] The present results indicate that the process of TSRO in a-CuTi was strongly accelerated by applying ϵ. The current theory of the electromigration mechanism[6] predicts acceleration of atomic diffusion by ϵ. In this case, the rate constant K may be given by

$$K = K_0 \exp[-(E - A\epsilon)/kT] , \tag{2}$$

where A is a proportional constant measuring the effect of ϵ on E. Then, with $E = 2.1$ eV and the assumption that K at a given $(dR/dt)/R$ is the same for two temperatures in Fig. 3, A can be estimated to be about 0.8 eV/(V/cm). In contrast, the conventional electromigration mechanism predicts A of the order of 10^{-8} eV/(V/cm) which is too small to compare with the present value of A. On the other hand, since hydrogen contained in a-CuTi is mobile above room temperatures,[7] transport of hydrogen under ϵ might be expected. For an effect of hydrogen, we observed the following: Precharging of hydrogen by about 2 at.% caused a small decrease in ϵ_T by about 0.1 V/cm at 413 K, but hydrogen charging by about 2 at.% during the R decrease did not change the time dependence of the R decrease. Therefore, one can say that for the present specimens without hydrogen charging, the effect of hydrogen is negligible. It was further observed that alternation of the polarity of ϵ during the R decrease did not change the subsequent time dependence of the R decrease. This fact suggests that a preferential transport of specific atoms under ϵ is not the case here. All of these results indicate that the usual electromigration mechanism cannot explain the present results.

As already mentioned, we observed a good similarity between the present effect of ϵ and the reported effect of temperature. Then one can expect that the present R decrease can also be described by Eq. (1). In Fig. 4 curve 1 shows the JMA plot of the results shown in Fig. 1. The JMA exponent reported for the decrease in R above 600 K is 3.0.[3] On the other hand, the tangent of curve 1 gradually decreases from 4 at $t \sim 150$ s to 0.4 at $t > 2500$ s. This result probably reflects the fact that the decreasing rate of R became slower and slower at later t because of decreasing ϵ (note that i was kept constant). To take into account this fact, we assume that the rate constant K can be described by Eq. (2). For a three-dimensional nucleation and growth process, the JMA model[4] predicts the following general relation:
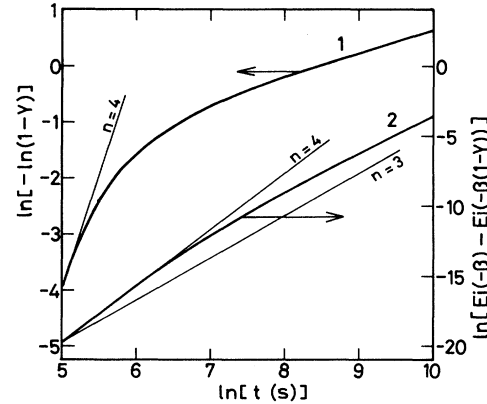
$$Y = 1 - \exp(-K't^n) , \tag{3}$$

FIG. 4. Curve 1 shows the JMA plot using Eq. (1) for the results shown in Fig. 1. Curve 2 shows the modified JMA plot using Eq. (5′) for the same data (see text for details).

where $3 \leq n \leq 4$. In the later stage of the process where all nucleation centers were exhausted, Eq. (3) becomes equivalent to Eq. (1) with $n = 3$ and $K' = K^3$. In the early stage where the nucleation rate is effectively constant, the nucleation rate is involved in K' and n becomes 4. For the sake of simplicity, we apply Eq. (1) to the present results at first. Then one has the following relation:

$$dY/dt = nK^n(1 - Y)t^{n-1} , \tag{4}$$

where K is given in Eq. (2). Using $Y = (\epsilon - \epsilon_0)/(\epsilon_\infty - \epsilon_0)$ where ϵ_∞ is ϵ at $t = \infty$, integration of Eq. (4) gives

$$Ei(-\beta) - Ei[-\beta(1 - Y)] = at^n , \tag{5}$$

or

$$\ln\{Ei(-\beta) - Ei[-\beta(1 - Y)]\} = \ln a + n \ln t , \tag{5'}$$

where

$$Ei(-x) = -\int_x^\infty z^{-1}\exp(-z)dz ,$$

$a = \{K_0\exp[-(E - A\epsilon_\infty)/kT]\}^n$, $\beta = nA(\epsilon_0 - \epsilon_\infty)/kT$. For the data in Fig. 1, values of $\ln\{Ei(-\beta) - Ei[-\beta(1 - Y)]\}$ calculated assuming $n = 3$ and $A = 0.8$ eV/(V/cm) are plotted against $\ln t$, with the results shown by curve 2 in Fig. 4. The slope of the later part of curve 2 gives $n = 3$ which is consistent with Eq. (5′). Further, the slope of the early part of the curve tends to $n = 4$ which is also consistent with the JMA model. Therefore, the TSRO process under ϵ can be said to be in good general agreement with the JMA model for a three-dimensional nucleation and growth process.

Now we can say that the application of ϵ caused the strong decrease in the effective activation energy by about 0.8 eV/(V/cm), for the TSRO process in a-CuTi specimens. In order to explain this anomalous decrease in the effective activation energy, the usual electromigration mechanism requires a local concentration of the electromigration force of atoms of the order of 10^8 onto one atom. For amorphous alloys, the free volume model of the glass transition[8] predicts the existence of clusters of liquidlike cells[9] even below the glass transition tempera-

ture. However, the number of atoms in such a cluster is considered to be too small to compare with 10^8. To clarify the underlying mechanism, further investigation is now in progress.

In conclusion, we found that passing current which corresponds with applying low electric field ϵ of 0.5 V/cm to a-$Cu_{50}Ti_{50}$ specimens caused the dramatic decrease in the effective activation energy, 0.8 eV/(V/cm), for the TSRO process which can occur for thermal annealings above 600 K with $E = 2.1$ eV. This dramatic effect of ϵ on the TSRO process cannot be explained by the usual electromigration.

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