Observation of transitionlike behavior and a slow thermal relaxation process in icosahedral quasicrystals

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Thermal relaxation effects on AlPdRe icosahedral quasicrystal samples quenched from high temperature have been studied. A systematic and rapid increase in electrical resistivity versus annealing temperature is seen below 700° C, near which an abrupt change in reversibility behavior is also observed, while the samples retain the *i*-phase structure. Samples quenched from above 700 °C show relaxation time constants many orders of magnitude larger than those for metallic glasses. The unusual features observed are ascribed to the possibility of a structural transition in AlPdRe *i* alloys.

I. INTRODUCTION

Recently, we reported[1] surprisingly large annealing effects on the transport properties of AlPdRe icosahedral (i) alloys, namely the high-temperature annealed *i* alloys became much more insulating upon further annealing at lower temperatures of 600–700 °C. The low-T resistivity, $\rho(0.45\ \mathrm{K})$, increased from 1 to 10 Ω cm. The large increase of ρ upon annealing indicates the presence of significant thermal relaxation effects in *i* alloys. For many years, thermal relaxation effects in metallic glasses have been studied extensively by measuring properties such as resistivity, superconducting transition temperature, thermal conductivity, and Curie temperature,[2] in an effort to reveal the microscopic nature of relaxation. The latter is ascribed to atomic ordering.[3] Structural transformation in quasicrystals (QC) is intriguing in its own right in view of the unique quasicrystalline structure. Although several investigations of structural transformation in *i*-AlCuFe have been carried out, the interpretations of these measurements are still being debated.[4] Realizing that the large thermal effect on resistivity of *i*-AlPdRe alloys may help to shed light on the nature of structural transition in *i*-QC, we conducted detailed studies of thermal relaxation effects in AlPdRe *i* alloys using resistivity as a very sensitive probe. We also investigated the reversibility of these relaxation effects between pairs of temperatures. The rapid change in ρ upon relaxation and the unusual thermal cycling behavior of samples give signatures of a phase transition around 700 °C, while the macroscopic structure remains *i* phase, as shown by x-ray-diffraction studies.[4] The thermal relaxation effects measured will be compared to those previously seen in metallic glasses. Plausible scenarios to account for the new features will be discussed.

II. EXPERIMENTAL PROCEDURE

Ingots of $Al_{70.5}Pd_{21}Re_{8.5}$ were made by melting appropriate combinations and quantities of high-purity elements sequentially in an arc furnace, under argon atmosphere. The procedure was carried out to maximize ingot homogeneity in alloying aluminum with high melting point refractory metals. Alloyed ingots were then annealed under a highly purified condition at 950 °C for 12 h to produce single *i*-phase samples. Samples cut from annealed ingots that showed high resistivity ratios $\rho(4.2\ \mathrm{K})/\rho(295\ \mathrm{K}) \sim 30$ were used in the thermal relaxation study. About 100 quality samples were collected. In order to yield reproducible results from annealing studies that involve multistep heat treatments, it is imperative that samples of comparable high quality be used. Samples were annealed in evacuated small quartz tubes to ensure rapid rise to the desired temperatures ($\sim$2 min; Ref. 5). At the end of each heat treatment, samples were rapidly quenched in chilled water. X-ray diffraction was performed using a SCINTAG diffractometer with a resolution of $<0.13°$ (Cu Kα). Resistivity measurements were carried out using a four-lead probe. The first series of isothermal annealing was performed on 950 °C annealed samples and $\rho(T)$ was measured. Experiments were repeated on samples "equilibrated" at 800 °C and 700 °C.

III. RESULTS AND DISCUSSION

A. Organization of data

In view of the multistep annealing process involved, we need to introduce parameters to label samples for their various thermal states. In order to minimize the effect of uncertainty in the value of ρ, the resistivity ratio given by $\bar{\rho}=\rho(4.2\ \mathrm{K})/\rho(295\ \mathrm{K})$ is used to characterize samples. Values of $\rho(295\ \mathrm{K})$ are given in Table I. The isothermal annealing temperature is denoted by T_a, annealing time by t, and the temperature at which samples are equilibrated prior to isothermal annealing by T_i. $\bar{\rho}$ then depends on T_i and T_a as well as implicitly on t and is written as $\bar{\rho}(T_i,T_a)$, and $\bar{\rho}(T_i)$ represents the value before isothermal annealing. Finally, the apparent maximum of $\bar{\rho}$ obtained from the isothermal curve of $\bar{\rho}$ versus t at given T_i and T_a is denoted by $\bar{\rho}^{\max}(T_i,T_a)$. For clarity, Fig. 1 only shows data taken at $T_a=600$ °C and 650 °C for samples treated at three T_i's in the form $[\bar{\rho}(T_i,T_a)-\bar{\rho}(T_i)]/\bar{\rho}(T_i)$ versus $\ln t$. Values of $\bar{\rho}(T_i)$ are given in Table I. Reasons for making isothermal annealing stud-

TABLE I. T_i is the temperature at which samples were "equilibrated" prior to the annealing study. $\bar{\rho}(T_i)$ represents the value of ρ (4.2 K)/ρ(295 K) for samples equilibrated at T_i before isothermal annealing. $\bar{\rho}^{\max}(T_i, 600\,^\circ\mathrm{C})$ is the maximum value obtained from isotherm (T_i, 600 °C), as explained in more detail in the section on data organization. There is an estimated ±10% deviation in the value of relaxation time constant τ_0 and activation energy E_0 due to the uncertainty of the exact annealing time in the furnace and the slight variation of sample quality.

T_i	ρ (295 K) (mΩ cm)	$\bar{\rho}(T_i)$	$\bar{\rho}^{\max}$ (T_i, 600 °C)	τ_0 (sec)	E_0 (eV)
950 °C	12±2.5	~30	~110	$\sim 1\times10^{-3}$	~1.1
800 °C	14±4.0	~35	~110	$\sim 5\times10^{-5}$	~1.4
700 °C	16±4.0	~60	~110	$\sim 3\times10^{-8}$	~1.9

ies on samples treated at various T_i's will become clear later.

B. Key findings

Several trends in $\bar{\rho}(T_i, T_a)$ are noted. It is seen that $\bar{\rho}$ increases with annealing time t, and its "saturation value" $\bar{\rho}^{\max}(T_i, T_a)$ increases as T_a decreases. Such enormous increase in $\bar{\rho}$, or more distinctly in the value of ρ(4.2 k) that reaches 2 Ω cm upon annealing, has not been previously reported for quasicrystals. Figure 2 sums up one of the trends and shows the rather rapid increase in $\bar{\rho}^{\max}(T_i, T_a)$ below T_i. We also observed $\bar{\rho}^{\max}$ decrease below $\bar{\rho}(T_i)$ for $T_a > T_i$, consistent with the trend. Values of $\bar{\rho}^{\max}$ (T_i, 600 °C) are listed in Table I. However, it is noted that a rapid rise in $\bar{\rho}^{\max}$ (950 °C, T_a) and $\bar{\rho}^{\max}$(800 °C, T_a) occurs at $T_a < 700\,^\circ\mathrm{C}$, much below T_i. Thus for all samples the mechanism of thermal relaxation is most effective below ~700 °C. Another distinct trend noticed is that the annealing time needed to reach $\bar{\rho}^{\max}(T_a)$ decreases as T_i decreases (Fig. 1). It is important to point out that all the thermal-resistivity features reported here were reproducible on a large number of samples whose $\bar{\rho}$(950 °C) values vary over a range of ~20%, the minimum variation one can practically achieve with these i alloys. In spite of the large increase in resistivity observed upon thermal relaxation at decreasing temperature, x-ray-diffraction measurements on samples show no apparent change in shape for all the diffraction peaks as a function of T_a. The apparent absence of peak broadening or splitting in the low-resolution x-ray-diffraction pattern for a sample annealed at 600 °C contrasts sharply with observations on i-AlCuFe,[4] especially for the three low-angle peaks as shown in the inset of Fig. 2. In short, AlPdRe appears to retain its i-phase structure at low temperature, and any structural change that has taken place must have been subtle. Further assessment of i-phase structure over a wide temperature range awaits high-resolution x-ray-diffraction measurement.

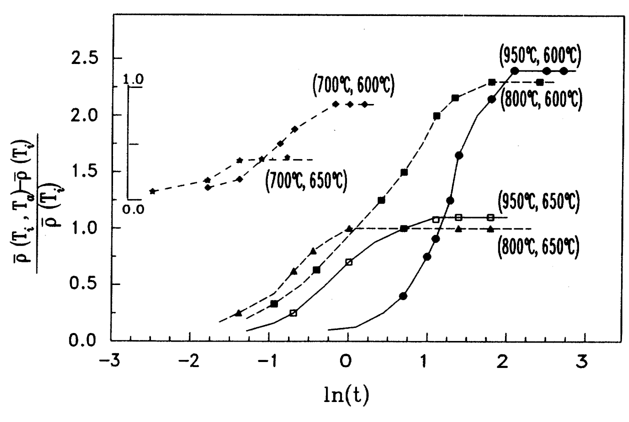

FIG. 1. Isothermal data at $T_a = 600\,^\circ\mathrm{C}$ and 650 °C for samples first equilibrated at three T_i's in the form of $[\bar{\rho}(T_i, T_a) - \bar{\rho}(T_i)]/\bar{\rho}(T_i)$ vs ln$t$, with t in units of h. $T_i = 700\,^\circ\mathrm{C}$ data is plotted with a different y scale for clarity. Thermal history each isotherm is labeled as (T_i, T_a). Lines are drawn as guides for the eye.

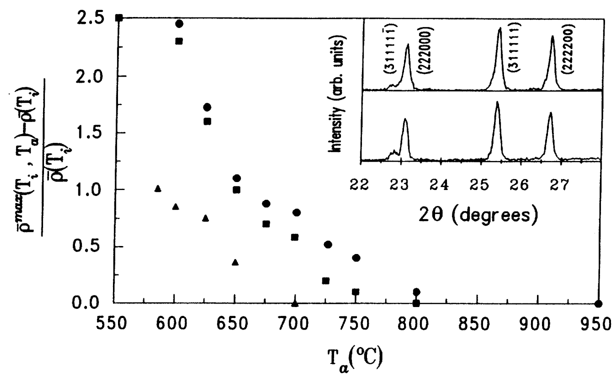

FIG. 2. Dependence of "saturation value" $\bar{\rho}^{\max}$ on annealing temperature T_a for samples equilibrated at 950 °C (●), 800 °C (■), 700 °C (▲), plotted in the form of $[\bar{\rho}^{\max}(T_i, T_a) - \bar{\rho}(T_i)]/\bar{\rho}(T_i)$ vs T_a. The inset shows x-ray-diffraction pattern for a sample annealed at 940 °C (lower pattern) and with additional annealing at 600 °C for 2 h (upper pattern). The trend of x-ray pattern is described in text. Peaks are labeled by 6 D index, as explained in Ref. 1.

It is plausible that the thermal effects on resistivity seen here are due to some kind of subtle structural change in the i phase, while the quasicrystallinity remains unchanged. To shed light on the structure-property states of i-AlPdRe, we have studied effects of thermal cycling on these states. Similar experiments on metallic glasses (MG) are well documented.[2,3] In MG, reversible cycling effect in electrical resistivity was attributed to reversible change in chemical short-range order (CSRO), and irreversible effect was ascribed to the relaxation of defects or free volume which led to irreversible change in topological short-range order (TSRO). Our studies were carried out on samples initially equilibrated at 800°C followed by cyclic annealing between two T_a's (labeled as T_{a1}, T_{a2}). The $\bar{\rho}^{\max}$ from the isothermal curve at each T_a was attained during the cycling. Two kinds of behaviors were seen as illustrated in Fig. 3, namely, reversible relaxation with $\bar{\rho}^{\max}$ similar to those obtained in regular isothermal annealing, and irreversible relaxation with $\bar{\rho}_{\max}$

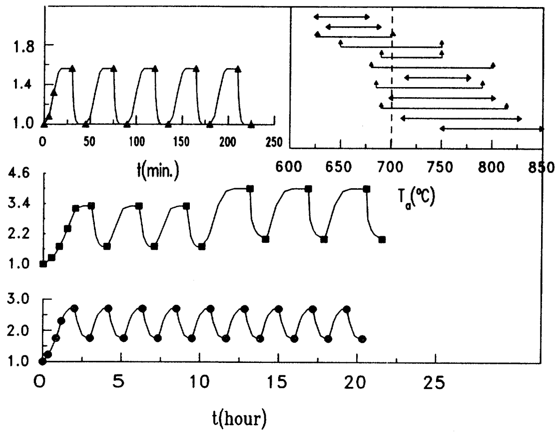

FIG. 3. Observation of reversible relaxation between $T_{a1}=700\,°C$, $T_{a2}=800\,°C$ (▲); $T_{a1}=625\,°C$, $T_{a2}=675\,°C$ (●), and irreversible relaxation (■) between $T_{a1}=625\,°C$ and $T_{a2}=700\,°C$. The inset summarizes results of cycling experiments for 12 pairs of T_a's, with reversible change (↔) and irreversible change and irreversible change (↑——↑) symbolized.

exceeding those obtained in regular isothermal annealing. A summary of thermal cycling experiments for twelve pairs of T_a's is given in the inset of Fig. 3, with those exhibiting reversible and irreversible change symbolized. It is seen that reversible change is observed only when both T_{a1} and T_{a2} lie above or below a narrow temperature region ($\sim 10\,°C$) near 700 °C, while irreversible change is only seen when samples are thermally cycled across 700°C, while irreversible change is only seen when samples are thermally cycled across 700 °C. Although the reversible behavior within each of the two temperature regions bordering near 700 °C resembles that reported for MG,[2,3] the enormous change in resistivity due to thermal relaxation and the partition of reversible regions by a well defined temperature across which irreversibility in thermal cycling occurs have not been seen in MG. We should stress that the isothermal annealing (Figs. 1 and 2) and thermal cycling (Fig. 3) results reported are very prominent and they are not due to extraneous effects. Precipitation of impurity phase(s) in *i*-alloy samples will tend to decrease their resistivity.[6] On the other hand, the polycrystalline nature of *i*-phase samples was found to have no observable effects on transport properties.[7,8]

C. Some plausible explanation of results

We first analyze our results from isothermal annealing. Based on previous experiments,[7,8] we assert that $\bar{\rho}$ increases with improved structural order of the quasicrystal. Thus the various dependencies of $\bar{\rho}$ on T_a and T_i reflect changes in the structural order of *i*-AlPdRe. In the absence of models on thermal relaxation in quasicrystals, a simple Arrhenius-type analysis adopted from activation energy models applied to metallic glasses[2,5] will be used. The analysis, in spite of its simplicity, has been of considerable value in obtaining kinetic parameters such as the characteristic energy of an activation energy spectrum and relaxation time constant from isothermal curves. Isotherms for the $T_i=800\,°C$ and 950 °C samples shown in Fig. 1 clearly do not follow. *T*ln*t* dependence, suggesting there are at least two structural relaxation processes. To feature the influence of slow relaxation in the high-T_i samples, it suffices to take a simple approach, rather than one that involves many fitting parameters. Here, we assume that $\tau(T_i,T_a)$ [half time defined at half of $\bar{\rho}^{\max}$-$\bar{\rho}(T_i)$ at each T_i,T_a] follows the simple activation energy model, $\tau=\tau_0 \exp[E_0/K_BT_a]$. Activation energy E_0 and time constant τ_0 for each T_i were obtained by plotting $\ln\tau(T_i,T_a)$ versus $1/T_a$, as shown in Fig. 4. Values of E_0 and τ_0 are given in Table I. It is seen that values of τ_0 for the $T_i=800\,°C$ and 950 °C samples are orders of magnitude larger than 10^{-8}–10^{-14} sec commonly seen in MG, and E_0 for the $T_i=950\,°C$ samples is lower than the 2–3 eV reported for the same materials.[2] In contrast, results for the $T_i\equiv 700\,°C$ samples are close to conventional values of MG. The disparity in kinetic behavior may be ascribed to the slow relaxation process inherent to the *i*-phase structure, quenched in from above 700 °C, the onset temperature of irreversible relaxation.

Based on experimental facts, but in lieu of models of structural relaxation for quasicrystals, one can only discuss possible scenarios that may account for the unusual features observed. Accepting the assertion that resistivity increases with improved structural order, it is clear from Fig. 2 that structural order is enhanced precipitously below 700 °C. Reversible change in the two temperature regions bordering 700 °C reflects reversible change in structural order within each of the two regions. Meanwhile, the onset of irreversibility upon cycling across 700 °C suggests an abrupt change in the nature of reversible structural order between the two regions. Structural order in *i* alloys, which includes long-range quasilattice (QL) order and chemical order, are far from being perfect even in those *i* alloys that exhibit single-crystal quality x-ray-diffraction patterns.[9] Drawing an analogy with the much discussed CSRO and TSRO effects in MG, which involve only short-range order, the reversible change in *i* alloys may be attributed to chemical order, or CSRO effect in MG, and irreversible change to configurational reshuffling of QL, or TSRO effect in MG. However, a clear distinction between the two sys-

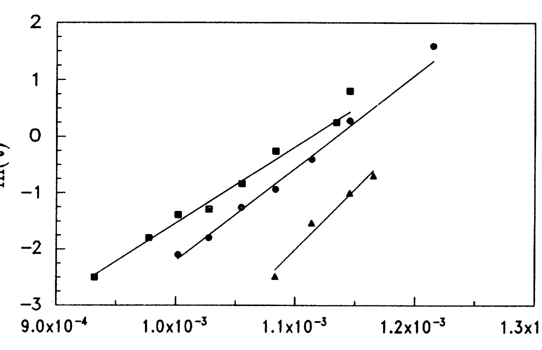

FIG. 4. ln τ vs $1/T_a$ (τ in units of h), for samples equilibrated at $T_i=950\,°C$ (■), 800 °C (●), 700 °C (▲). Activation energy E_0 and characteristic time constant τ_0 are given in Table I.

tems must be noted, that is, continuous structural change can account for the results in MG, but not those underlined for *i* alloys. To interpret the nonmetallic-glasslike irreversible change which only occurs when samples are thermally cycled across a well defined temperature region around $T = 700\,^{\circ}\mathrm{C}$, one may refer to the existing quasicrystal models. Several models have discussed the possibility of transition in QL order[10,11] between a perfect-tiling ground state, which is phason locked, and a random-tiling excited state, which is phason unlinked, at T_c. One of the models predicts a nonzero T_c for the three-dimensional (3D) QL.[11] In *i* alloys, the extent of perfect-tiling order below T_c will be restricted by the degree of chemical order, and only chemical order can continue to improve in the phason-locked state. Heating this ordered structure above T_c to allow it to reshuffle in the phason-unlocked state, a structure which is less disordered than that quenched from the same high temperature will develop. If one now returns this more ordered high-temperature phase to below T_c, one should obtain an *i* structure which is now more ordered than previously at the same low temperature. Clearly, this procedure of enhancing structural order upon repeated thermal cycling across $700\,^{\circ}\mathrm{C}$, if this temperature is taken to be T_c, would result in an irreversible effect. As for the reversible effects seen in the partitioned regions, they can be ascribed to reversible chemical order, possibly also reversible QL order in the phason-unlocked state above T_c. The trend of kinetic parameters derived from isotherms (Table I) is also in accord with the notion of a QL phase transition. For the high $T_i(>T_c)$ samples, the long time constant can be explained by slow phason diffusion[12] and the small activation energy by a low excitation barrier for phasons,[13] manifested while equilibrating from their "as-quenched" metastable states. In comparison, the $T_i = 700\,^{\circ}\mathrm{C}$ samples reveal mostly chemical ordering effects, which produce metallic-glasslike parameters.

In closing, it is suggested that chemical ordering and structural transition may also be seen in other ordered *i* phases, however, their relatively small resistivities have rendered thermal relaxation features much less robust for detection.

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