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E. Balanzat, C. Mairy, J. Hillairet. QUENCHED-IN RESISTIVITY IN RELATION TO ATOMIC MOVEMENTS IN AMORPHOUS Fe₄₀Ni₄₀P₁₄B₆ AND Cu₅₀Ti₅₀. Journal de Physique Colloques, 1980, 41 (C8), pp.C8-871-C8-874. 10.1051/jphyscol:19808215 . jpa-00220321

HAL Id: jpa-00220321

<https://hal.science/jpa-00220321>

Submitted on 4 Feb 2008

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QUENCHED-IN RESISTIVITY IN RELATION TO ATOMIC MOVEMENTS IN AMORPHOUS
 $\text{Fe}_{40}\text{Ni}_{40}\text{P}_{14}\text{B}_6$ AND $\text{Cu}_{50}\text{Ti}_{50}$

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A reversible process has been evidenced recently with the help of electrical resistivity studies conducted in an amorphous $\text{Fe}_{40}\text{Ni}_{40}\text{P}_{14}\text{B}_6$ alloy cycled thermally at subcrystallization temperatures in the range 220°C to 380°C (Balanzat 1980). The present paper is intended at a presentation of the detailed features of the relevant resistivity variations as measured at liquid helium temperatures, after repeated heating and quench cycles. The Metglas alloy under consideration was chosen despite its complex chemical composition partly for experimental convenience and also because the annealing behaviour of its magnetic properties has been the object of extensive studies in the last few years. In particular, Hall resistivity measurements and magnetic anisotropy experiments have shown a similarly reversible effect to occur for both the Curie temperature and the field induced magnetic anisotropy in a series of FeNi base alloys of the same Metglas type (Egami 1978, Malmhäll 1979, Chambron 1980 a,b).

The presence of compositional short range order (CSRO) and its evolution with anneal temperature in terms of the pair ordering of the transition metal atoms have been postulated to explain the magnetic behaviour and the resistometric results as well. This assignment will be discussed together with the influence of topological short range order (TSRO). The possible role of the metalloid elements will be considered also. On the other hand, preliminary results obtained in a $\text{Cu}_{50}\text{Ti}_{50}$ alloy are given : they are part of a more general investigation into the properties of atomic ordering in metal-metal alloys.

Experimental

Ribbon samples 50 μm x 2 mm x 2 cm of amorphous $\text{Fe}_{40}\text{Ni}_{40}\text{P}_{14}\text{B}_6$ (Allied Chemical Metglas alloy 2826) obtained by melt spinning were studied. Specimens

for resistivity testing were made by spot welding two wire leads 2 cm apart from each other. A d.c. current was used to monitor the resistance changes. All measurements were carried out at 4.2 K. For the thermal treatments, the specimens were put in a cryostat surmounted with a furnace which was basically a heated block of aluminium with a slot. All the temperature cycles were conducted in the vapors emanating from a liquid helium bath under normal pressure. These cycles consisted of a 10 min. anneal at the selected temperature followed by a quench. Quenching was by lowering the specimen holder rapidly from the slot down into the cold gas. Initial cooling rates were about 500°C x sec⁻¹. Some tests were also conducted on melt-spun $\text{Cu}_{50}\text{Ti}_{50}$ samples.

Results

The specimens were first given a preanneal treatment for 30 min. at 320°C, that is about sixty degrees below crystallization. Fig. 1 shows the typical resistivity variations observed as a function of quenching temperature, for repeated quenches. Quench temperatures were varied sequentially from 320°C down to 135°C and back. In these conditions the data points lie on a straight line down to about 200°C. Below this temperature, a plateau occurs. The most striking feature of the results is that the data points for both up and down runs are, within experimental error, located on the same curve, which denotes a reversible effect. This suggests that an "equilibrium" was achieved in the time scale of the thermal cycles.

Complementary information was obtained by isochronal anneals after quenching. Fig. 2 shows the corresponding evolution spectras for the quenched-in resistivity. The observed features are the same whatever the quench temperature, 250°C or 320°C ;

the major result is that above a certain temperature the resistivity increases, that is tends towards the "equilibrium" value. The relevant kinetic parameters have been analyzed in some detail with the help of isothermal anneals. The results indicate that the

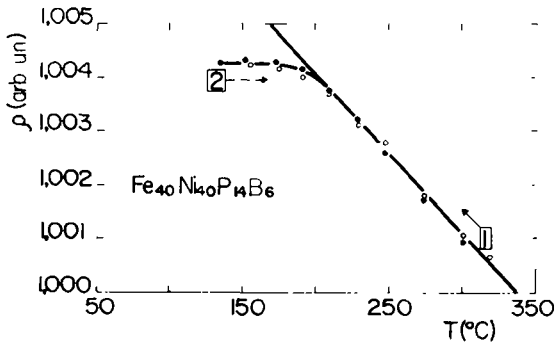


Fig. 1 - Quenched-in resistivity in $Fe_{40}Ni_{40}P_{14}B_6$ preannealed at $320^\circ C$.

1. o : first run, at decreasing temperatures
 2. ● : second run, at increasing temperatures
 The slope of the straight line is $5.6 \times 10^{-3} \mu\Omega cm (^{\circ}C)^{-1}$

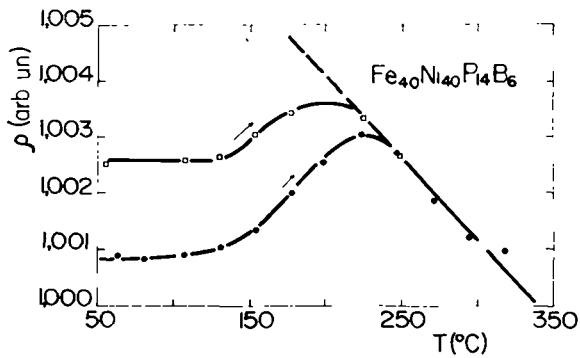


Fig. 2 - Isochronal resistivity curves in $Fe_{40}Ni_{40}P_{14}B_6$ for annealing sequences after quenching from $250^\circ C$ (□) and $320^\circ C$ (●).

evolution rate can be parametrized by two variables, the mean ordering rate and the ordering rate distribution width. The mean rate is well described by a Boltzmann expression, with a preexponential factor of $10^{14 \pm 1} \text{ sec}^{-1}$ and an activation energy of $1.6 \pm 0.1 \text{ eV}$ (Balanzat 1980).

A different series of experiments has been performed in as-received specimens to check whether such effects occur after the initial quench from the melt. Fig. 3a indicates unambiguously that the resistivity spectrum during the first heating sequen-

ce from ambient temperature up to crystallization is quite similar to those described above, with a pronounced maximum around $200^\circ C$. However the equilibrium line although its slope is unchanged, within experimental error, is progressively shifted downwards for anneal temperatures up to $350^\circ C$, then upwards until the vicinity of the crystallization temperature. Finally, the slope of the equilibrium line is significantly altered only at the start of crystallization and it falls to zero when crystallization is completed. The non-reversible resistivity decrease is plausibly assigned to structural relaxation while the sharp increase followed by a downturn at $380^\circ C$ are

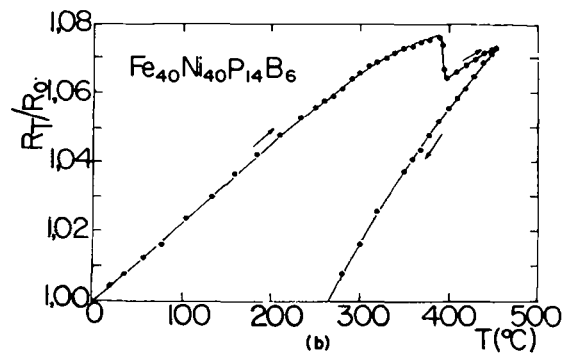
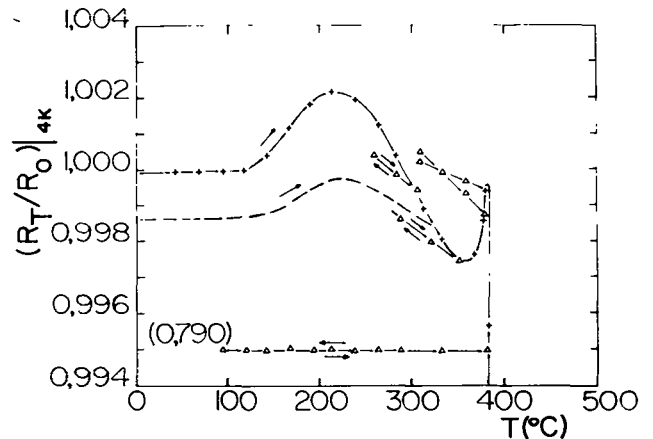


Fig. 3 - (a) Isochronal resistivity curve for a $Fe_{40}Ni_{40}P_{14}B_6$ specimen in the as-received condition. The isochronal anneal sequence at increasing temperatures was periodically stopped to examine whether reversibility was still present and to measure its specific contribution. The dashed line is just to recall and locate the evolution spectrum found in a preannealed specimen, Fig. 2.

(b) resistivity values as measured at the anneal temperature in a fresh specimen.

associated with incipient crystallization (Marcus 1979) and the steep descent is a reflection of the further progress of crystallization. Fig. 3b indicates the corresponding resistivity variations measured directly at the anneal temperature. It is interesting to mention that structural relaxation has been observed recently in the same alloy by Egami (1978) with use of energy dispersive X-ray diffraction. It is to be noted that the X-ray detect mainly the position of the metal atoms, not the metalloids, and that they do not discriminate between Fe and Ni.

The same experimental procedure was applied to a $\text{Cu}_{50}\text{Ti}_{50}$ in the melt-spun condition. Fig. 4 offers clear evidence of an identical behaviour as described for the Metglas alloy. Detailed description of the quench and anneal curves is superfluous, since all features correspond point to point to the ones in $\text{Fe}_{40}\text{Ni}_{40}\text{P}_{14}\text{B}_6$.

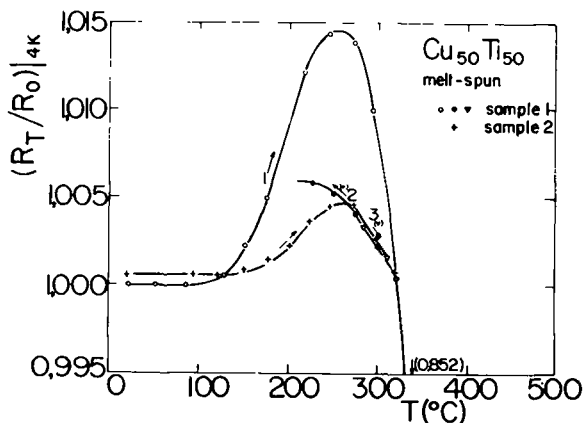


Fig. 4 - Evolution spectra for the quenched-in resistivity in a $\text{Cu}_{50}\text{Ti}_{50}$ specimen : (o) on heating from the as-received condition, (+) after a pre-anneal treatment at 321°C followed by a quench.

Discussion

1 - Separation between reversible and non-reversible quenched-in resistivities and assignment to CSRO and TSRO.

The resistivity results are quite informative about the atomic rearrangements which occur during thermal treatments and their relation to topological and/or compositional SRO. Consideration of the following experimental facts is used as a guide :

i) the isochronal value of the quenched-in electrical resistivity is not a monotonic function of annealing temperature (fig. 2). It is difficult to explain this feature in terms of TSRO only, since this would imply that the resistivity does not vary monotonically with structural relaxation.

ii) in fact, during the first heating sequence of specimens in the as-received condition, the isochronal recovery spectrum appears to result from the superimposition of two contributions, non-reversible and reversible (fig. 3,4). The latter is presumably associated with some type of CSRO.

iii) after a preannealing treatment at elevated but subcrystallization temperatures to achieve structural relaxation, only reversible effects are still occurring on thermal cycling, between 220°C and the preanneal temperature (fig. 1).

iv) interestingly enough, the temperature dependence of this reversible resistivity variation is, within the range studied up to 370°C , insensitive to the specimen history (fig. 3). This situation holds until a few degrees below the crystallization temperature. Thus it can be concluded that the corresponding short range ordering process is not dependent upon structural relaxation, that is upon TSRO.

These observations, together with the kinetic study which is discussed below, lead to the important conclusion that the reversible effect detected is due to CSRO. Along this line, the evolution pattern for the residual resistivity is satisfactorily accounted for by the following scheme : in the as-received condition, the amorphous alloy is strongly disordered and ordering is expected but it is delayed until 130°C , when the atomic mobility starts being significant. Resistivity increases as a result of the increasing degree of order. The kinetics of this evolution is controlled by atomic motion. Above 220°C , the ordering rate is sufficiently fast for the equilibrium state of order to be completed during the anneal. In this region up to the crystallization temperature both the CSRO and the associated resistivity vary reproducibly. The higher the temperature, the lower the degree of order and hence, the smaller the resistivity. Incidentally it is to be noted that, in crystalline alloys, the resistivity effect associated with disordering is

generally an increase, but effects of the opposite sign have been reported also on the basis of both theoretical and experimental considerations (Schulze 1972, Rossiter 1979). To our knowledge, no information exists in the open literature about this feature in amorphous alloys.

A further step in the understanding of the ordering process at an atomic level is the identification of the atom species involved in ordering. This point is discussed in the next section.

2 - Identification of the defect species involved in CSRO.

Interestingly, the measured preexponential factor and activation energy match to a first approximation those reported for the induced magnetic anisotropy in the same Metglas alloy (Chambron 1980.a), a result in agreement with the idea of a common underlying physical mechanism. We are inclined to think that both reversible effects, resistometric and magnetic, are linked to the motion of the metal atoms, although no straightforward argument exists at the moment. This problem has been discussed in some detail elsewhere (Chambron 1980a). It is recalled that Egami (1979) argued that the Curie temperature in the Metglas is determined primarily by the distribution of the Fe atoms to explain its reversibility on thermal cycling in terms of the local redistribution of the metal atoms. The analogy observed in the present work in the respective resistometric behaviour of a Metglas alloy and a metal-metal alloy also suggests that the relevant atomic rearrangements in the latter deal with pair ordering of the metal atoms, rather than with a redistribution of the metalloids.

As for the CuTi amorphous alloy studies, little doubt is left about the assignment of the reversible resistivity effect to compositional short range ordering. In particular, recent work based on neutron diffraction measurement of the structure factor of a $\text{Cu}_{66}\text{Ti}_{34}$ metallic glass has brought to evidence the existence of an intense 'prepeak' which has been associated with short range chemical ordering between copper and titanium atoms (Sakata 1979). More precisely, the value of the order parameter observed is found to be negative, in $\text{Cu}_{65}\text{Ti}_{34}$ and $\text{Cu}_{50}\text{Ti}_{50}$ as well, which indicates a preference for unlike neighbours. In addition, the degree of CSRO after the quench from the melt appears to lie

far from its theoretical maximum (Sakata, Cowlam and Davies, this Conf.). This means that more ordering is expected to occur on further annealing as soon as the atomic mobility becomes high enough. This brings further support to our interpretation of the resistivity stage in $\text{Cu}_{50}\text{Ti}_{50}$ in terms of chemical ordering. We hope to be able to make a detailed study of the relevant kinetic parameters and derive information about atom jump frequencies in this and other metal-metal alloys, in the near future.

Summary

We have used the resistivity quench method to study the changes in the atomic short range order upon annealing at subcrystallization temperatures. This method offers good accuracy and extended applicability to a variety of metallic glasses. A reversible thermally activated process is shown to occur in the alloys studied, $\text{Fe}_{40}\text{Ni}_{40}\text{P}_{14}\text{B}_6$ and $\text{Cu}_{50}\text{Ti}_{50}$. This is a reflection of a short range ordering process involving the component metal atoms. Further research is intended at the investigation of the nature and properties of the structural defects which are responsible for the corresponding atomic rearrangements.

Aknowledgements

The authors gratefully acknowledge Dr. H.U. Künzi (Institut für Physik, Basel), for the elaboration of the CuTi specimens.

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