Structural Relaxation and Chemical Decomposition in Amorphous TM–M Alloys

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Small angle X-ray scattering experiments performed on amorphous two-component transition metal-metalloid alloys have shown that these materials decompose on annealing clearly before crystallization starts. This process influences the behaviour of physical properties in a similar way as structural relaxation does. To separate the two effects mainly composition dependent properties must be compared with others which are mainly sensitive to structural changes. In this paper it is shown that the ratio of the annealing-induced changes of the temperature coefficient of the resistivity and of the residual resistivity is determined by the underlying elementary process. The two values resulting for predominating structural relaxation and for predominating decomposition seem to be universal and are compatible with a theory of phonon-controlled conductivity in high-resistance conductors.

Introduction

As was shown in previous papers [1, 2] in amorphous Co–P alloys structural relaxation is superposed by chemical decomposition prior to the onset of crystallization. This process was discovered with the aid of small angle X-ray scattering (SAX) after separation of the contribution of surface defects to the scattering intensities [1, 2]. Other authors observed phase separation in ternary and quaternary amorphous alloys [3–8]. The negative result reported by Wu and Spaepen [9] on Fe79.3B16.4Si4.3 may be due to the fact that their SAXS measurements ended at k≈0.7 nm−1 whereas in the case of the phosphorus alloys of iron, cobalt and nickel the relevant maximum appears in the range 1 nm−1<k<6 nm−1, Figs. 1 and 2.

Decomposition causes changes of physical properties but it is impossible to separate this effect from that due to structural relaxation solely on the basis of SAXS data. For this purpose we have to compare the behaviour of mainly composition dependent properties with that of mainly structure dependent properties. Some examples are presented in this paper. The electrical resistivity and its temperature coefficient are extensively discussed. Their annealing-induced changes are correlated in a characteristic manner which depends on the underlying process. Extended Ziman theories mostly applied to interpret transport properties in amorphous alloys are incompatible with the observations whereas a model regarding electron-phonon interaction yields quantitatively the just mentioned correlations.

Experimental

The material was electrodeposited onto well-polished copper plates which were chemically dissolved after preparation [10]. Composition and microstructure were varied by the composition of the electrolyte and the current density [11]. From the same original plate several samples were cut for small angle X-ray scattering (SAXS), for measurements of the electrical resistance and for chemical analysis.

SAXS experiments were performed with a Kratky camera and the Mo–Kα radiation of a tube working at 35 kV and 40 mA. The k-region under study ranged from 10−2 to 1.3 Å−1. Further experimental details and the procedure of data analysis are described in Ref. [1]. The amorphous state was checked with large angle X-ray scattering in a conventional goniometer or by measuring the magnetic coercivity [12].
The electrical resistance was detected applying an ac-Lock-In-technique on the four-point-method as has been described in Ref. [13]. The resolution was $10^{-5}$.

The samples were annealed in a small oven which included a sample chamber shaped as a narrow shaft. They were put into the pre-heated oven. As their heat capacities are small compared with that of the oven they reached the desired temperatures within only 5-10 s corresponding to a maximum heating rate of about 1,500 K/s. The heating period is so short that the effective starting point of an isothermal treatment could be found by extrapolating the experimental curves. This is not possible if an appreciable fraction of the relaxation has happened during the heating process [14]. Another advantage of the equipment was the high thermal stability of $\pm 0.1$ K during 3 days.

Results and Discussion

As our knowledges concerning decomposition have been derived from SAXS experiments at first the relevant results shall be summarized.

Results of SAXS

Figures 1 and 2 present the product of the corrected scattering intensities $i_c$ with the value $k$ of the scattering vector versus $k$ for two Co-P samples. They were both amorphous. As detailed in [1] the area below the curves, $\int_0^\infty i_c(k)kdk$, is proportional to $\Delta \rho^2$, which is the mean square of the electron density fluctuations. For a two-phase system it is given by

$$\Delta \rho^2 = V_1(1-V_1) \cdot \Delta \rho$$  \hspace{1cm} (1)

$\Delta \rho$ is the deviation of the electron density of the scattering centres from that of the matrix and $V_1$ the volume fraction filled by the scattering centres.

Real measurements are restricted to a limited $k$-range, $k_1 \leq k \leq k_2$. So we have to consider some assumptions concerning the contributions coming from the ranges below $k_1$ and above $k_2$. The high angle part could be estimated by extrapolating the measured intensity according to Porod's law [1].

$$i(k) = \frac{\mathcal{P}}{k^\alpha} + \bar{i}_b$$  \hspace{1cm} (2)

$\mathcal{P}$ is the Porod constant, $\bar{i}_b$ the background scattering intensity. Therefore

$$\bar{i}_c(k) = i(k) = \frac{\mathcal{P}}{k^\alpha} + \bar{i}_b$$  \hspace{1cm} (3)

and

$$\int_{k_2}^\infty i_c(k)kdk = -\frac{\mathcal{P}}{k_2}$$  \hspace{1cm} (4)

In the lowest angle regime below $k_1$ the scattering coming from irregularities on the surfaces of the samples superposes the intensity scattered by inhomogeneities in the bulk. The separation of the two contributions is not straightforward. Therefore we tried to