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EXAFS studies of intermediate crystallisation steps of amorphous Ni–Zr alloys

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Abstract. Metallic Ni–Zr glasses show characteristic exothermic processes during crystallisation as observed with differential scanning calorimetry (DSC). In the glassy alloy $\text{Ni}_{36.5}\text{Zr}_{63.5}$, after the first of the two exothermic reactions leading to complete crystallisation an intermediate amorphous stage is found. The x-ray absorption near-edge structure (XANES) and the extended x-ray absorption fine structure (EXAFS) of such an alloy are compared to those for the as-cast alloy and to those for an intermediate crystallisation step, an alloy with the nominal composition NiZr_2 .

1. Introduction

Metallic glasses are metastable and at sufficiently high temperatures they revert to the stable crystalline state via one or more exothermic reactions. Amorphous Ni–Zr glasses in the Zr-rich part of the phase diagram are produced by rapid quenching of the melt by melt spinning. In a previous paper (Frahm *et al* 1984b) the structural properties of the as-quenched alloys, as observed using x-ray absorption near-edge structure (XANES) and extended x-ray absorption fine structure (EXAFS), were described. The samples used in that work were heated in an apparatus for differential scanning calorimetry (DSC), and the DSC spectra, together with thermodynamic data on the alloys, are given by Frahm (1983). In the present work, data for $\text{Ni}_x\text{Zr}_{1-x}$ alloys with nominal compositions $x = 0.333$ and $x = 0.365$ —which have compositions as measured using an electron microprobe, x_{emp} , of 0.343 and 0.368, respectively—are presented. The DSC traces of both alloys show two exothermic processes, which are strongly overlapping in the $x = 0.333$ alloy but are well separated in the $x = 0.365$ case. If the latter alloy is quenched from a temperature between those at which the two exothermic peaks appear the material does not give sharp rings in the x-ray diffraction (Buschow *et al* 1981, Altounian *et al* 1983, McKamey *et al* 1986) and still remains ductile (Frahm 1983). The phase transformation leading to this intermediate crystallisation stage is accompanied by an increase in electrical resistance (Altounian *et al* 1983, Schulz *et al* 1984), but the details of the structural changes still remain unclear. For this reason EXAFS experiments have been performed, which probe the local environment of selected atoms in a mixture of several atomic

Table 1. (a) Structural parameters for the DSC-quenched alloys obtained from the Zr EXAFS data at 77 K (inter-atomic distance R , coordination number N , difference between the mean square displacements for the alloys and the pure elements $\Delta\sigma^2$). (b) The corresponding results obtained for the as-cast alloys (Frahm *et al* 1984b) are reproduced for ease of reference.

Neighbour	$x = 0.333$			$x = 0.365$		
	R (Å)	N	$\sqrt{\Delta\sigma^2}$ (Å)	R (Å)	N	$\sqrt{\Delta\sigma^2}$ (Å)
(a)						
Zr	3.22	12.55	0.177	3.21	5.97	0.114
Ni	2.66	2.25	0.094	2.63	1.81	0.064
(b)						
Zr	3.18	10.1	0.148	3.20	8.91	0.146
Ni	2.62	1.43	0.072	2.63	1.56	0.067

species. After the second exothermic DSC peak in the alloys the samples are crystalline and brittle. The EXAFS and XANES data for the crystallised materials have been presented by Frahm *et al* (1984a) together with a detailed description of the data reduction procedure—which has also been used for the present results. It is essentially based on the standard EXAFS formula for Gaussian radial distribution functions of the neighbouring atoms. The coordination numbers have been obtained from fits using experimental back-scattering amplitudes of Ni and Zr, which include the Debye–Waller factors of the pure elements. The differences $\Delta\sigma^2$ between the mean square deviations of the alloys and the elements are given in the present paper (see Frahm *et al* (1984a) for details). All the spectra were measured at a temperature of 77 K at the DORIS electron/positron storage ring at the DESY in Hamburg using synchrotron radiation.

2. Experimental results and structural parameters

2.1. The intermediate crystallisation stage of $Ni_{0.365}Zr_{0.635}$

The amorphous sample with $x = 0.365$ was quenched from a temperature between those at which the two exothermic peaks in DSC are found to a temperature of 80 K. It was checked by subsequent DSC measurements that the second transition, which leads to the crystallisation, is not affected by this treatment. The x-ray absorption near-edge structure (XANES) and the Fourier transform of the EXAFS above the Ni K edge measured at liquid nitrogen temperature are presented in figures 1(a) and 1(b). The back-transform of the main peak in figure 1(b) is compared with the back-transform of the corresponding peak of the as-cast alloy (see figure 5 of Frahm *et al* (1984b)) in figure 1(c). The XANES and the shapes of the EXAFS are essentially the same as for the untreated alloy; the main differences are between the absolute amplitudes of the structures. Using the value of $\Delta\sigma^2$ from the Zr-edge EXAFS (see below), a fit of the EXAFS with one Ni–Zr shell at the Ni edge yields a coordination number of 3.53, which is 45% higher than the one for the untreated alloy. Figure 2(a) shows the EXAFS at the Zr edge. The Fourier transform and a back-transform performed over the range $1.5 \leq r \leq 3.9$ Å are presented in figures 2(b) and 2(c) respectively. The back-transformed fine structure has been fitted using a two-shell model. The fit is included as a dotted curve in figure 2(c) and the resulting structural parameters are listed in table 1. At the Zr edge the increase of the Zr–Ni coordination

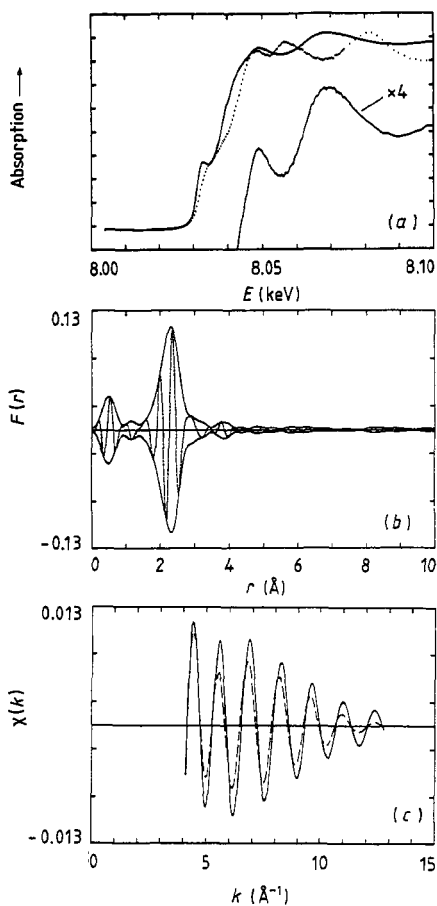


Figure 1. Ni-edge data for the DSC-quenched alloy with $x = 0.365$: (a) XANES data (dotted curve: Ni metal); (b) the Fourier transform of the EXAFS data (Kaiser-Bessel window, $k = (3.5\text{--}13.9) \text{ \AA}^{-1}$, k^1 -weighting); (c) the back-transform of the main peak of (b) (full curve) compared with that for the untreated alloy (broken curve).

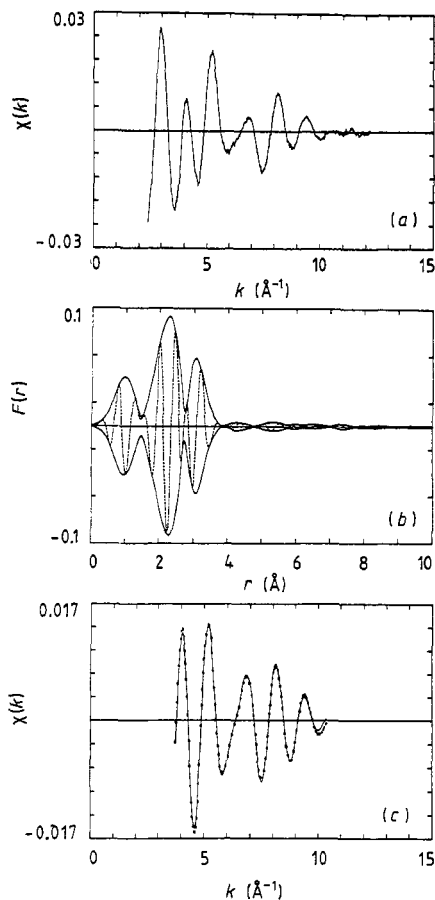


Figure 2. Zr-edge EXAFS data for the DSC-quenched alloy with $x = 0.365$: (a) the EXAFS spectrum; (b) the Fourier transform (Kaiser-Bessel window, $k = (2.45\text{--}12) \text{ \AA}^{-1}$, k^1 -weighting); (c) the back-transform of the main peaks of (b) (full curve) and fitted data (dotted curve; see table 1).

number relative to that for the as-cast alloy amounts to 16%. The atomic distances are unchanged within the experimental accuracy of $\pm 0.02 \text{ \AA}$. After quenching, the Zr-Zr contribution has sharpened significantly and the coordination number is decreased.

2.2. The intermediate crystallisation stage of $Ni_{0.333}Zr_{0.667}$

The sample $Ni_{0.333}Zr_{0.667}$ reveals two exothermic effects on annealing in DSC, which may be indicative of a slight deviation with respect to the ideal $NiZr_2$ composition. The quenching was done from a temperature intermediate between those of the two overlapping DSC peaks. In subsequent DSC runs it was found that the second crystallisation peak was smaller and shifted in temperature, and that the sample was brittle. Only the Zr-edge EXAFS were measured and the results are presented in figure 3. The spectrum is similar to the one found for $x = 0.365$. The structural parameters obtained from a two-shell fit are listed in table 1. These data show some differences with respect to the

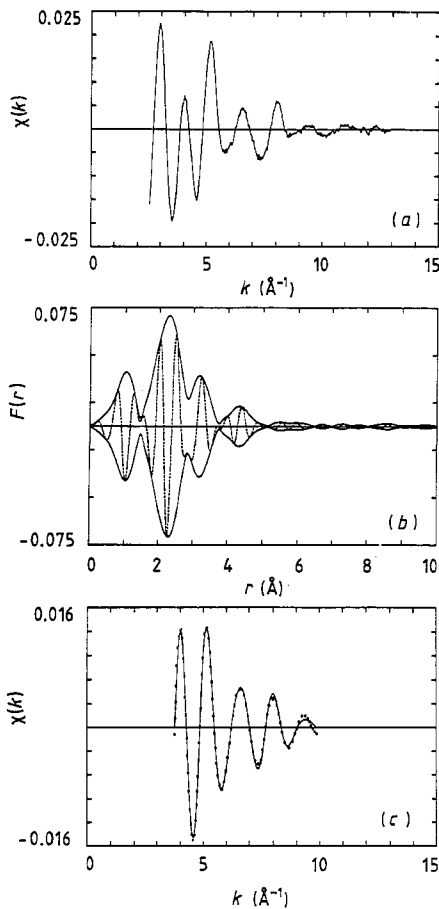


Figure 3. Zr-edge EXAFS data of the DSC-quenched alloy with $x = 0.333$: (a) the EXAFS spectrum; (b) the Fourier transform (Kaiser-Bessel window, $k = (2.45-12) \text{\AA}^{-1}$, k^1 -weighting); (c) the back-transform of the main peaks of (b) (full curve) and fitted data (dotted curve; see table 1).

untreated alloy in all the parameters. The Zr-Zr as well as the Zr-Ni distributions broaden and yield higher coordination numbers and increased atomic distances, indicating the atomic rearrangements. The beginning of the crystallisation is visible from the additional peak in the Fourier transform in figure 3(b). It indicates the beginning of a long-range order. EXAFS spectra have also been measured for an alloy annealed isothermally at 530 K for two hours. This temperature is well below the temperatures where the exothermic processes in the DSC occur. For the alloy with $x = 0.333$ such a treatment leads to no significant changes at either absorption edge. In contrast an annealing of metal-metalloid glass at those temperatures results in embrittlement and structural changes (Werner 1979).

3. Discussion

The Ni K-edge EXAFS of the intermediate phase during the crystallisation of the alloy containing 36.5 at. % Ni indicates an increased number or a growing of some kind of structural unit compared to the case for the as-cast alloy due to the increasing EXAFS amplitude. Similar structural units have been proposed in a previous paper (Frahm *et al* 1984b). The preference and stability of these units is indicated by the fact that the Ni-Zr bond distance remains unchanged in passing the first DSC peak. The Zr K-edge EXAFS

shows that after quenching the Zr-Zr pair distribution becomes smaller and some atoms have been removed from this coordination sphere according to the decrease in coordination number. The next crystallisation step is an increase of the Ni-Zr distance as can be seen from the data for the alloy with $x = 0.333$. From the Fourier transform in figure 3(b) it can be seen that there is a long-range order established before the rearrangements of the first shells have been completed.

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