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High temperature ^{1}H spin–spin relaxation in Zr–Ni–Cu–H amorphous alloys

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Abstract

^{1}H spin–spin relaxation time (T_2) and complementary hydrogen content, PMR spectrum width and spin–lattice relaxation time (T_1) have been measured in $Zr_y(Ni_{1-x}Cu_x)_{1-y}$–H ternary amorphous alloys of different hydrogen content at $0 \le x \le 33$ at.% Cu and $y=33$, 50 and 67 at.% Zr concentrations using Carr–Purcell–Meiboom–Gill (CPMG), solid-echo and saturation recovery pulse sequences, respectively. At high hydrogen contents the T_2 measured by the slope of the CPMG echo train depends on both the Zr and Cu content, but is independent of the hydrogen content. The differences in the spin–spin relaxation behaviours can be attributed to the substantial change of correlation time and not to the change of activation energy or local fields. The measurements were made in the ‘‘motional narrowing’’ state, consequently our E_a and τ_∞ quantities are averaged to the diffusion motion of protons taking part in this process. At small hydrogen contents T_2 depends on hydrogen content and the T_2 vs. $1/T$ curves cannot be fitted by single Arrhenius plots. The hydrogen content measured by echo train has turned out to be systematically smaller than that measured by weight increase, demonstrating that not all the hydrogen takes part in the diffusion process.

Keywords: Magnetic resonance; Relaxation; Zr–Ni–Cu–H; Hydrogen; Amorphous alloy

1. Introduction

The paper is an extension of our work [1] for two other Zr–Ni–Cu alloys of different Zr content; following a similar philosophy and structure a study of the proton magnetic spin–spin relaxation is presented. Our aim is consequently to measure simultaneously, as precisely as possible, the required NMR parameters and the hydrogen content. Using the CPMG pulse sequence [2], the extrapolated amplitude of the echo-train (normalized to the same quantity in water) is a direct measure for the hydrogen content in the alloy. At the same time, the slope of the CPGM echo-train provides a value for the spin–spin relaxation time.

As far as the methodical details are concerned, Ref. [1] and the literature mentioned there are cited, using the same notations. Similarly to Ref. [1], if the diffusion term is nearly zero, we can use a simple formula, namely

$$M(t) = M_0 \exp(-t/T_2) \tag{1}$$

in the evaluation of the CPMG echo-train, where t is the time elapsed from the beginning of the first rf pulse. Eq. (1) gives the opportunity to measure M_0, i.e. the proton magnetization (that is the hydrogen content) and the spin–spin relaxation time simultaneously in our samples.

The simple model proposed by Redfield and Slichter [3] is used in the interpretation of the spin–spin relaxation at high temperatures, where ‘‘motional narrowing’’ exists. This model replaces the bodily motions of protons by fluctuating magnetic fields. The fluctuations of the field in reality arise from the diffusion motion of protons, and in the case of dipole coupling the fluctuating fields are of dipole origin. According to this model the spin–spin relaxation is given as

$$\frac{1}{T_2} = \gamma^2 \overline{H_z^2} \tau_0 + \frac{1}{2T_1} \tag{2}$$

The first term on the right side is the secular broadening containing the square average of local fields $\overline{H_z^2}$, and the correlation time:

$$\tau_0 = \tau_\infty \exp(E_a/kT) \tag{3}$$

where E_a is the activation energy for diffusion, τ_∞ is the value of τ_0 for infinite temperature ($T=\infty$) and k is the Boltzmann constant. In the original form of the BPP theory [4], the second moment of the NMR spectrum replaces $\overline{H_z^2}$ in Eq. (2). In our case, $\overline{H_z^2}$ can be measured by the square of the PMR spectrum width. The spin–lattice relaxation

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time, T_1, in the second term of Eq. (2) gives the nonsecular contribution.

The main goals of this investigation are:

1. To study the dynamic neighbourhood of hydrogen at substantially different Zr, Cu and hydrogen content by measuring the spin–spin relaxation time;
2. To monitor the effects of increasing nuclear magnetization on certain NMR parameters by adding Cu nuclear spins to protons;
3. To measure the hydrogen content by an NMR method not used before in this field.

2. Experimental

The measurements were made at 87.6 MHz frequency using a BRUKER and an SMIS pulse NMR spectrometer with a 1.7 μs π/2 pulse length and a 4 μs dead-time. The CP echoes and the echo peaks in the CPMG echo trains were collected and averaged by a Hewlett-Packard storage scope linked to an IBM PC computer via a HPIB card. The experimental error in both M_0 and T_2 measurements is less than 5%. The T_1 and the supplementary solid echo measurements were performed using the saturation-comb-τ-$\pi/2$ and the $\pi/2$-τ-$(\pi/2)_{90^\circ}$ pulse sequences, respectively, and the same technique for data accumulation system was used. The error in the $\overline{H_z^2}$ measurements is less than 10% and in T_1 is less than 5%.

The CPMG measurements were made in the temperature range of 294–384 K and the $\overline{H_z^2}$ measurements at liquid nitrogen temperature. The temperature of the samples was controlled by an Oxford cryosystem.

Zr–Ni–Cu alloys were prepared by melt spinning from 3N (Zr), 4N (Ni) and 5N (Cu) purity metals after electron beam melting and the non-crystalline state of the samples was checked by X-ray diffraction. The samples were charged at least two times with hydrogen from the gas phase at 30 MPa pressure at temperatures between ambient and 370 K. The smaller H content was achieved by discharging. The discharge caused partial crystallisation in alloys of 67 at.% Zr content. In this paper only the samples that remained amorphous are discussed.

3. Results and discussion

Following the logic of the introduction the first step was to prove that Eq. (1) is valid, that is, the diffusive term does not significantly influence our results. Similarly to the results in Ref. [1] the CPMG train and the single echoes give exactly the same amplitude for all of our alloys, proving that the diffusion does not directly reduce the magnetization.

Eq. (1) points to the measurements of both M_0 and T_2. From M_0, the number of protons can be evaluated. An absolute scale for the proton number in the metal–hydrogen system can be deduced by calibrating the method performing exactly the same measurement on a water sample. Similarly to the results of Fig. 2 in Ref. [1], the hydrogen/metal ratio (H/M) values measured by CPMG echo train and the values measured by weight increase are different. CPMG echoes give a smaller hydrogen content. The higher the hydrogen content the larger the deviation. The hydrogen content was also measured by gas chromatography in a few cases [5]. The results prove that not all of the protons contribute to the CP echoes, that is, not all of them take part in the diffusion process. The H/M scale measured by CPMG echoes is used in our figures.

The room temperature spin–spin relaxation times vs. H/M are given in Fig. 1 for binary alloys of different Zr content. The measured T_2 values can be separated into two ranges; in the high H/M range T_2 is independent of the hydrogen content, but is strongly dependent in the low H/M range. The boundary between the two ranges and the maximal soluble hydrogen content also depends on the Zr content; the higher the Zr content the higher are these values.

As a next step T_1, the spin–lattice relaxation time, was measured in the same temperature range as T_2 in order to eliminate the life time contribution in Eq. (2). The T_1 values are in the 0.13–0.43 s range, decreasing with temperature and hydrogen content, and increasing with Zr and Cu content (the details will be published elsewhere). From that data and from the measured T_2 values one can easily deduce that the nonsecular term is always smaller than 10% and can be neglected. Neglecting it causes maximal overestimation of the same order in the diffusion parameters in the samples containing 33 at.% Zr.

Because we concentrate our efforts on the τ_0 measurements (Eq. (2)), $\overline{H_z^2}$ was also measured independently by the solid echo sequence (the earlier results were published

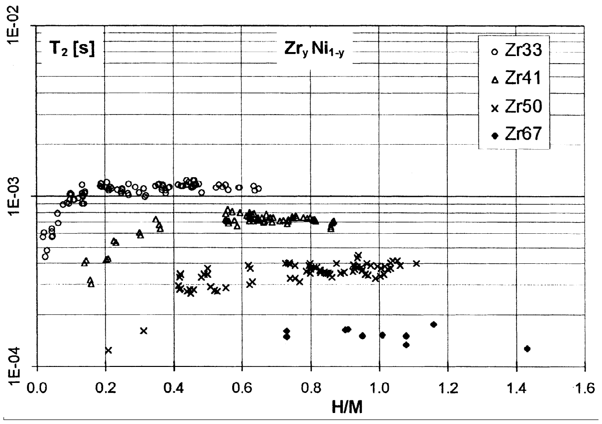

Fig. 1. The room temperature spin–spin relaxation times vs. hydrogen/metal ratio (H/M) for binary alloys of different Zr content. The measured T_2 values can be separated into two ranges. T_2 is independent of the hydrogen content in the high H/M range, but strongly dependent in the low H/M range. The boundary between the two ranges and the maximal soluble hydrogen content also depends on the Zr content.

Table 1

Alloy ⇒	$Zr_{33}(Ni+Cu)_{67}$			$Zr_{50}(Ni+Cu)_{50}$		$Zr_{67}Ni_{33}$
Parameters ⇓	Cu = 0	Cu = 16	Cu = 33	Cu = 0	Cu = 29	Cu = 0
$\overline{H_z^2}$ [G^2]	11.0	12.1	14.2	14.7	17.5	21.7
E_a [eV]	0.34	0.35	0.33	0.34	0.31	0.25
τ_∞ [10^{-12}s]	0.25	0.30	1.44	*0.54	*2.34	25.5

in [6]). These data and the new ones are given in Table 1, together with the estimated diffusion parameters. They were used to separate the local fields from the measured T_2 in order to obtain τ_0 independently from the other physical quantities.

Fig. 2 shows T_2 in binary alloys vs. inverse temperature. Data were selected that refer to samples belonging to the H/M independent ranges of Fig. 1. The slopes of the nearly parallel straight lines show a weak dependence on Zr content.

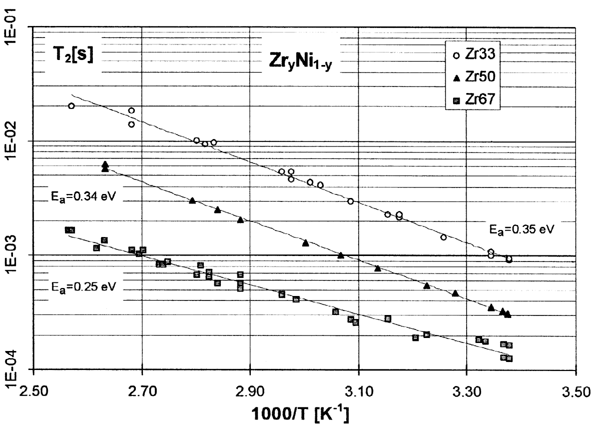

Fig. 2. T_2 in binary alloys vs. inverse temperature. Data were selected that refer to samples belonging to the H/M independent ranges of Fig. 1. The slopes of the nearly parallel straight lines show only a weak dependence on Zr content.

The inverse temperature dependence of T_2 is shown in Fig. 3, for the Zr 33 at.% alloys and with Cu content as a parameter. The parallel set of curves together with Eq. (2) and Eq. (3) demonstrate that the slopes are independent of Cu content (similarly to the results on $Zr_{50}Ni_{50}$ in Ref. [1]) and the pre-exponential factors change with Cu content.

Fig. 4 demonstrates the inverse temperature dependence of T_2 for the $Zr_{33}Ni_{51}Cu_{16}$ alloys at different H/M values. The results show the independence of H/M at high hydrogen content and demonstrate that the linearity and independence are decreasing in samples of low H/M. Similar results were found for $Zr_{50}Ni_{50}$ alloys.

4. Conclusions

The results shown in the figures are typical of the whole investigated alloy system. The spin–spin relaxation in samples of low hydrogen content cannot be characterized by a single exponential temperature dependence, that is, by a single activation energy. The temperature dependence of spin–spin relaxation in the samples of high H/M value is of Arrhenius type. The evaluated parameters of the Arrhenius function and the averaged local magnetic fields are

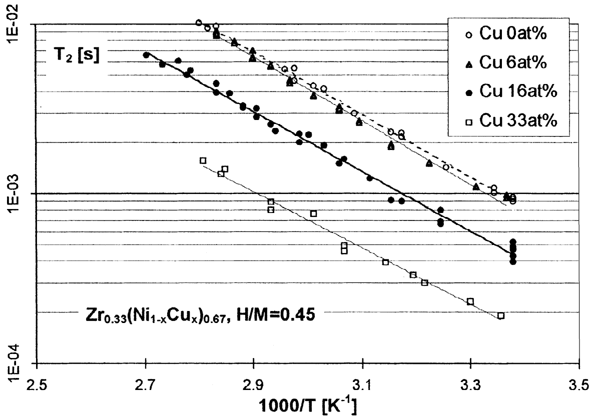

Fig. 3. The inverse temperature dependence of T_2 is shown for the Zr 33 at.% alloys and with Cu content as a parameter. The parallel set of curves together with Eq. (2) and Eq. (3) demonstrate that the slopes are independent of Cu content and the pre-exponential factors change with Cu content.

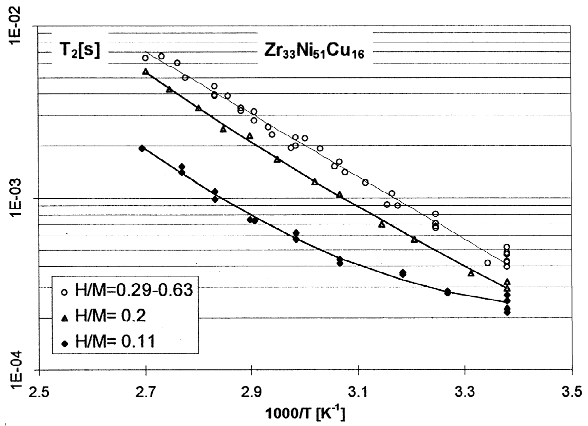

Fig. 4. The curves demonstrate the inverse temperature dependence of T_2 for the $Zr_{33}Ni_{51}Cu_{16}$ alloys at different H/M values. The relaxation time is independent of H/M at high hydrogen content, but the linearity and independence are failing in the samples of low H/M.

given in Table 1, (the data marked by * are not correct in Ref. [1]).

It is impressive that the correlation time exhibits approximately an order of magnitude change as a function of Cu contents, and two orders of magnitude for Zr composition, contrary to the activation energy which is independent of these concentrations in the two alloy systems of smaller Zr content. A smaller E_a value in $Zr_{67}Ni_{33}$ is probably the consequence of the higher atomic diameter of Zr. The data refer to the samples of maximal H/M ratio, 0.63, 0.98 and 1.41, respectively.

The differences in the spin–spin relaxation behaviours can be attributed to the substantial change of correlation time and not to the change of activation energy or local fields. The measurements were done at high temperature in the ‘‘motional narrowing’’ state, consequently our E_a and τ_∞ quantities are averaged to the diffusion motion of protons taking part in this process.

The proton content measured by the CPMG pulsed NMR method is systematically smaller than the hydrogen content measured by weight increase. The probable explanation is that not all the protons are diffusing, i.e. they are not in a motional averaged state and consequently not all the protons contribute to the Carr–Purcell echoes. For a deeper but not complete understanding of hydrogen diffusion in metals the literature is invoked [7–10].

Acknowledgments

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