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Hydrogen-induced internal friction in $NiZr_2$

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Abstract

The H-induced internal friction (IF) in the C16 compound $NiZr_2$ was measured, at temperatures between 80 and 500 K and H concentrations from about 0.3 to 3 at.%, on samples crystallized from amorphous ribbons using the vibrating reed technique. With some variation between individual ribbons, three IF peaks (I–III) were found at temperatures near 160 K, 250 K, and below 100 K respectively. Peaks I and II are interpreted as reorientation peaks and discussed in terms of a recent microscopic model relating interatomic distances to activation energies, which can account qualitatively also for the large difference in width between these two peaks. A preliminary explanation for the third peak is a 'reaction mode' (an exchange of H atoms between two types of interstitial sites without reorientation), but other processes are also possible.

1. Introduction

In contrast to amorphous alloys where hydrogen-induced internal friction (IF) peaks have hitherto been observed in at least 20 systems [1], comparatively little is still known about IF phenomena produced by hydrogen in crystalline intermetallic compounds (see ref. 2 for a brief overview). The so-far most intensely studied effect is the reorientation relaxation of hydrogen in the tetragonal C16 ($CuAl_2$-type) structure, which has recently been described by a quantitative, atomistic model relating activation energies to interatomic distances and lattice parameters [3].

Whereas most of the experimental observations of this effect were made on $CoZr_2$ [4, 5], a few preliminary results have also been obtained on $NiZr_2$ [5, 6]. At H concentrations below 1 at.%, these results revealed a single, broad IF peak (at $T=150$–175 K for $f=450$ Hz) in one sample of nominal composition $Ni_{35}Zr_{65}$ but a double-peak behaviour with an additional peak near 240 K in another sample of composition $Ni_{33}Zr_{67}$.

To obtain a better characterization of the H-induced IF phenomena in $NiZr_2$, additional IF results over a larger range of H concentrations will now be presented and discussed with respect to microscopic mechanisms and theoretical predictions. This might also contribute to improve our understanding of H-induced IF in the C16 compounds in general.

2. Experimental procedure

The IF Q^{-1} of thin $NiZr_2$ ribbons was measured using the vibrating reed technique, with electrostatic excitation and an HF detection circuit, on clamped-free flexural vibrations with (fundamental) resonance frequencies between 10^2 and 10^4 Hz. The H-induced IF spectra were usually obtained under vacuum, at a constant heating rate of 2 K min^{-1}, in a temperature range between 80 and 500 K. More details of this technique have been given elsewhere [4].

The C16 phase $NiZr_2$ was produced from melt-spun amorphous ribbons, about 1 mm wide and 20 μm thick, of nominal composition $Ni_{33}Zr_{67}$, which already contained a 'quenched-in' hydrogen content of about 0.2–0.3 at.% as an impurity. The amorphous samples were clamped into the vibrating reed holder and then crystallized *in situ* by a heat treatment (up to about 900 K) in the vibrating reed chamber, making use of the known crystallization behaviour of this metallic glass [7–9]. The crystallization reactions were followed *in situ* by the related changes in IF and resonance frequency, and also checked independently by differential scanning calorimetry.

After crystallization into the C16 phase, it was possible to increase the H concentration in the samples by gas charging treatments at atmospheric or even lower H_2 pressures (usually, $p=90$ kPa and $T=470$ K for various times). Because this also was done *in situ*, IF spectra at different, successively increasing H concentrations could be measured on the same sample without any change in geometry. For charging at higher H_2 pressures (normally at $T=373$ K), a special pressure chamber was also available. In some cases, H concentrations were measured by heat extraction analysis.

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3. Results

Among the different series of IF spectra observed in individual samples, two major types can roughly be distinguished, as shown in Figs. 1 and 2 by two representative examples. In these logarithmic Q^{-1} plots (without any subtraction of background) three main IF peaks labelled I–III can be identified.

At the lowest H concentrations in Fig. 1, the two IF peaks (I and II) reported earlier for $Ni_{33}Zr_{67}$ (ref. 6, see above) are found again, albeit somewhat less resolved. With increasing H concentration, peak II is predominantly growing, whereas at the highest concentrations a third and finally still higher peak (III) enters from low temperatures. The very broad peak I, on the contrary, transforms into a plateau and finally disappears between its neighbours II and III.

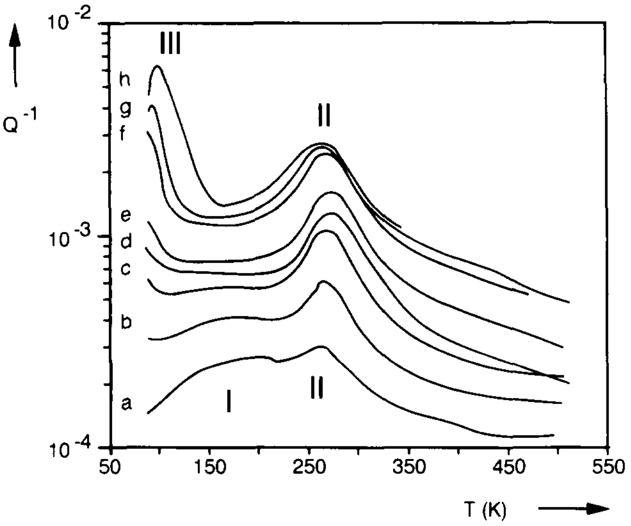

Fig. 1. IF spectra (at 390±30 Hz) of an $NiZr_2$ sample after successive hydrogen charging at $p = 90$ kPa and $T = 470$ K. Charging times are 0 h (curve a), 10 h (curve b), 20 h (curve c), 28 h (curve d), 36 h (curve e), 48 h (curve f), 52 h (curve g) and 56 h (curve h).

The example of Fig. 2, measured on a sample from another melt spinning charge of nominally the same alloy, starts with a single-peak spectrum very similar to that reported earlier for the composition $Ni_{35}Zr_{65}$ [5, 6]. Peak II is only observed at higher H concentrations but is less pronounced than in Fig. 1 and with an additional high temperature shoulder. Peak I now clearly shifts to lower temperatures with increasing H concentration, before it again seems to be masked behind the flank of a big third peak coming from low temperatures but apparently not yet reaching the accessible temperature range. After the last measurement (curve i), an H concentration of 3 at.% was found in the sample of Fig. 2 by heat extraction.

As shown in Fig. 3, peaks II and III are both of a thermally activated nature, *i.e.* they shift to higher temperatures when the frequency is increased (for peak I, this has already been stated earlier [5]). However, there is considerable scatter for peak II and a strong additional variation in peak height especially for peak III, the origin of which is not yet clear. Taking into account also the still rather limited frequency variation in Fig. 3 (obtained by successive shortening of the sample), we do not yet consider these measurements as sufficient for a reliable determination of activation energies.

Although there are large apparent differences between individual ribbons as seen in Figs. 1 and 2, it can nevertheless be stated that all the peaks I–III can in principle be found in any of our $NiZr_2$ samples. Considered at constant frequency, the general properties of these peaks with increasing H concentration can be summarized as follows.

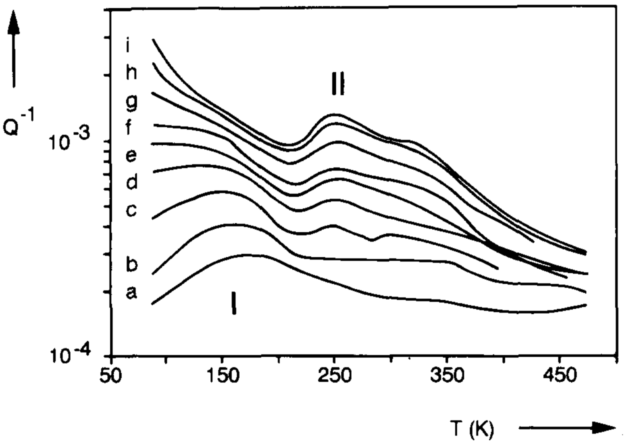

Fig. 2. IF spectra (at 315±20 Hz) of an $NiZr_2$ sample from a second charge after successive H charging at $p = 90$ kPa and $T = 470$ K. Charging times are 0 h (curve a), 10 h (curve b), 20 h (curve c), 30 h (curve d), 40 h (curve e), 50 h (curve f), 60 h (curve g), 70 h (curve h) and 80 h (curve i).

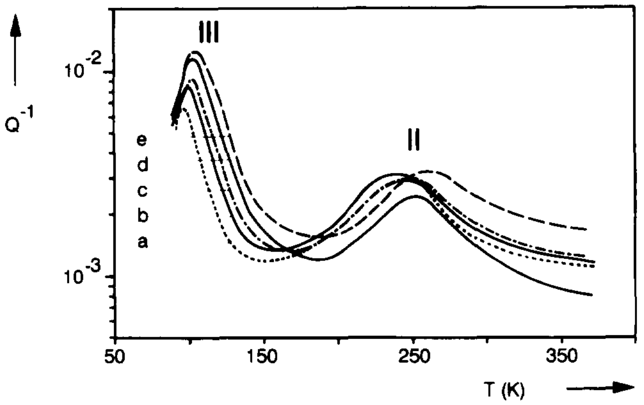

Fig. 3. Frequency dependence of the IF peaks II and III measured on an $NiZr_2$ sample from the same ribbon as in Fig. 1, after a two-step H_2 charging treatment (30 MPa and 373 K for 52 h and 90 kPa and 470 K for 60 h). Frequencies are 453 Hz (curve a), 720 Hz (curve b), 1230 Hz (curve c), 1878 Hz (curve d) and 2680 Hz (curve e).

(1) All the peaks are growing.

(2) Peak I is distinctly broader than the other two peaks. It shifts to lower temperatures and simultaneously still broadens so that it finally loses its identity as a peak.

(3) Peak II first shifts slightly to higher temperatures, but at higher H concentrations this shift seems to be reversed.

(4) Peak III seems first to be situated at temperatures below the range accessible with our vibrating reed equipment but then exhibits apparently a strong shift to higher temperatures.

4. Discussion

In a previous paper [6], the IF peaks I and II in $NiZr_2$ have already been interpreted in terms of the above-mentioned model of H reorientation relaxation in the C16 compounds [3], which assumes non-interacting, thermally activated jumps of the H atoms between Zr-surrounded interstitial sites. As can be seen in Fig. 4, there are two different types of Zr_4 tetrahedral sites in the C16 lattice, called here 'type 1' and 'type 2'. A reorientation relaxation is possible by a redistribution of H atoms between the four different orientations (α–δ) of the type 2 sites having monoclinic symmetry. By applying the appropriate expressions of the model [3] to the case of $NiZr_2$, peak I was essentially attributed to the direct jump of H atoms between neighbouring type 2 sites and peak II to the 'indirect' jump via a type 1 site. The shift of both peaks with increasing H concentration was found in qualitative accord with the predictions of the model [6].

What has not been considered so far, however, is that the widths of the peaks are much broader than a Debye peak, especially in the case of peak I. Apart from microstructural reasons [6], this broadening may be due to lattice-induced H–H interactions, which are indeed expected because the H concentrations cannot really be considered as 'dilute', but which were neglected in the model (except a uniform change in lattice parameters with H concentration which should not influence the peak width).

Assuming a non-uniform variation of interatomic distances by a superposition of long-range strain fields, *e.g.* around dissolved H atoms, there will be a corresponding variation in site and saddle point energies. Since for the two reorientation jumps the site energies are the same, a different peak broadening for both processes can only be related to the variation in saddle point energy. This in turn is related to the variation in d_1+2d_4 for the direct jump and that in d_1+2d_3 for the indirect jump [3] (*cf.* Fig. 4). Considering the Zr–Zr distances d_3 and d_4 as a function of the lattice parameters a and c [10], it follows that the saddle point of the direct jump is predominantly influenced by variations in a and that of the indirect jump more by variations in c.

Since for $NiZr_2$ a responds more sensitively on changing the H concentration than c [3, 6], the relaxation peak due to the direct jump will indeed be expected to exhibit a stronger broadening than that of the indirect jump. In addition, the broadening of the latter peak will be reduced further by the averaging effect of the two partial nearest-neighbour jumps constituting the indirect reorientation jump. Thus, the above identification of peak I with the direct jump and of peak II with the indirect reorientation jump is also consistent with the differences in width observed for these peaks.

A further discussion of the shift of peaks I and II with increasing H concentration, in addition to what has been said above, will not be given here since there are not yet sufficiently detailed crystallographic data for the range of H concentrations considered.

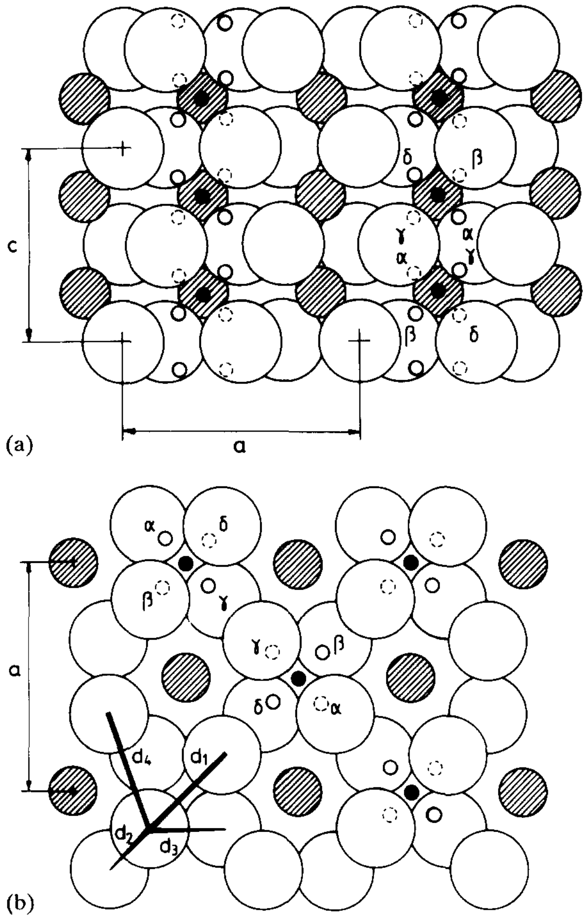

Fig. 4. The (a) (100) and (b) (001) projections of the C16 lattice of $NiZr_2$ with the positions of the Zr-surrounded interstitial sites: ○, Zr; ▨, Ni; ●, type 1 (4b) tetrahedral sites; ○, type 2 (16 l) tetrahedral sites, with orientations α, β, γ, δ. Indicated are also the four slightly different Zr–Zr distances d_1–d_4.

According to the general crystallographic theory of relaxation kinetics [11], the above type of reorientation relaxation can in principle account for two independent relaxation times, so that (if the above explanation of peaks I and II is correct) peak III must have another origin. One possibility is the so-called 'reaction mode' [12], *i.e.* a net exchange of H atoms between the type 1 and type 2 sites without any reorientation among the type 2 sites. This reaction mode is, however, only sensitive to highly symmetric stress components, *e.g.* hydrostatic pressure and uniaxial stresses parallel to the *c* axis in tetragonal crystals. Its relaxation time is determined by the sum of jumping probabilities from site 1 to site 2 and vice versa, and hence mainly by the faster of these processes [12]. Except for the case of identical site energies of the type 1 and type 2 sites, its activation energy should therefore be lower than that of the indirect reorientation jump (which averages between the two partial jumps), with a difference of up to half the site energy difference. For $NiZr_2$ this would correspond, according to the appropriate characteristic lengths of the relaxation model [6], to a value still somewhat lower than that of the direct reorientation jump.

Thus, the temperature range of peak III seems reasonable for an interpretation as a reaction mode between the type 1 and type 2 sites. What look rather surprising in that case and need closer examination, however, are the apparently large height and temperature shift of this peak. At present we cannot decide whether it is indeed the reaction mode or some other process, perhaps based on the interaction of hydrogen with some other defects, that is responsible for peak III.

After this first overview over the H-induced IF phenomena in $NiZr_2$ and possible explanations, there is now a need for more experimental effort, especially with respect to lower temperatures, lower ('dilute') H concentrations (*i.e.* the use of high purity ingots and sample preparation), more detailed crystallographic data on H-containing samples, and also a resolution of the fine compositional and microstructural variations probably underlying the differences between samples such as those of Figs. 1 and 2.

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