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Journal of Alloys and Compounds 356–357 (2003) 305–309

Journal of ALLOYS AND COMPOUNDS

www.elsevier.com/locate/jallcom

New aspects of mechanical relaxation by hydrogen in metals: a combined study of long- and short-range mechanisms

H.-R. Sinning*, R. Scarfone

Institut für Werkstoffe, Technische Universität Braunschweig, Langer Kamp 8, D-38106 Braunschweig, Germany

Received 1 June 2002; accepted 26 October 2002

Abstract

Anelastic relaxation from hydrogen in metals may be subdivided into mechanisms of long-range diffusion, short-range reorientation, and processes coupled with motion of matrix defects. Among recent discoveries in this field, i.e. Snoek-type effects in quasicrystals, Zener mechanism in intermetallic compounds, and intercrystalline Gorsky effect, the latter two are studied in a combined way using different polycrystalline Zr–Cu(–Ni–Al) alloys with $CuZr_2$-type structure. This combined approach, concerning kinetics as well as concentration-dependent magnitudes of the respective damping peaks, is helpful for a better understanding of both processes. The results generally confirm the two mechanisms considered, but also give some new insight, for example, into the probable influence of an attractive H–H interaction on the Zener mechanism. The potential of these new effects for different kinds of application is also discussed briefly.

Keywords: Intermetallics; Point defects; Acoustic properties; Anisotropy; Mechanical spectroscopy

1. Introduction

Hydrogen-induced changes of mechanical properties of metallic materials not only affect strength, ductility, and elasticity, but also anelastic relaxation and mechanical damping [1–4]. Such relaxation is generally caused by hydrogen diffusion, in the form of either long-range (Gorsky effect) or short-range (Snoek- or Zener-type) mechanisms. The present contribution gives a brief overview over these relaxation mechanisms, with emphasis on the recently discovered intercrystalline Gorsky effect, and on the tentative observation of a Zener mechanism in an intermetallic compound like $CuZr_2$. From the experimental point of view, it will be shown that a combined study of both effects may contribute to a deeper understanding of both of these relaxation types, and that the resulting damping spectra are also interesting with respect to different kinds of applications.

2. Relaxation mechanisms

2.1. Overview

Within the general framework of point-defect relaxation [5], anelastic relaxation by hydrogen in metals may be classified in different ways, as discussed in some detail elsewhere [4]. For instance, we may distinguish between the following three major groups of mechanisms: long-range H diffusion, short-range reorientation of interstitial H atoms, and coupled processes involving both H diffusion and the motion of matrix defects.

2.1.1. Long-range H diffusion

The classical Gorsky effect, predicted as early as 1935 [6] but observed only 33 years later (first for H in Nb [7,8]), is now a standard method in hydrogen diffusion studies [9]. Again more than 30 years later, an intercrystalline version of the Gorsky effect could be identified as the origin of previously unexplained damping peaks in polycrystalline intermetallic compounds [4,10,11]; a closer look at this recent progress will be given below.

2.1.2. Short-range reorientation

This second, most extensive class of H-induced relaxation mechanisms may be subdivided into Snoek- and Zener-type processes, depending on the nature of the reorienting elastic dipoles (single H atoms or H–H bonds) in a comparatively immobile metallic matrix. Especially in the former case, a large number of observations exists in dilute and concentrated b.c.c. and f.c.c. alloys, in metallic

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*Corresponding author.
E-mail address: hr.sinning@tu-bs.de (H.-R. Sinning).

0925-8388/02/$ – see front matter
doi:10.1016/S0925-8388(02)01275-6

glasses and in some intermetallic compounds [1–4]. The close relation between the relaxation parameters and the nature of the metal atom cages around the jumping H atoms also makes it possible to use the Snoek-type relaxation as a local probe especially in disordered phases [3,4,12–14]. However, this interesting aspect, as well as the most recent discovery of related damping peaks also in quasicrystals [14–17], is beyond the scope of this paper; instead, we will focus more on the second (Zener) type of reorientation mechanisms.

2.1.3. Coupled processes

There are also some relaxation effects which do not fall into the above categories of motion of H atoms alone, but which require a coupled motion of both H atoms and matrix defects. The most important case is the hydrogen Snoek-Köster effect (hydrogen–dislocation interaction) [3,18], but also an example of H-enhanced host atom diffusion [19] should be mentioned in this context.

2.2. The intercrystalline Gorsky effect

Generally, the Gorsky effect is produced by a H diffusion current in a gradient of hydrostatic stress. However, whereas in the classical case this stress gradient is produced by external bending, the new *intercrystalline* Gorsky effect comes from internal mismatch stresses between elastically anisotropic crystallites in a polycrystal. Analogous to the thermoelastic case [5], the relaxation strength Δ_{IG} and relaxation time τ_{IG} can be written as [11]

$$\Delta_{IG} = R(\mathrm{tr}\ \lambda)^2 \Omega\, K_U c_H / k_B T \qquad (1)$$

and

$$\tau_{IG} = d^2/3\pi^2 D = \tau_0 \exp(Q_a/k_B T), \qquad (2)$$

where R is an elastic anisotropy factor, tr λ is the H-induced lattice dilatation, Ω the atomic volume in the matrix, K_U the unrelaxed bulk modulus, c_H the H concentration, d the grain diameter, and D the hydrogen diffusion coefficient with activation energy Q_a; the other quantities have their usual meaning.

2.3. The Zener mechanism in $CuZr_2$

Although the term 'Zener relaxation' originally meant a substitutional pair reorientation [5], anelastic effects by interstitial H–H interaction were afterwards also called 'Zener effects' [1]. This was justified later by the lattice gas model of Wipf and Kappesser [20], which applies to both the substitutional and interstitial cases. The hydrogen Zener mechanism was reported in pure f.c.c. and h.c.p. metals (for reviews, see Refs. [1,4]) before we found evidence for it also in the tetragonal ($C11_b$) $CuZr_2$ phase [10], which then is the first case of this mechanism in an intermetallic compound. Without going into the theory in detail, we may assume that the strength Δ_Z of the 'Zener effect' is proportional to the product $(\delta\lambda_{H-H})^2\ n_{H-H}$, where $\delta\lambda_{H-H}$ and n_{H-H} are the elastic dipole strength and the number, respectively, of the reorienting H–H pairs or bonds. Consequently, the H concentration dependence of Δ_Z will depend mainly on the relationship between n_{H-H} and c_H which will be discussed further below.

3. Combined studies of long- and short-range processes

3.1. Damping spectra of $CuZr_2$-type polycrystals

As described in more detail previously [4,11,21], vibrating-reed experiments were performed on Zr-based, polycrystalline intermetallic phases prepared from melt-spun amorphous precursors by thermal crystallization. After additional hydrogen charging from the gas phase, strong H-induced damping effects could be observed over a very broad temperature range of sometimes more than 500 K. These wide damping spectra (wider even than in amorphous alloys) often contain several peaks and may be rather complex, especially in multi-phase polycrystals. It is obvious that in such cases more than one relaxation mechanism must be active, but identification is sometimes difficult.

More favorable under the aspect of relaxation mechanisms is the situation in phases with $CuZr_2$ structure ($Zr_{65}Cu_{27.5}Al_{7.5}$ and $Zr_{65}Cu_{17.5}Ni_{10}Al_{7.5}$ [22,23] in addition to $CuZr_2$) showing two well-defined hydrogen damping peaks associated with the two mechanisms mentioned above in Sections 2.2 and 2.3 [10,11,21]. In Fig. 1 two examples of such spectra, for an estimated H concentration of a few atomic percent, are shown on a reciprocal temperature scale; the individual peaks are compared to Debye peaks calculated for an activation energy of 0.5 eV (this value was found experimentally for $Zr_{65}Cu_{17.5}Ni_{10}Al_{7.5}$ [11]).

The main differences between the two alloys in Fig. 1 concern chemical composition (affecting the occupancy of the Cu sublattice in the $CuZr_2$ structure) and grain size. These differences influence the positions and relative heights of the two peaks in different ways, to be discussed in the following two sections. There we will also see that such a combined consideration of long- and short-range processes may be helpful for a better understanding of both kinds of mechanisms, because for each of them there are specific questions which can be answered better when, respectively, the other mechanism is taken as a reference.

3.2. Relaxation kinetics and diffusion distances

Looking at the positions of the hydrogen damping peaks, the main effect is that the *high-temperature peak* (on the left side in Fig. 1), identified with the inter-

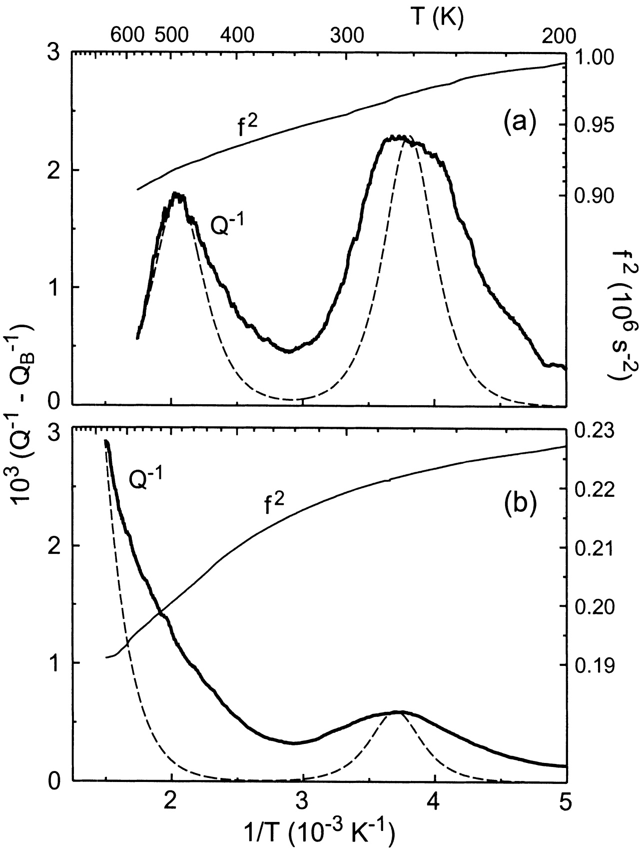

Fig. 1. H-induced internal friction Q^{-1} (after subtraction of a linear background Q_B^{-1}) and square of the resonance frequency f as a function of reciprocal temperature. (a) $Zr_{65}Cu_{17.5}Ni_{10}Al_{7.5}$ (grain size ~30 nm [11]) after 62-h hydrogen charging at 473 K and 1 bar H_2; (b) $CuZr_2$ (grain size: a few µm [10,21]) after 80-h hydrogen charging. The dashed lines correspond to Debye peaks with an activation energy of 0.5 eV.

crystalline Gorsky effect [4,10], shifts to higher temperatures with increasing grain size. It could be measured as a real peak only at sub-micrometer grain sizes, whereas in the case of Fig. 1b the maximum is beyond the accessible temperature window so that only the low-temperature side of this peak is seen. On the other hand, the position of the *reorientation peak* at 260–270 K practically does not change: apparently, the rate of the local hydrogen jumps in the $CuZr_2$ lattice is neither affected by grain boundaries nor, thanks to the strong affinity between H and Zr, by some Ni or Al atoms on the Cu sublattice.

This relative stability of the position of the reorientation peak, which is also rather insensitive to H concentration [4,10,15], was indeed the key for the experimental confirmation of the intercrystalline Gorsky effect: by a normal Arrhenius analysis of the frequency shift, it was shown that in the case of Fig. 1a the activation energy Q_a is the same for both peaks, but that the respective pre-exponential time constants τ_0 differ by the ratio d^2/a^2, where d is the grain size and a the lattice parameter [11]. Assuming for the reorientation a diffusion distance of the order of a lattice parameter (which should essentially be true for any reorientation, so that there is no need at this point to know the process exactly), this means that the second peak comes from H diffusion over the distance of the grain size, as expected for the intercrystalline Gorsky effect. Then, the deviations of this intercrystalline peak from a Debye peak, which are surprisingly small at least at the high-temperature side in the case of Fig. 1a, in principle reflect the grain-size distribution in the sample. (This latter problem is in fact more complicated in detail, which is beyond the scope of this paper.)

3.3. Relaxation strength and H–H interaction

The identification of the low-temperature peak in Fig. 1 with a hydrogen 'Zener effect' was as yet mainly based on crystallographic arguments [10], whereas the question of the H concentration dependence still remained open; another open question is why, in relation to the intercrystalline Gorsky peak, the 'Zener peak' is much smaller in Fig. 1b than in Fig. 1a. In the ideal case of a random ('non-interacting') distribution of the H atoms, the number n_{H-H} of reorienting H–H pairs should be proportional to $c_H^2(1-c_H^2)$, i.e. for $c_H << 1$ a relaxation strength $\Delta_Z \propto c_H^2$ should be expected. If, however, a stronger association or clustering of H atoms occurs, then the c_H dependence of Δ_Z should be weaker, e.g. in form of a power law $\Delta_Z \propto c_H^m$ with $m<2$. Two artificial examples might illustrate this latter statement: first, if all the H atoms were associated to form isolated pairs ($n_{H-H}=n_H/2 \propto c_H$) then $m=1$ would be expected; second, if hydrogen formed spherical clusters, with relaxation contributions only from the surface, then $m=2/3$ would be the result.

Even though direct c_H data are not available for most of the damping spectra (often measured stepwise on the same sample), it is nevertheless possible to approach this question of c_H dependence: knowing from Eq. (1) that Δ_{IG} should be proportional to c_H, the intercrystalline Gorsky effect may be taken as a reference. When the heights of the two peaks are plotted against each other as in Fig. 2, exponents m are found which are ~1.4 in the four-component cases, but even below 1 for the binary and ternary alloys.[1]

To understand this behavior, the role of H–H interaction in these $CuZr_2$-type phases has to be considered as the most crucial point. It is known that a strong, elastic H–H attraction exists both in b.c.c. metals [24] and in hexagonal zirconium [25]; hence, one might expect this also in $CuZr_2$ which has a b.c.c.-type superstructure. Also the strong broadening of the reorientation peaks in Fig. 1, compared

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[1] For $CuZr_2$ showing only the low-temperature side of the 'Gorsky' peak, the H-induced damping level at $T=635$ K was taken for this purpose, so that the true 'Gorsky' peak height is underestimated in this case. This means that the exponent $m=0.83$ might be still too high for $CuZr_2$.

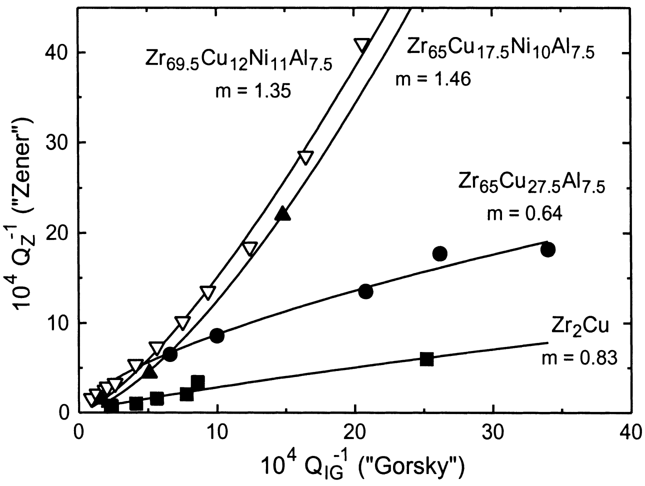

Fig. 2. Concentration dependence of the strength of the hydrogen reorientation relaxation in four polycrystalline $CuZr_2$-type alloys, as obtained from a plot of the heights of the hydrogen 'Zener' and 'intercrystalline Gorsky' peaks (in part taken from published damping spectra [10,14,15,21]) against each other. The exponents m are the result of power-law fits of the form $y = ax^m$.

to a Debye peak, points in this direction. With this information, the low m values in $CuZr_2$ and $Zr_{65}Cu_{27}Al_{7.5}$ are not in conflict with the Zener mechanism but may possibly indicate some clustering of hydrogen in these phases. On the other hand, alloying with nickel may weaken this clustering effect, which could explain the higher exponents observed in the four-component alloys. In fact, these latter values are too high for a Snoek-type process (which was also rejected by other arguments [10]) but support again the Zener mechanism.

3.4. Applied aspects

Especially for the intercrystalline Gorsky effect as a new mechanism, there are several interesting possibilities for potential applications in H-absorbing materials. Because the effect is based on elastic anisotropy [Eq. (1)], and is therefore not found in elastically isotropic quasicrystalline or 'big cube' phases [17,21], it might be used to detect elastic crystal anisotropy even in the range of micro- to nanocrystalline grain sizes. Corresponding grain-size distributions might be obtained from an analysis of the peak shape, as already mentioned above. If, on the other hand, the polycrystalline microstructure is well characterized, the intercrystalline Gorsky effect may serve as an additional method to study hydrogen diffusion on a mesoscopic scale.

More generally, the extended possibilities of combining different short- and long-range H relaxation mechanisms, related not only to crystal type and composition but also to the grain microstructure, might in principle give a greater variability in tailoring damping properties of materials, possibly also in a reversibly adjustable way.

A further applied aspect, briefly mentioned in the overview of Section 2.1 above, is the use of the reorientation (especially Snoek-type) relaxation of hydrogen as a local atomic probe; this has been treated in more detail elsewhere [3,4,12–14].

4. Conclusions

Some 'synergetic effects' of a combined study of long- and short-range hydrogen relaxation effects were demonstrated.

(i) With reorientation as a reference for the diffusion distance, it could be shown that the diffusion currents of the long-range process occur on the scale of the grain size, which confirms the intercrystalline Gorsky effect.

(ii) The concentration dependence of the height of the reorientation peak, with the intercrystalline Gorsky effect used as a measure of H concentration, is generally consistent with the Zener mechanism, but it also indicates some possible clustering of hydrogen in $CuZr_2$ and $Zr_{65}Cu_{27.5}Al_{7.5}$ under the influence of an attractive H–H interaction. Alloying with Ni apparently reduces this latter influence.

Potential applications may include H diffusion studies, characterization of elastic anisotropy and microstructure, and tailoring of damping properties.

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