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Effects of relaxation on hydrogen absorption in Fe–Ti produced by ball-milling

L. Zaluski [a], A. Zaluska [a], P. Tessier [a], J.O. Ström-Olsen [a], R. Schulz [b]

[a] Centre for the Physics of Materials, Department of Physics, McGill University, 3600 University St., Montréal, Québec H3A 2T8, Canada

[b] IREQ, Institut de recherche d'Hydro-Québec, Technologie des matériaux, Varennes, Québec J3X 1S1, Canada

Abstract

Powders of FeTi ball milled with Pd were found to absorb hydrogen in the as-ball-milled state, without activation. This allows a study of relaxation effects on hydrogen absorption in nanocrystalline and amorphous FeTi. Hydrogen absorption characteristics (at room temperature) for powders in the unrelaxed state and after annealing were determined and compared with those for conventionally activated FeTi.

Keywords: Relaxation effects; Hydrogen absorption; Ball-milling

1. Introduction

Ball-milling involves heavy deformation of the powders so that the material as prepared is far from equilibrium and contains a high concentration of strain and defects [1]. Hydrogen absorption of unrelaxed FeTi powders (i.e. in the as-ball-milled state) was previously inaccessible to study because the samples did not absorb hydrogen without activation. A typical activation of polycrystalline FeTi consists of annealing at 450 °C under hydrogen at high pressure, usually several times [2]. These activation processes are sufficient to relax out strains and defects. However, an enhancement in hydrogen absorption of FeTi can be accomplished by the catalytic effect of a very small addition of Pd (less than 1 wt.%). FeTi with Pd exhibits an excellent activity in both amorphous and nanocrystalline powders in the as-ball-milled state [3,4]. Such powders require no activation and readily absorb hydrogen at room temperature, even when stored for a prolonged time in air before hydrogenation. By examining FeTi powders ball-milled with a Pd catalyst it is therefore possible to determine hydrogen absorption for the ball-milled powders in the unrelaxed state (for both amorphous and nanocrystalline material) and the results can be compared with those for annealed powders.

2. Experimental methods

Mechanically alloyed FeTi samples (nanocrystalline and amorphous) were fabricated from elemental Fe and Ti powders (99.9% purity) by high energy ball-milling. The milling was performed in a high energy ball mill from SPEX (Spex 8000) using WC balls and vial (for details see [5]). The final structure of the material is critically dependent on oxygen contamination. High (3 at.%) oxygen content in the samples promotes the formation of an amorphous structure, whereas under oxygen-free conditions nanocrystalline samples are produced [5]. A small amount of Pd (less than 1 wt.%) was used to modify the powders of nanocrystalline and amorphous FeTi in the course of ball-milling. X-ray studies were performed on a Nicolet-Stoe powder diffractometer (Cu Kα and Mo Kα radiation). The microstructure and chemical composition of the ball-milled material were studied using a Philips CM20 (200 kV) transmission electron microscope equipped with an energy-dispersive X-ray analysis system (EDAX 9900) with a thin Be window. Thermal analysis of the powders was performed by differential scanning calorimetry (Perkin-Elmer DSC-2). Pressure–concentration isotherms were obtained using an automated volumetric apparatus, a modified version of that described in [6].

To determine relaxation effects, pressure–concentration isotherms were measured at room temperature for the unrelaxed samples and for samples previously annealed at different temperatures. Microstructures of the powders were examined by X-ray diffraction and transmission electron microscopy (TEM) before and after hydrogenation cycles and also before and after annealings, to check for crystallization or grain growth caused by heat treatments.

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3. Results and discussion

Relaxation effects in alloys prepared by ball-milling are usually very large, much larger than in alloys prepared by other non-equilibrium processes (e.g. melt-spinning) [1,7]. However, there is still no complete, quantitative description of the relaxation phenomena in ball-milled materials owing to the experimental difficulties in the direct measurements of structural and chemical changes in the materials [7]. Relaxation effects are usually characterized by the release of enthalpy and stress on annealing [7,8]. A large amount of energy can be stored in nanocrystalline FeTi fabricated by high energy ball-milling, as a result of mechanical deformation, leading in turn to a high concentration of structural defects and chemical disorder. DSC studies of as-ball-milled FeTi show a large enthalpy release on heating to 600 °C. An enthalpy release of 8 kJ mol^{-1} was obtained for the nanocrystalline samples used in the present study, which compares well with previous results for nanocrystalline FeTi ball-milled with lower energy, 7.5 kJ mol^{-1} [9]. By comparison, the enthalpy stored in heavily deformed, cold-worked polycrystalline materials does not usually exceed 1–2 kJ mol^{-1} [1].

Relaxation of ball-milled materials may be also described as annealing out of strain. It was shown that ball-milled nanocrystalline FeTi exhibited a high level of internal strain, 0.73% [9]. (For comparison, a strain of up to 1% may be obtained in cold worked metals [10].) Annealing reduces the internal strain to 40% of the initial value after heating to 400 °C, with the size of the crystallites remaining unchanged (as determined by X-ray diffraction). After heating to 600 °C the material is practically strain free [9].

Chemical ordering in nanocrystalline FeTi is also affected by annealing. Chemical disorder can be estimated from X-ray diffraction. FeTi has a b.c.c. structure of CsCl type with an ordered occupation of the sites by Fe and Ti atoms. Non-equilibrium crystalline structures of FeTi may be characterized by different degrees of disorder. It was calculated from the X-ray diffraction patterns that the long-range order parameter (determined as the relative intensity ratio of (100) to the (200) line) is about 0.8 for the as-ball-milled sample [11] and increases after annealing. Similar results, i.e. chemical disordering caused by ball-milling, were obtained for other compounds with the CsCl structure [12].

To reveal effects of relaxation on hydrogen absorption, the unrelaxed FeTi powders (amorphous and nanocrystalline) and samples annealed at different temperatures were studied. TEM and X-ray diffraction of the samples before and after hydrogenation cycles showed that no apparent changes of the material occurred either with annealing, or with hydrogen absorption. Amorphous samples did not crystallize and grain sizes in nanocrystalline samples remained unchanged.

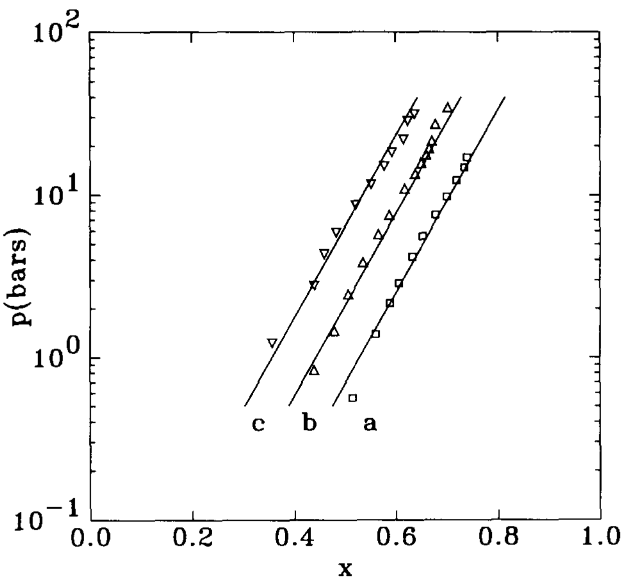

Fig. 1. Pressure–composition isotherms at room temperature for amorphous FeTi (modified by Pd) in as-produced state (a), after annealing at 300 °C (b) and at 400 °C (c); $x=[\mathrm{H}]/[\mathrm{FeTi}]$.

Fig. 1 shows pressure–composition (*p–c*) isotherms of hydrogen absorption at room temperature for amorphous FeTi powders, in both an unrelaxed sample and in samples annealed at 300 °C and 400 °C. The measurements correspond to the first hydrogenation of each sample. Both the as-prepared and the relaxed samples exhibit a solubility-type behavior (i.e. no plateau in the isotherm), with a very similar *p–c* slope. This behavior is believed to be a result of the random local arrangements of atoms in the amorphous structure, which provides a wide distribution of energy of possible hydrogen sites. As a consequence the amount of adsorbed hydrogen is significantly reduced, compared with the ordered hydrogen packing in crystalline FeTiH at comparable hydrogen pressures. Annealing does not change the slope of the hydrogen absorption curve for amorphous samples but only shifts it towards lower hydrogen contents at the given pressure. For example, after annealing at 300 °C the amount of absorbed hydrogen is lower by 0.09 H per FeTi and after annealing at 400 °C by 0.17 H per FeTi, as compared with the as-obtained sample at the same hydrogen pressure (10 bar).

Fig. 2 shows hydrogenation curves for nanocrystalline FeTi in the as-ball-milled state and after different annealing. *p–c* isotherms measured for the as-made material show no well defined plateau in the curve. Analogously to the amorphous material, annealing causes a shift of the *p–c* isotherm towards higher pressures. However, unlike the amorphous samples, annealing gives rise to the appearance of a plateau. For the sample annealed at 300 °C the pressure plateau becomes more evident. Annealing at 400 °C gives the *p–c* isotherm with well defined plateau (Fig. 2(d)), similar to that presented in [5] for activated nanocrystalline FeTi.

To interpret the above results the structure of the nanocrystalline FeTi is assumed to consist of two components: crystalline nano-grains and highly disordered (amorphous-like) grain-boundary regions, similar to what was presented in Ref. [13]. The presence of some amorphous component in the nanocrystalline FeTi may be detected by X-ray dif-

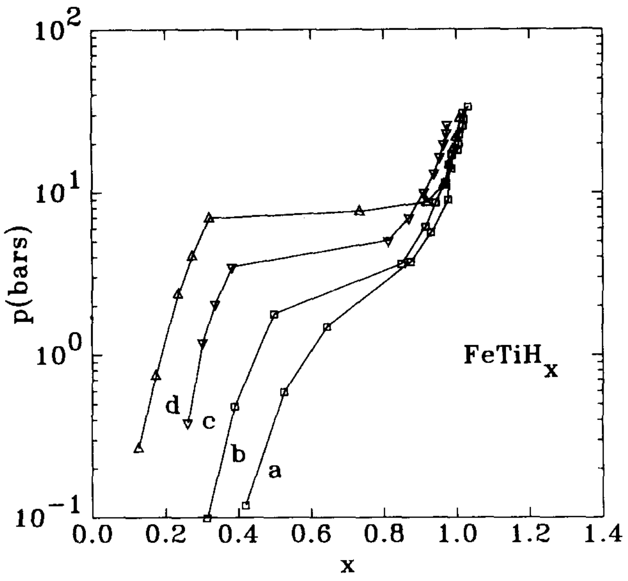

Fig. 2. Pressure-composition isotherms at room temperature for nanocrystalline FeTi (with Pd) in as-ball-milled state (a), and after annealing at 300 °C for 0.5 h (b), at 400 °C for 0.5 h (c). A p-c isotherm after prolonged annealing at 400 °C is also shown (d).

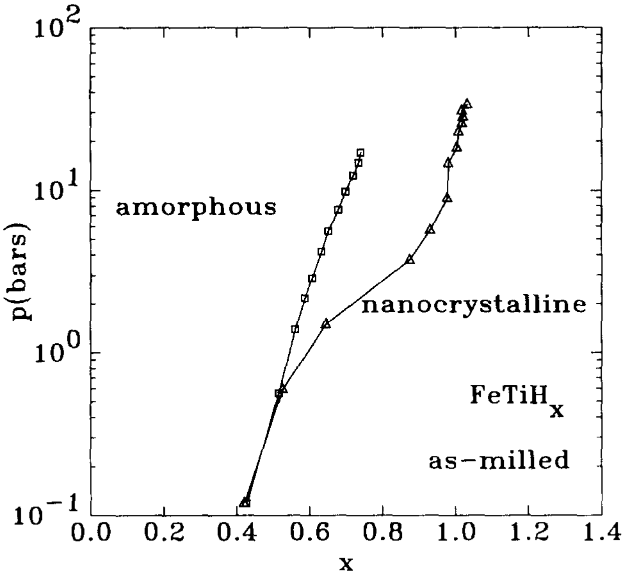

Fig. 3. Pressure-composition isotherms for nanocrystalline and amorphous FeTi (with Pd) in as-ball-milled state.

fraction [11] and the calculated amount of amorphous phase reaches a fraction of 20%-30% of the material. The amorphous-like nature of the grain boundary regions can be confirmed by comparison of the hydrogenation characteristics for amorphous and nanocrystalline samples, as shown in Fig. 3. For the as-ball-milled powders the isotherms overlap at low pressure (below plateau), i.e. where the absorption is solid solution type. Overlapping of isotherms for the amorphous and nanocrystalline samples was also found for different annealings (Fig. 4) and was surprisingly well correlated with annealing temperature. These results strongly support the amorphous-like character of the grain-boundary regions in the ball-milled nanocrystalline FeTi.

However, there is still a controversy in the literature about the nature of the grain boundary regions in nanocrystalline materials. For example, Kirchheim and coworkers [14,15] concluded from the analysis of hydrogenation in nanocrystalline Pd that the grain boundary phase was highly disordered, but other authors [16] reported that grain boundaries in nanocrystalline Pd were similar to the grain boundaries in polycrystalline material. It should be stressed that these results were obtained for materials produced by the gas condensation method. Grain boundaries formed in ball-milling may have a different character, because they are mostly affected by local stress and deformation. Ball-milling can also eventually lead to amorphization of the alloy [5], starting presumably at interfaces of the ball-milled powders.

Irreversible relaxation in amorphous metals (e.g. in metallic glasses) is characterized by an increase in density [17]. According to this approach the structure of the unrelaxed glass provides more accessible sites for hydrogen, with lower energy. For annealed samples a higher hydrogen pressure must be applied to obtain the same amount of absorbed hydrogen as for the unrelaxed sample. Annealing does not change the slope of the hydrogen absorption curve but shifts it towards lower hydrogen contents at the given pressure. Similar results were obtained for hydrogen absorption measured at various temperatures (from room temperature to 170 °C) for amorphous NiZr ribbons [6]. An increase in the hydrogenation temperature caused a shift of isotherms towards lower hydrogen contents without any change in the isotherm slope.

The fact that relaxation does not change the slope of the isotherm but only shifts it to higher pressures suggests that the distribution of site energies is not changed in form but is

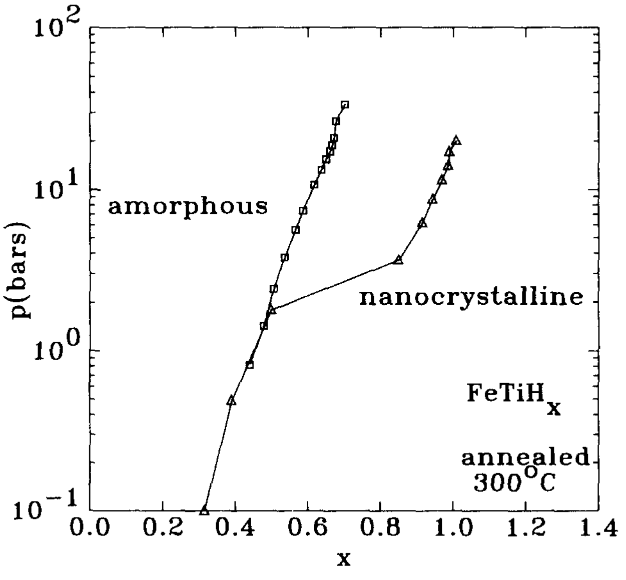

Fig. 4. Pressure-composition isotherms for nanocrystalline and amorphous FeTi (with Pd) after annealing at 300 °C.

only shifted to higher energies. Assuming that displacement is caused only by a densification, it is possible to calculate the change in specific volume v_{M} from the pressure shift of the isotherm. Using a linear potential between protons and metal atoms and a hard core repulsion between protons [18], together with an isotropic and diagonal force-dipole tensor and replacing its diagonal component P by

$$P = -Bv_{\mathrm{H}} \tag{1}$$

where B is the bulk modulus of the material and v_{H} the volume expansion per hydrogen atom absorbed, we find

$$\Delta H = -Bv_{\mathrm{H}}\left(\frac{\Delta V}{V}\right)N \tag{2}$$

where N is the number of dissolved protons. The correction to the chemical potential is

$$\Delta\mu = -Bv_{\mathrm{H}}\left(\frac{\Delta V}{V}\right) \tag{3}$$

The pressure in the relaxed material corresponding to a given concentration of hydrogen is related to that for the as-made material by the expression

$$\frac{1}{2}kT\ln P' + Bv_{\mathrm{H}}\frac{\Delta v_{\mathrm{M}}}{v_{\mathrm{M}}} = \frac{1}{2}kT\ln P \tag{4}$$

The change in specific volume is

$$\frac{\Delta v_{\mathrm{M}}}{v_{\mathrm{M}}} = \frac{kT}{2Bv_{\mathrm{H}}}\ln\frac{P}{P'} \tag{5}$$

Although there are no precise figures for v_{H}, the literature [19] on amorphous transition metal alloys suggests it should be around 2.8 Å. The bulk modulus of crystalline FeTi is 189 GPa [20]. The bulk modulus of amorphous metals is generally 4% smaller than that of their crystalline counterparts [21]. We therefore use 180 GPa in this calculation. Taking the hydrogen pressure for the relaxed amorphous powder as about 10 times larger than that for the unrelaxed sample (for the same hydrogen content) (Fig. 1), we find $\Delta v_{\mathrm{M}}/v_{\mathrm{M}} \approx -0.9\%$ and $\Delta\mu \approx 0.03$ eV. Again, it should be emphasized that this simple estimation of the change in specific volume ($\Delta v_{\mathrm{M}}/v_{\mathrm{M}}$) is based on the assumption that densification is the only factor in the increase in hydrogen pressure due to irreversible relaxation. The estimated value of $\Delta v_{\mathrm{M}}/v_{\mathrm{M}} \approx -0.9\%$ is larger than the observed density change caused by irreversible relaxation for rapidly solidified metallic glasses. It may be found in the literature that the density change due to irreversible relaxation is equal in metallic glasses to 0.5% [22]. The difference between the estimated value of density change for the amorphous ball-milled powder and metallic glass ribbons is consistent with previous reports that relaxation effects are much larger in ball-milled powders than in rapidly solidified materials [7]. As mentioned before, the enthalpy of irreversible relaxation for ball-milled materials is usually several times larger than that for metallic glasses [7]. Amorphous FeTi exhibited a heat of irreversible relaxation of the order of 4–6 kJ mol^{-1} and the values of relaxation of metallic glasses are in the range 0.4–1 kJ mol^{-1}.

Relaxation in nanocrystalline powders involved two features: a shift of the p–c curve towards the lower hydrogen contents (analogous to the above discussed for amorphous structure) and a change in inclination of the plateau. From Figs. 3 and 4 it can be concluded that changes in the initial solubility of hydrogen before the formation of the FeTiH hydride can be attributed to the disordered grain-boundary regions. For the unrelaxed nanocrystalline sample, the lack of the well defined plateau in the region of the hydride formation may involve two overlapping and interconnected effects: a narrowed miscibility gap in the metal–hydrogen phase diagram and a tilting of the isotherm.

We suggest that the change in hydrogen absorption characteristics for the nanocrystalline FeTi (in the range of formation of the FeTiH hydride) is caused by the influence of structural defects and internal strain on the metal–hydrogen phase diagram. At equilibrium there is a very limited solubility of hydrogen in FeTi [2] at room temperature (0.1 H per FeTi), although it increases significantly with temperature [2]. The presence of internal strain and chemical disorder may change the metal–hydrogen phase diagram by shifting the increasing solubility curve towards lower temperatures. The unrelaxed material exhibits a broader spread in energy of hydrogen sites which leads to a decrease in the critical temperature T_{c}, according to theoretical predictions [23,24].

It was observed, for example for crystalline Pd [25], that hydrogen storage properties were very sensitive to the internal strain in cold-worked samples. Internal strain caused increased solubility of hydrogen in Pd. A narrowing of the Pd–H miscibility gap (increase in hydrogen concentration in solute phase) was also recently observed for nanocrystalline Pd produced by gas condensation [26] and in Monte Carlo simulations [27]. It was shown for Pd–tritium and V–tritium systems [28] that pressure–concentration isotherms exhibit inclination of the plateau at elevated temperatures of hydrogenation and the effect is most pronounced for temperatures closer to the critical temperature of mutual solubility. Ternary intermetallics also exhibit a plateau slope [29], which may be connected with a chemical segregation that occurs during solidification. The plateau slope can be minimalized by annealing [29].

In general, it may be concluded that the presence of structural defects and internal strain in ball-milled FeTi reduces the miscibility gap (i.e. increases the solubility of hydrogen in FeTi) and also lowers the critical temperature of mutual solubility, which manifests in shortening and inclination of the pressure plateau in the p–c isotherm.

4. Conclusions

Relaxation effects were studied in ball-milled FeTi in the amorphous and nanocrystalline states. Hydrogen absorption characteristics at room temperature for the unrelaxed material were determined and compared with those for annealed samples.

For amorphous samples annealing does not change the character of hydrogen absorption, but only shifts the hydrogenation curves towards lower hydrogen contents. This effect can be explained by densification of the amorphous structure due to annealing, which reduces the easily accessible hydrogen sites with low energy.

Relaxation effects in nanocrystalline FeTi involve two interconnected features: a decrease in the solubility of hydrogen in FeTi (increase in the miscibility gap) and a change in inclination of the plateau. We suggest that the hydrogenation characteristics of the unrelaxed nanocrystalline powder result from the lowered critical temperature of mutual solubility in the metal–hydrogen phase diagram. The decrease in critical temperature occurs owing to the presence of internal strain and disorder in the unrelaxed material, which causes broadening of the energy spectrum for the hydrogen sites.

Additionally, it was shown that the nanocrystalline FeTi produced by ball-milling consists of two components: crystalline nano-grains and highly disordered (amorphous-like) grain-boundary regions, which may reach a fraction of 20%–30% of the material.

References

[1] W.L. Johnson, *Prog. Mater. Sci., 30* (1986) 81.
[2] J.J. Reilly and R.H. Wiswall, Jr., *Inorg. Chem., 13* (1974) 218.
[3] L. Zaluski, A. Zaluska, P. Tessier, J.O. Ström-Olsen and R. Schulz, *J. Alloys Comp., 217* (1995) 295.
[4] L. Zaluski, A. Zaluska, P. Tessier, J.O. Ström-Olsen and R. Schulz, unpublished results.
[5] L. Zaluski, P. Tessier, D.H. Ryan, C.B. Doner, A. Zaluska, J.O. Ström-Olsen, M.L. Trudeau and R. Schulz, *J. Mater. Res., 8* (1993) 3059.
[6] E. Batalla, J.O. Ström-Olsen, Z. Altounian, D. Boothroyd and R. Harris, *J. Mater. Res., 1* (1986) 765.
[7] R. Brüning, Z. Altounian, J.O. Ström-Olsen and L. Schultz, *Mater. Sci. Eng., 97* (1988) 317.
[8] R. Schulz, M.L. Trudeau and A. van Neste, *Mater. Sci. Eng., A134* (1991) 1354.
[9] M.L. Trudeau, R. Schulz, L. Zaluski, S. Hosatte, D.H. Ryan, C.B. Doner, P. Tessier, J.O. Ström-Olsen and A. Van Neste, *Mater. Sci. Forum, 89–90* (1992) 537.
[10] M.B. Bever, D.L. Holt and A.L. Titchener, *Prog. Mater. Sci., 17* (1973) 1.
[11] P. Tessier, L. Zaluski, Z.-H. Yan, M.L. Trudeau, R. Bormann, R. Schulz and J.O. Ström-Olsen, *Mater. Res. Soc. Symp. Proc., Nanophase Nanocomposite Mater., 289* (1993) 209.
[12] E. Hellstern, H.J. Fecht, Z. Fu and W.L. Johnson, *J. Appl. Phys., 65* (1989) 305.
[13] H. Gleiter, *Prog. Mater. Sci., 33* (1989) 223.
[14] R. Kirchheim, T. Mutschele, W. Kieninger, H. Gleiter, R. Birringer and T.D. Koble, *Mater. Sci. Eng., 99* (1988) 457.
[15] T. Mutschele and R. Kirchheim, *Scr. Metall., 21* (1987) 1101.
[16] G.J. Thomas, R.W. Siegel and J.A. Eastman, *Scr. Metall. Mater., 24* (1990) 201.
[17] J.O. Ström-Olsen, D.H. Ryan and Z. Altounian, *Mater. Sci. Eng., A133* (1991) 403.
[18] W. Wagner and H. Horner, *Adv. Phys., 23* (1974) 587.
[19] Yuh Fukai, *The Metal–Hydrogen System*, Springer, Heidelberg, 1993.
[20] U. Buchenau, H.R. Shober, J.-M. Welter, G. Arnold and R. Wagner, *Phys. Rev. B, 27* (1983) 955.
[21] G. Knuyt, L. De Schepper and L.M. Stals, *Mater. Sci. Eng., 98* (1988) 527.
[22] H.S. Chen, *J. Appl. Phys., 49* (1978) 3289.
[23] P.M. Richards, *Phys. Rev. B, 30* (1984) 5183.
[24] R. Griessen, *Phys. Rev. B, 30* (1983) 7575.
[25] R. Kirchheim, *Acta Metall., 29* (1981) 835.
[26] J.A. Eastman, L.J. Thompson and B.J. Kestel, *Phys. Rev. B, 48* (1993) 84.
[27] R.J. Wolf, M.W. Lee and J.R. Ray, *Phys. Rev. Lett., 73* (1994) 557.
[28] R. Lasser and T. Schober, *Mater. Sci. Forum, 31* (1988) 39.
[29] G. Sandrock, S. Suda and L. Schlapbach, *Topics Appl. Phys., 67* (1992) 197.