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Mechanical instability in amorphous metal alloys–hydrogen systems

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Abstract

In the present study, we report the hydrogenation and deuteration of amorphous iron-, cobalt- and nickel-based alloys. Hydrogenation of these materials leads to a multiple acceleration of the creep deformation at room temperature. After hydrogenation, an almost full reduction of the shear resistance was observed on the iron-based alloys. The physical and mechanical characteristics of the alloys return to the initial values after a complete evacuation of hydrogen from the samples.

Keywords: Amorphous materials; Hydrogen storage materials; Elasticity; Magnetic measurements

1. Introduction

In a recent past, the interaction of hydrogen (or deuterium) with Fe-, Co- and Ni-based amorphous metal alloys (AMA) was systematically investigated [1–3]. For example, it is shown on Fig. 1 that hydrogenation of AMA in the creep mode under loads that constitute 0.1–0.3 of the yield stress, activates the deformation of the alloys. The creep deformation was investigated immediately in hydrogenation process, at room temperature.

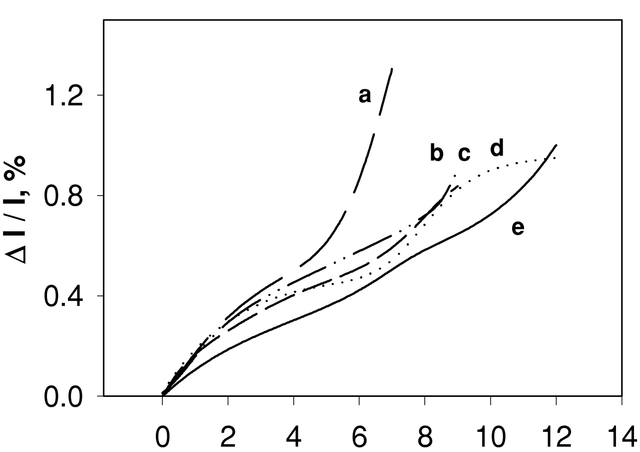

Fig. 1. Dependence of the hydrogenation time ($i_c = 100$ A m^{-2}) on the deformation of alloys. $\sigma = 110$ MPa (σ = tension stress): (a) $Fe_{81}B_{14}Si_5$; (b) $Fe_{65}Co_{20}Si_5B_{10}$; (c) $Fe_5Co_{58}Ni_{10}Si_{11}B_{16}$; (d) $Fe_5Co_{70}Si_{15}B_{10}$; (e) $Co_{83}Ni_{6.4}Si_{8.4}B_{2.2}$.

However, the sample had not been charged with hydrogen the value of the creep deformation measured was about zero. It is important to mention that it is not the presence of hydrogen in the samples but rather its continuous charging with hydrogen that is responsible for the increase of the creep deformation.

At any stage of creep, the deformation process interrupts when the charge with hydrogen procedure is stopped. Prolonged hydrogenation leads to disproportion of the alloys. By studying the deformation response of Finemet-type alloys, a solid state physics phenomenon that has never been reported before was evidenced. During the charge with hydrogen procedure, the reversible loss of shape was found out alloy $Fe_{78}Nb_{3.5}Cu_1B_4Si_{13.5}$ (known as ‘Finemet’). The sample of Finemet alloy charged of hydrogen lose their load carrying ability and become shapeless with shear modulus values almost zero. According to these characteristics, the state of the alloy appearing after hydrogenation was called a quasi-liquid state [1,2].

2. Mechanical properties

In the present work we have studied Fe and Co-based alloys produced by melt spinning in the form of a ribbon.

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The thickness of the ribbons was varied from 20 to 40 μm for different samples.

The samples were subjected to a treatment of two different types: the first one was the 30 min annealing in vacuum at different temperature; the second one was an electrolytic hydrogenation of the samples in acid electrolyte at room temperature. The hydrogenation time was varied from 5 to 15 min. The samples were serving as a cathode and a platinum wire was chosen as an anode. At first, a sample of Finemet alloy was fixed as a cantilever. Under hydrogenation one was transformed and exhibits the so-called quasi-liquid state as shown on Fig. 2.

In order to quantify the characteristics of the deformation several parameters were used such as *d*, a measure of the ratio of the vertical displacement *x* of the free end of the sample to its initial length *L*. It was established that the variation of the *d* parameter induced by hydrogenation was markedly dependent on the extrinsic quality of the surface resulting from the fast quenching technique. In fact one has to distinguish the glassy from the matt surface of a ribbon sample, the former (latter) being that who was in contact (no contact) with the cold wheel during the fast quenching procedure. The variation of the *d* ratio upon hydrogenation was found to depend essentially if the glassy (matt) side is facing up (down): the shape loss effect appears to be much stronger when the glassy surface of the Finemet sample is facing up (Fig. 3). Similar results were as well obtained for $Fe_{78}Ni_1B_{12}Si_9$ and $Fe_{5.5}Co_{71}Ni_{11.7}B_{3.4}Si_{8.6}$ samples. Furthermore, it is worth to note that the variation of the *d* parameter is a two-step process as observed for all the alloys presently under investigation. Moreover, the *d* parameter changes faster during the initial period of hydrogenation than during the second ending phase.

The virtually loss of elasticity after completing the hydrogen load can not be interpreted in terms of Gorskii's effect only. In the later effect which is of diffuse relaxation type, a hydrogen treated sample retains its characteristic elasticity properties. Furthermore, using the hydrogen coefficient of diffusion $D_H = 10^{-12}$–10^{-10} $cm^2\ s^{-1}$ of iron based AMA samples of 30 μm thickness, we evaluate the relaxation time of elastic properties. It is found higher by two to three orders of magnitude for the effect of reversible loss of shape than that calculated from the Gorskii's effect. The effect of reversible loss of shape doesn't explain the effect of dislocation mobility because in our case we have a fully reversible deformation.

A natural aging time t_a of the alloy can be defined as the time elapsed since the manufacture of the material; it influences the characteristics of the AMA deformation process under hydrogenation. Effectively, it was observed [4] that the deformation of the alloys during the hydrogenation procedure, and after subsequent storage periods in atmosphere, essentially depends on the age of the alloys. The sample fastening method of a glassy (matt) side is facing up becomes insignificant when t_a increases up to 1–1.5 years. Based on this fact, we believe that upon hydrogenation of recently produced alloys, three different features can be well observed as to occur simultaneously. These are the reversible loss of shape, the relaxation of the stresses appeared during quenching and the relaxation of the free volume [5].

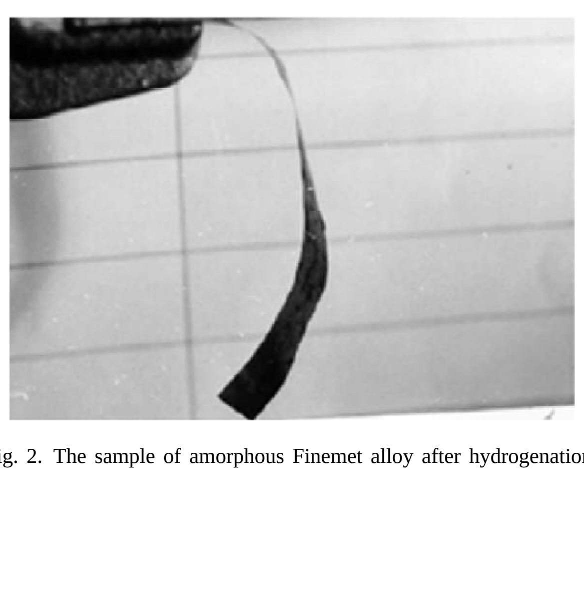

Fig. 2. The sample of amorphous Finemet alloy after hydrogenation.

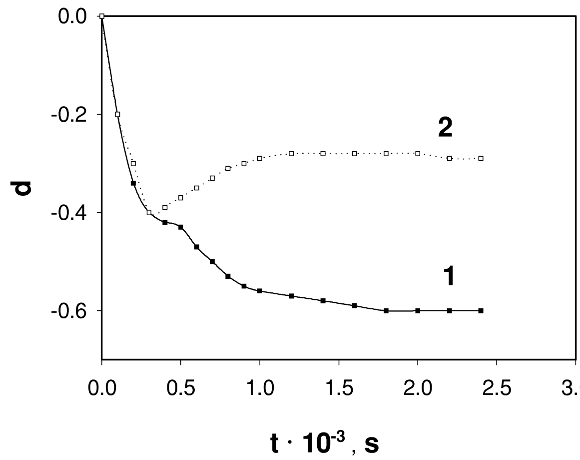

Fig. 3. Behaviour of amorphous alloy under hydrogenation: (1) glassy side is facing up; (2) matt side is facing up.

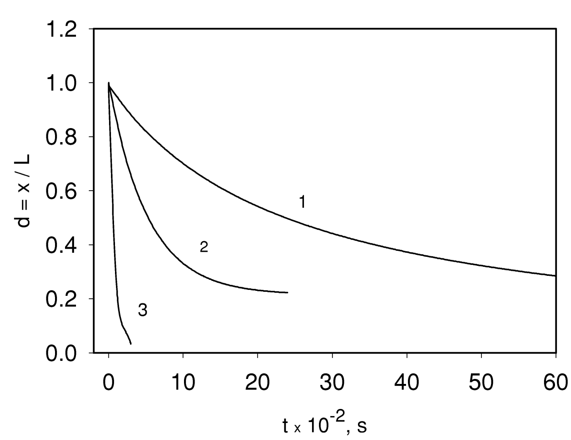

Fig. 4. Dependence the parameter *d* on temperature (1) 60 °C, (2) 100 °C, (3) 150 °C and duration of annealing.

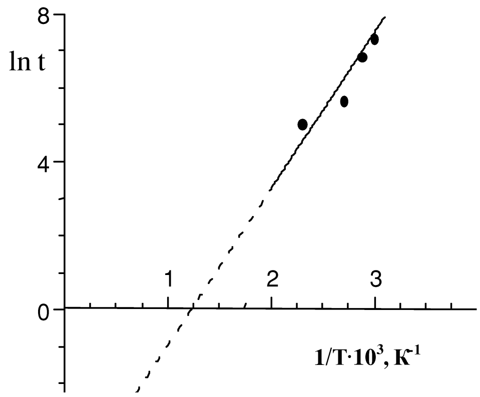

Fig. 5. The data of Fig. 4 for parameter d = constant.

The alloys recover their elastic properties within 10–15 min after the end of hydrogen charging. After 60–80 h of storage, the samples return to their initial state (which is horizontal position for the sample fixed as a cantilever). Cycles of hydrogenation–relaxation process leads to the disproportion of the samples, since hydrogenation induces changes in both topological and short-range orderings. Besides, we made an estimate of the activation energy E_a related to the restoration process of the alloys. For the Finemet type alloys this value was found to be E_a = 0.4±0.1 eV (that correlate with Refs. [6–8]), with a characteristic time of 10^{-2} s. These quantities have been extracted from the experimental results presented in Figs. 4 and 5.

The complete recovery of elastic properties after hydrogenation may be interpreted in terms of a slow transition occurring in the AMA, from one equilibrium state to another one. The rate of this transition seems likely controlled by diffusive mobilities of both hydrogen and matrix atoms [4,9]. The mechanical instability resulting from (accompanying this) this transition appear very similar to the loss of the load-carrying ability of the materials upon phase transformations when submitted to stress fields, i.e. effect of transformation-induced plasticity [10].

3. Magnetic properties

We established that hydrogenation of the alloys markedly influences the typical spectrum of Barkhausen noise as seen on Fig. 6. Finemet alloys is a magnetically softened material. After hydrogenation the intrinsic value of coercive force has increased.

At room temperature, during the period of storage of

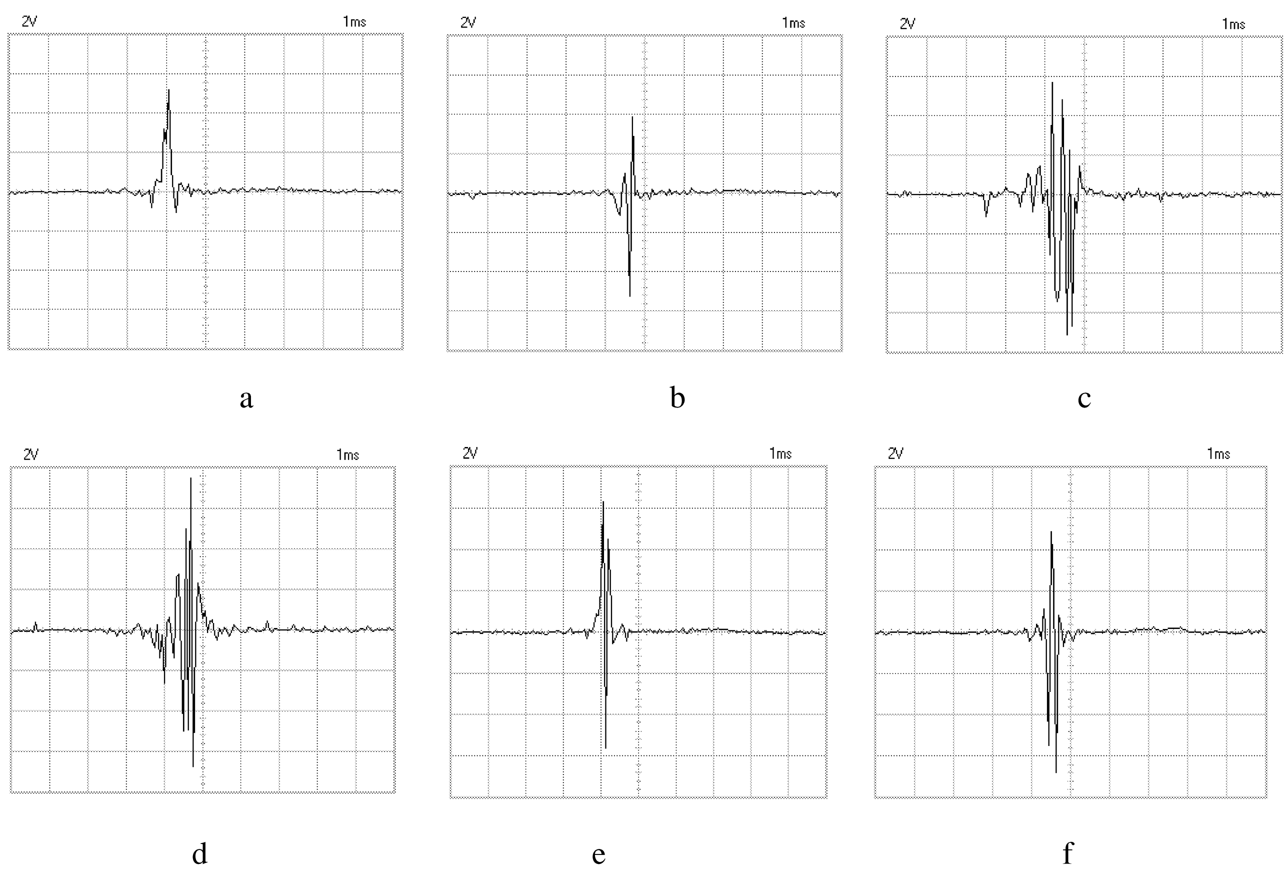

Fig. 6. The structure of Barkhausen jumps for a cycle of magnetic reversal of $Fe_{78}B_{12}Si_9Ni_1$ alloy. Two independent experiments are shown for each case: (a) and (b) initial state, (c) and (d) after charging with hydrogen, (e) and (f) after annealing at 400 °C.

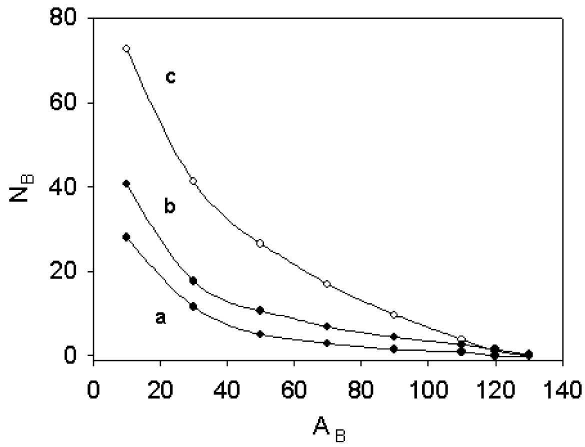

Fig. 7. Behaviour of the magnetic state of a $Fe_{78}Ni_1B_{12}Si_9$ alloy: correlation between the number of Barkhausen jumps N_B after 50 reversal cycles and the amplitude A_B of the jumps expressed in arbitrary units. (a) Initial state, (b) annealing at 400 °C, (c) just after hydrogenation.

hydrogenated samples, the magnetic characteristics of the alloys gradually return to the initial state. However a complete recovering of the initial properties is achieved only after annealing of the alloys at 120 °C for 30 min under neutral atmosphere. Hydrogenation of the ribbons does not change significantly the amplitude of the Barkhausen jumps as seen on Fig. 6c,d. However, an increase of the range of magnetic fields in which occur the Barkhausen jumps is noticed as reported in Fig. 7.

Moreover, it was determined that depending on the time of hydrogenation saturation, a change of number of Barkhausen jumps operates via a two steps process. This phenomenon is fully correlated with the changes of the elastic properties of hydrogenated on one side and deuterated alloys in the other side [3,11,12]. It is worth to note

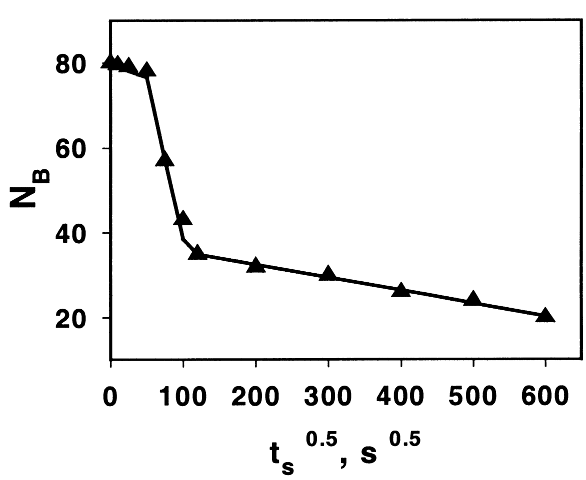

Fig. 8. Dependence of the number of Barkhausen jumps, after application of 50 cycles of magnetic field reversal, versus the square root of storage time t_s.

that the Barkhausen jump—storage time (t_s) data as represented versus the number N_B of Barkhausen jumps—$t_s^{0.5}$ allows to directly evidence a two-site effects as seen on Fig. 8. This indicates that the relaxation process operates in two well-identified steps. However, both steps are fully controlled by the rate of evacuation of hydrogen isotopes from the AMA, with a linear time-dependence of $\sqrt{t_s}$-type.

4. Conclusion

The elastic properties of amorphous alloys (AMA) are found to be reversibly changed by hydrogenation.

A complete loss of the elastic properties—so-called effect of reversible loss of shape—is observed upon hydrogenation of Finemet-type alloys.

Hydrogenation of Finemet-type alloys leads to reversibility change of some magnetic properties of AMA.

Acknowledgements

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