

The nature of deformation effects in metal–hydrogen systems

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Abstract

The hydrogen effect on mechanical properties of metals and alloys is usually studied after ending hydrogenation. In our work we used a new methodological approach. The investigation of metals took place directly during hydrogenation. The measurements of shear modulus, electrical resistivity, mechanical properties (creep deformation, stress relaxation, mechanical after-effect) were accompanied by X-ray diffraction, SEM, DCS analysis and magnetic investigations. The relative complexity of our results as recorded from pure metals and alloys either in amorphous or in crystalline state underline the various changes of the structure of the materials during hydrogenation. Then, hydrogen-activation of the phase transformations already existing as alloy characteristics (e.g. B2 \leftrightarrow B19' in TiNi) can be easily induced. Charging with hydrogen the crystalline and amorphous compounds leads to a marked acceleration of the deformation effects related to modification of plasticity. It is worth to mention that these behaviors occur directly and uniquely under the hydrogenation process of the materials. The main reason for such types of effects is the decrease of the shear modulus in local regions of the alloy when reached by hydrogen.

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1. Introduction

More than 20 years ago, analysis of the mechanical properties of pure metals under electrolytic loading with hydrogen has retained specific attention, e.g. of Japanese groups [1–3] working more specifically on monocrystalline and polycrystalline iron. For such an electrolytic processing, the investigated iron sample was taken as the cathode while the used anode was made of platinum. Interestingly, unexpected results in terms of mechanism of deformation under loading were pointed out as illustrated on Fig. 1. During the plastic tensile deformation process initiated at the beginning of hydrogen charging, a very rapid decrease of the flow stress was observed. After stopping the hydrogenation process, a measurement of the strain-hardening traces has revealed that the level of stress has returned exactly to the original state of unloaded metal. From these pioneering but important works [1–3], it was concluded that the interaction of hydrogen with the dislocations was responsible for the typical mechanical

behavior generated under both hydrogen loading and application of external strain simultaneously, as illustrated in Fig. 1. However, further and renewed experiments have been devoted to these phenomena, leading to propose alternative explanations for the deformation processes resulting from hydrogen loading [4–6].

The present study is mainly addressed to the role of the shear modulus as a main parameter to question as responsible of typical metal deformation under the simultaneous loading of hydrogen and development of stress field.

2. Experimental results and discussion

2.1. Brief review of main distinct features that characterize deformation effects

More extensively, mechanical aspects of the behavior of metals and alloys in many forms, such as crystalline, nanocrystalline, even amorphous materials have been examined under the combined effects of stress torsion field and hydrogen charging. Then, systematic experiments and anal-

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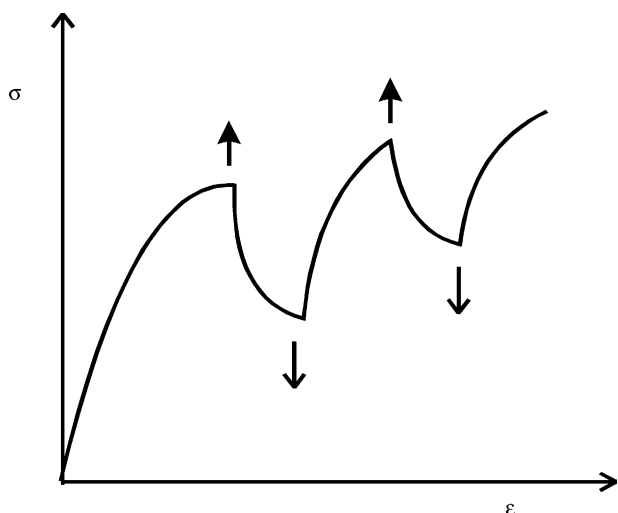


Fig. 1. Scheme of a strain-hardening trace of a monocrystalline and pure iron foil under hydrogenation. Arrows mean: \uparrow , the start; \downarrow , the end of hydrogenation, respectively.

yses were addressed to develop either direct (creep, stress relaxation) or reverse mechanical after-effects up to large amplitudes of strength [4]. In the past, the effects of hydrogen on the mechanical properties of metals and alloys were usually but very systematically studied after ending the hydrogenation process, typically for ex situ experiments. For the present work, we have used a new methodological approach in which the analysis of the metal properties took place directly during hydrogenation. So this is the main peculiarity of our in situ investigations.

The process here considered, e.g. the transformation of a structure inclined to deformation, is realized at room temperature where the mobility of the metal atoms must be considered to be definitively null. In this case the deformation effects observed on the metal arrangement are the unique result of the presence of hydrogen in the metal or the alloy. It is another aim of these studies to analyze how the mechanisms related to a given deformation can reveal insights in which will result a new structural arrangement. For example, the nucleation process and the precipitation of a given hydride take place at room temperature as the direct result of the increasing hydrogen concentration in the material. This is quite far from the conditions and the mechanisms are different to those involved and resulting from thermo-cycling a sample loaded with hydrogen.

In most cases, the deformation process is the result of a phase transformation based on shift mechanisms. A third peculiarity of our investigations is to better understand the cooperative mechanism associated with the phase transformation, since the structural changes associated with the hydrogen loading result from cooperative displacements of the matrix metal atoms. It is worth to note that such a type of deformation is labeled as a martensitic type transformation. In this context, our investigations aim at defining the transition exactly as a diffusion-cooperative type of phase conversion.

Hence, the absorption rate of hydrogen controls the kinetic of the phase conversion in which case the operating mechanism of transition is a martensitic transformation.

Additionally, we like to investigate the necessary and sufficient conditions to initiate the deformation process in metal–hydrogen systems. For that, it is worth to consider both the differential parameters that are the gradient of the stress field and the diffusion rate (gradient of concentration) of hydrogen in the sample. The former parameter connects with the torsion deformation coefficient, and the latter parameter is induced and monitored by the electrolytic conditions applied for hydrogen charging. However, the synergistic effects resulting from both the two activating parameters must be considered as deformation responsible. Reference to in situ analyses, we like to underline the general tendency for deformation effects in metal–hydrogen systems caused by the decreasing resistance to shear deformation (as well as shear modulus) induced by hydrogenation. Nevertheless, the intimate mechanisms of the deformation behavior depend on the nature of the materials under experimentation.

Deformation effects caused by hydrogenation are considered here as well as described by the classical model of plastic transformation effect (PTE) earlier proposed by Sauveur [7]. The detailed mechanisms of such types of deformation depend directly on intrinsic peculiarities of the tested materials, e.g. how and when occurs nucleation of the hydride, how the resulting crystalline lattice appears well distinguished from the initial metal arrangement with no direct symmetry relationship. Reference to experiments, here we aim to carry out a more extended classification of the deformation effects, thus successively considering three classes of metal materials known to actively react with hydrogen.

2.2. First type of materials typically with solid solution to metal–hydride transitions

The class of materials we consider first is based on the early transition metals such as Zr, Nb, V, Ta. These elements are well known to form defined metal–hydrides. In such cases the diffusion-cooperative phase transformation occurring in these metals are essentially accompanied by a PTE deformation. The specific phenomenon that takes place in these metal–hydrogen systems, including the formation of a defined hydride, is a hydrogen diffuse redistribution mode in the crystalline metal lattice. Ordering of hydrogen atoms in interstitial sites results in the formation of metal–hydride for this group of materials. The principle that drives hydrogen atoms to fill the interstitial sites of the considered group of metals are the chemical (thermodynamics) parameters, namely the enthalpy ΔH and entropy ΔS of formation of hydrides. The metal to hydride phase transition appears as a diffusion-cooperative type of phase transformation. If the kinetics of such phase transitions are based on diffusion process modes, the relevant mechanism is of martensite type of transformation, meaning that ordering of hydrogen atoms leads to the cooperative shift of metals atoms.

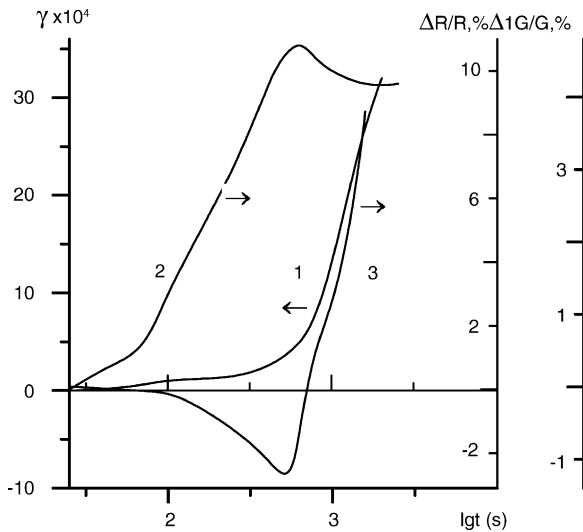


Fig. 2. Creep deformation in vanadium ((1) load is 25 MPa), alteration of the electrical resistivity (2) and of the shear modulus (3) as a function of the hydrogen load duration.

From our studies we have found that saturation metals with hydrogen, namely for the well known cases of specific metals that are V, Zr, Nb, Ta . . . , accelerates the creep deformation (γ) and decreases the shear modulus ($\Delta G/G$) simultaneously and finally increases the electrical resistance ($\Delta R/R$), as reported in Fig. 2. For the starting step of the hydrogenation process, the first part of recording of the hydrogen loading mimics fairly well that of the increase of the electrical resistance signal. This stage corresponds well to the development of a disordered solid solution MH_ϵ of hydrogen in metal. When approaching the border limit of the $\alpha \rightarrow \alpha + \beta$ phase transition, a decrease of the shear modulus is observed and simultaneously the creep deformation starts. Nuclei of a specific hydride phase are initiated first and their growth, thanks to the induced stress gradient, can be understood in terms of acceleration of the creep deformation process. X-ray diffraction data we recorded confirms exactly the previous analysis as developed here above.

Procedures consisting of the measurement of the creep deformation and its behavior during hydrogen loading have been developed quite successfully to investigate metal–hydrogen systems, e.g. the Nb–H phase diagram. First, it was evidenced that the deformation effects reveal peculiar not only of the $\alpha \rightarrow \alpha + \beta$ type of conversion. Thus, it was demonstrated that the transition $\alpha \rightarrow \alpha' + \alpha$ obeys to the same type of effect as shown in Fig. 3. The clusters of the newly initiated hydride resulting from the continuous hydrogen load were found oriented with respect to the applied stress field. Consideration to several arguments we propose that the transformation of the metal–hydride phase M_xH_y following the decomposition of the MH_ϵ solid solution is likely a spinodal transformation. Such a process of M–H transformation appears quite comparable to the bainitic transformation of austenite in steels, thus resulting here in the generation of metal–hydride crystals. This effect was already pointed out

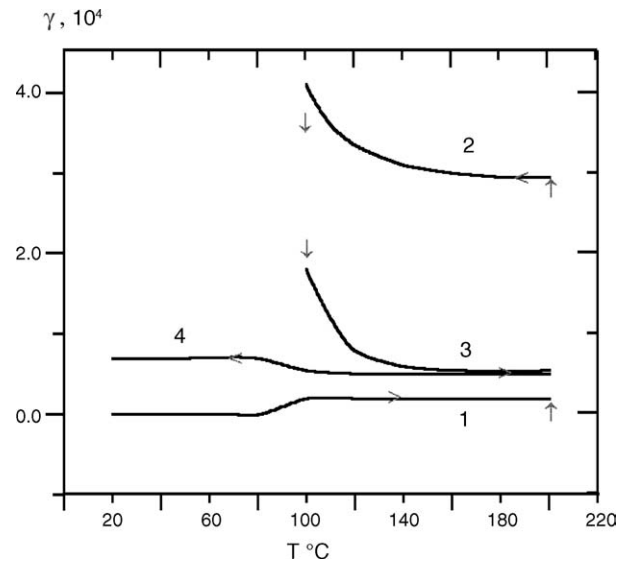


Fig. 3. Thermal cycles recorded for a Nb–H_{0.2} sample as a function of temperature during heating and cooling down. (1) Heating without stress load; (2) cooling down under load for 18 MPa; (3) heating without stress load; (4) cooling down without stress load.

to take place in the Pd–H system. The results here obtained lead to believe that the deformation behavior as found in the Pd–H system in the vicinity of the spinodal decomposition is to relate with distortions originating from H-enriched clusters. Their specific mode of growth, i.e. rate and direction, are determined by the strength and the orientation of the applied external stress field.

2.3. Second type of materials exhibiting displacive phase transformations

The second group of materials to consider here comprises alloys where a martensitic phase transformation occurs without any hydrogen loading. A corresponding typical type of these alloys can be found in alloy systems related to the binary TiNi. These types of materials exhibit a phase transformation well known as the shape memory effect. Here, it is to underline first that hydrogenation leads to a new series of sequences of the successive phase transformations [8,9]. Thus, it appears that new structural forms can be stabilized, different to those typical for the alloys, e.g. at room temperature (it is temperature of saturation with hydrogen). However we have found that a phase transformation as initiated by hydrogen loading may be accompanied by distortion effects. Besides, there are many evidences that a net softening of the shear modulus has anticipated this process of global transformation [10,11]. Hydrogen has initiated a larger softening of the shear modulus.

2.4. Third type of materials based on short range metal ordering

The classes of materials we consider here cover alloys basically possessing short-range order only, such as either

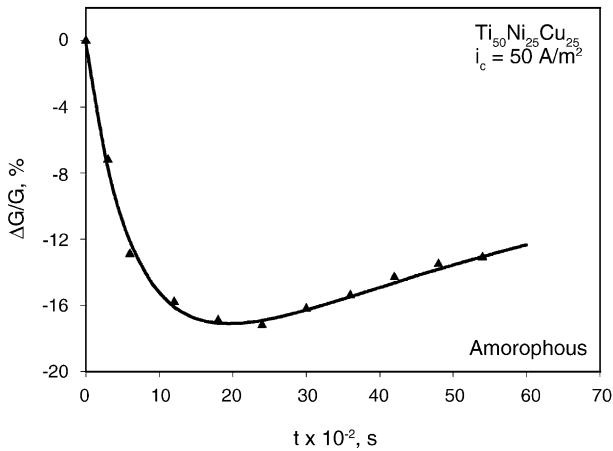


Fig. 4. Alteration of the shear modulus as a function of the electrolytic H-charging for a $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon in amorphous state.

amorphous or alloys exhibiting a superfine microstructure e.g. nanocrystalline alloys. In both cases, it appears that the deformation effects are more intensive when compared to the above discussed materials of the first and the second types. The creep deformation induced in the third type of alloys is from 1 to 2 orders of magnitude larger as compared with crystalline materials. For example, in the amorphous $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ alloy, a dramatic drop of the shear modulus was measured as shown in Fig. 4. Besides, it was found that saturation with hydrogen of $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ in a nanocrystalline form leads to the generation of a new type of structural state as shown in Fig. 5. A simple and reasonable analysis can be provided. When hydrogen atoms penetrate in the structure of the third class of less ordered alloys, it rapidly decreases the interaction forces bonding the metal atoms. Then, metastable

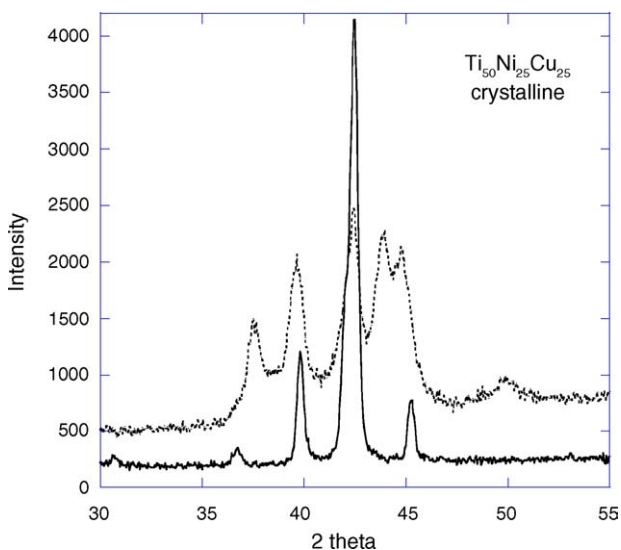


Fig. 5. X-ray diffraction data (λ_{Cu} , K_{α}) as recorded on a $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ alloy in crystalline state: black line, before hydrogenation (B19 phase); dot line, after hydrogenation (B2+B19+B19' phases). The temperature to initiate a martensitic transformation is $T \sim 60^\circ\text{C}$.

alloys appear more effectively predisposed to synergistic deformation effects.

3. Conclusion

1. A dramatic decrease of resistance to a shear deformation was found to occur in open thermodynamic metal–hydrogen systems simultaneously subjected to H-loading and to internal or external stress fields. For metals and alloys developing a martensitic-type of phase transformation under hydrogenation, the main cause of PTE deformation result from a corresponding decrease of the shear modulus.
2. Even if the hydrogen loading induces effects smaller than the yield stress of the considered metals or alloys, it can lead to increase any potential deformation such as creep deformation, stress relaxation. . . under the simultaneous action of both gradients of a stress field and that resulting from hydrogen flowing.
3. Specific mechanisms to achieve such types of deformation modes are made clear for metals and alloys. There are well identified cases to take into consideration:
 - a hydride conversion that regulates the ordering hydrogen atoms in interstitial sites;
 - from a spinodal decomposition;
 - via a martensitic type of phase transformation;
 - a hydrogen-induced conversion in systems with short-ordering.

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