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DYNAMICS OF STRESS INDUCED HYDRIDE FORMATION IN VANADIUM*

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Introduction

In large amplitude oscillations of a reed sample, linear anelasticity is no longer valid (1,2). Under certain conditions such as crystallographic orientation and/or temperature, the nonlinear characteristic of twinning or phase transitions triggered by large amplitude oscillations is manifested by the occurrence of automodulation (2,3,4). The automodulation phenomenon is said to occur whenever the amplitude of oscillation varies periodically with time around a steady state amplitude, even though the externally applied driving force is kept constant. This phenomenon has been investigated for twinning (2,3) and martensitic transformation (4) and interpreted in terms of the nonlinear anelasticity theory developed by the authors (1,2). Automodulations have also been observed in the course of an internal friction study of α -titanium near the β transformation temperature (5).

This letter describes the occurrence of automodulation in a V-H alloy and how it relates to the hydride precipitation in the alloy. The automodulations were triggered by varying applied stresses at temperatures up to about 60°C above the solvus temperature. It will be shown that this is directly related to the effect of stress on the precipitation of the β -phase.

A few relationships will be useful to discuss the experimental results. The effect of stress on the solvus (6) may be written as

$$\frac{\alpha\Delta V_{\alpha-\beta}}{RT} = k_1 - \ln C_H - \frac{\Delta H_s}{RT}, \quad (1)$$

where $\Delta V_{\alpha-\beta}$ is the volume change which accompanies the α - β transformation; C_H is the terminal solubility of hydrogen in vanadium expressed as $[H]/([V] + [H])$; ΔH_s is the heat of solution of hydrogen in vanadium saturated with respect to vanadium hydride; and k_1 is a constant.

The external driving force, D , is proportional to the stress, σ , on the sample and it is expressed as

$$\sigma = k_2 D \quad (2)$$

where k_2 is a constant. The combination of equations (1) and (2) gives

$$D/RT = K_1 - K_2/RT, \quad (3)$$

where K_1 and K_2 are constants given by

$$K_1 = (k_1 - \ln C_H)/k_2 \Delta V_{\alpha-\beta}$$

and

$$K_2 = \Delta H_s / k_2 \Delta V_{\alpha-\beta}.$$

The heat of solution ΔH_s can now be calculated from the expression,

$$\Delta H_s = \frac{K_2}{K_1} \cdot (k_1 - \ln C_H), \quad (4)$$

and the solvus temperature at zero stress is given by $T = \frac{K_2}{K_1 R}$. (5)

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Experiments

The internal friction apparatus used in this study has been described in previous publications (2,7). It is constructed in such a way that the driving force is proportional to the voltage driving the oscillation. The reed specimen was prepared from a polycrystalline vanadium sheet of 99.97% purity (by weight). The 1mm-thick reed was annealed in an evacuated quartz tube at 1000°C for 18 hours, then outgassed at 800°C in a vacuum (4×10^{-6} Pa) for 30 minutes. Subsequently it was hydrogenated by cathodic charging at room temperature in a solution of 10% H_2SO_4 . The hydrogen concentration as determined by weighing was approximately 2.6 at %. The known solubility data (8) indicate a transformation temperature of 36°C. The internal friction data were taken on the 5th cooling cycle during cooling at a rate of approximately 2°K/min and holding an average of 30 minutes at selected temperatures. The eigenfrequency of the reed was approximately 82 Hz.

Results and Discussion

A plot of the internal friction as a function of temperature for a selected driving force can be seen in Fig. 1 (open circles). For this driving force, the automodulation occurs at a threshold temperature of $T_S = 44^\circ C$ and below. As the driving force is increased, the threshold temperature T_S shifts to higher temperatures. As can be seen from Fig. 1 (closed circles), the internal friction has about the same value at all threshold temperatures, which justifies Fig. 2.

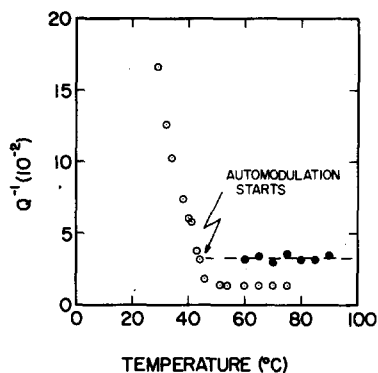


FIG. 1

Internal friction of a V-2.6 at % H alloy as a function of temperature (open circles). The values of the internal friction at the onset of the automodulation at various driving forces (and hence threshold temperatures) are indicated by closed circles.

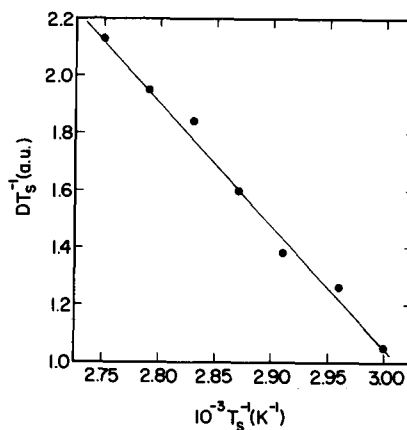


FIG. 2

The reduced threshold driving force D/T_S (in arbitrary units) as a function of the inverse temperature.

Fig. 2 shows a plot of the reduced threshold driving force D/T_S as a function of the inverse threshold temperature. This curve is represented by

$$D/T_S = 1.41 \times 10^3 - .87/RT_S . \quad (6)$$

The heat of solution can now be found by combining this experimental relationship (6) with equation (3). The result is $\Delta H_S = 14.5$ kJ/mole (3.5 kcal/mole, 0.15 eV/atom). In the above calculation, the numerical value of the constant k_1 of equation (4) given by Yoshinari and Koiva (9) was used. This choice is justified on the basis of the close similarity of the

experimental parameters (their cooling rate 1.7°C/min, ours ≈2°C/min; their hydrogen concentration 0.7 at % ≤ C_H ≤ 3.2 at %, ours 2.6 at %). The value of 3.5 kcal/mole compares favorably with their result, 3.4 kcal/mole (9). The transformation temperature obtained from equation (5) is 36°C.

The automodulation frequencies at the temperatures studied did not vary much. They stayed at approximately 0.16 Hz. This is not surprising in view of the fact that the diffusivity of hydrogen in vanadium in the temperature range studied varies less than 10% (10). The significance of the period of the automodulation can be obtained from an estimate of the distance over which the hydrogen diffuses during that period. Using an extrapolation of the known hydrogen diffusion data in vanadium (11) to the present hydrogen concentration of 2.6 at % and combining this value of D_H with the known expression for the period τ of an oscillating reed of thickness d

$$D_H \tau = (d/\pi)^2 \quad (7)$$

yields d = 0.6mm. This value is almost equal to one half the thickness of the reed used in this experiment, 0.5mm. The close agreement suggests strongly that the automodulation reflects the migration of hydrogen from the stressed to the unstressed zones. The observed automodulation has thus one of the characteristics of the Gorski effect. It must be realized, however, that the Gorski effect is a linear phenomenon whereas the automodulation is totally nonlinear in character. The Gorski effect, on one hand, consists of a reversible periodic enrichment in certain areas of the sample. The automodulation, on the other hand, is a manifestation of the reversible periodic precipitation of hydrogen in certain areas of the sample. It can therefore be said that the automodulation represents a Gorski effect for enrichments so large that they exceed the solute solubility.

In conclusion, automodulations have now been observed in conjunction with twins, martensite and hydride particles. In each case the period of the automodulation reflects the reaction time, which makes it a valuable tool for transformation studies.

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