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SHAPE MEMORY EFFECT IN THE VANADIUM-HYDROGEN SYSTEM

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The shape memory effect (SME) has been investigated in alloys of the V−H system at concentrations in the range 0.2-0.5 H/V. It is shown that SME occurs over the entire H/V range indicated, but the magnitude of the stresses, the reversibility of the deformation during heating, as well as the magnitude of the thermal hysteresis depend essentially on the hydrogen concentration. The conclusion is drawn that the transformation in this system is of a martensitic character.

It was shown in [1] that hydrogenated vanadium alloy possesses a shape memory effect which is typical of an alloy with a thermoelastic martensite transformation [2].

The detection of SME in a system in which the transformation cannot be completely classified as being martensitic [3], since it is accompanied by hydrogen diffusion, is of unquestionable scientific interest and deserves more detailed investigation.

The aim of the work reported here was to study the manifestation of SME over a wider range of hydrogen concentrations in the V−H system than in [1]. Moreover, VNM-1 vanadium was selected to be the starting material.

The initial strip vanadium had (according to the certificate) a total content of 0.36% of the impurities Si, Fe, and Al and about 0.007 wt.% of the substitutional impurities (H, C, O, and N). Specimens 4 mm wide and 100-110 mm long were cut from strips 0.5 and 1 mm thick. The specimens were annealed in a vacuum of 10^{-5} torr at 1450-1500°C for 30-40 min by heating with an electric current in a cold furnace. Such annealing not only promotes cleansing of films and contaminants from the surface of the specimen but can also cause carbon to burn up because of the presence of a small amount of oxygen in the atmosphere in the furnace [4]. The grain size after annealing reached 1-3 mm in the middle part, i.e., exceeded the thickness of the specimen.

The specimens were hydrogenated at room temperature electrolytically in a 20% solution of H_2SO_4 in water at a voltage of 3 V (the specimen was the cathode). The quantity of hydrogen absorbed was controlled by the hydrogenation time. The hydrogen concentration was determined in the middle part of the specimen from the weight loss after mechanical tests by the method of vacuum extraction at 700-750°C. The weighing was done on an analytical balance to within 0.1 mg. It was found that after sufficiently long continuous hydrogenation cracks form in the specimen, making it unsuitable for mechanical tests. The appearance of cracks can be avoided and the high mechanical properties can be preserved if the specimen is subjected to intermediate heating to 240-250°C for 5 min after every 15-30 min of hydrogenation. As shown by further investigations, such annealing promotes homogeneous distribution of hydrogen throughout the specimen and this substantially reduces the internal stresses and eliminates crack formation.

The shape memory effect was studied in a vacuum tensile testing machine which permitted a constant load to be maintained while the specimen was being cooling and heated. The elongation of the specimen during the testing was measured with a cathetometer from fiducial lines previously drawn on the specimen 60 mm apart to within ±0.003 mm. The temperature of the specimen was measured with a Chromel−Copel thermocouple with an accuracy of ±1°. During the heating−cooling process the length was measured every 10-20°.
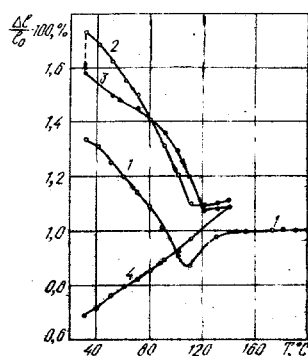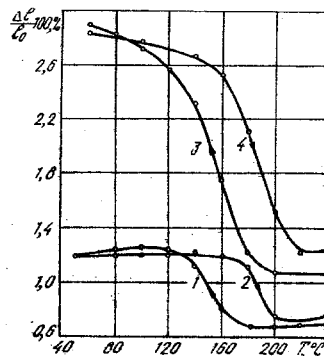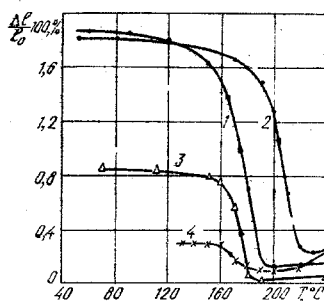
Fig. 1

Fig. 2

Fig. 3

Several experiments were conducted on each specimen with cooling under various loads, starting at 2 kg/mm². After each load the specimen was heated in the unloaded slate to 240°C with the elongation being measured during the heating process.

Figure 1 gives the results of the experiment for a specimen with a hydrogen concentration H/V = 0.2. (The numbering of the curves here and below corresponds to the sequence in which the experiment was conducted.)

Appreciable deformation during cooling under a load is observed only at loads $\sigma > 0.5\sigma_y$ (σ_y is the yield point at 240°C) ($\sigma = 9.8$ kg/mm² for curve 1 and $\sigma = 12$ kg/mm² for curve 2). Deformation appears at 100-120°C and grows right down to room temperature. During heating without a load (curve 3) reverse deformation (SME) is observed, leading to reduction of the length of the specimen. This deformation ends at 10° above the temperature at which deformation begins during cooling, i.e., there is a thermal hysteresis.

About 15-20% of the deformation accumulated during cooling is not restored. The magnitude of the irreversible deformation increases as the load grows during cooling. With multiple cycling the magnitude of the stored deformation remains practically constant in each cycle. And so does the magnitude of the irreversible deformation, which leads to the gradual elongation of the specimen. Curve 4 in Fig. 1 was obtained when the specimen was cooled without a load and it reflects the change in volume during cooling [1]. Although spontaneous elongation is not observed during cooling without a load, the cooling curve does not coincide with the initial heating curve, as has already been noted in [1].

With an increase in the hydrogen concentration the temperature at which deformation begins during cooling under load rises and is ~190°C for a concentration of 0.4-0.5 H/V. The width of the hysteresis loop increases to 30-35° (Fig. 2) while the temperature range in which the deformation of the specimen becomes narrower: for 0.4 H/V it is ~90° (Fig. 2, curve 1 − $\sigma = 2.2$ kg/mm²; curves 2, 4 − heating without load; curve 3 − $\sigma = 5.5$ kg/ mm²) while for 0.5 H/V it is ~40° (Fig. 3).

The magnitude of the irreversible deformation essentially depends on the magnitude of the load during cooling (Fig. 2) and on the thickness of the specimens. In specimens 1 mm thick practically total reversal of the deformation during heating occurs in the unloaded state if the load during cooling does not exceed the critical value σ_{cr}. When σ_{cr} is exceeded, irreversible deformation is observed to grow as the load goes above σ_{cr}. The value of σ_{cr} decreases as the thickness of the specimens decreases.

At a hydrogen concentration ~ 0.5 H/V we can observe reversible SME which manifests itself in spontaneous deformation of the specimen during cooling without a load (curve 3 in Fig. 3). If the specimen had been
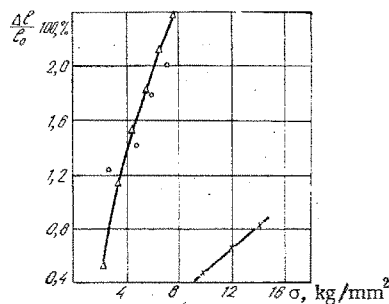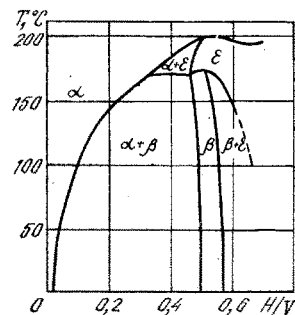
Fig. 4

Fig. 5

previously cooled at a load of 4.8 kg/mm² (curves 1 and 2). The magnitude of the deformation in this case depends on the preliminary load. If it is higher than σ_{cr} (6 kg/mm²), then the reversible SME decreases substantially (curve 4 of Fig. 3).

Figure 4 gives the plots of the stored deformation as a function of the load during cooling for specimens of three concentrations. This dependence is almost linear but its slope is different for different concentrations. The specimens with a concentration of 0.4(H/V) (Δ) to 0.5(H/V) ($\bigcirc$) display a high sensitivity to the magnitude of the load while the specimen with 0.2(H/V) ($\times$) has a much lower sensitivity. It must be pointed out that the maximum load which can be applied to the specimen should not exceed the yield point σ_y since at $\sigma \geq \sigma_y$ the specimens were observed to suffer brittle fracture at a temperature below 190°C (for concentrations of 0.4-0.5). Above 190°C the specimens possess the high plasticity which is characteristic of pure vanadium.

As is known [2], alloys which possess shape memory display a superelastic behavior under loading in a certain temperature range or SME under isothermal loading. It is of interest to trace the existence of these properties in the V—H system. Experiments with an isothermal load were carried out on specimens with a concentration of 0.5(H/V). No appreciable superelastic behavior was detected in the temperature range 20-250°C. Deformation which is reversible under heating appears during isothermal loading at temperatures below 190°C down to a temperature at which the rapid growth of deformation during cooling under load (~150°C) stops.

At lower temperatures induced deformation is practically not observed. In specimens with a low concentration of hydrogen a weak SME occurs under isothermal loading over the entire temperature range below the temperature at which deformation begins during heating, right down to room temperature, but only at loads near the yield point of the starting material.

In our view, the existence of SME in the vanadium—hydrogen system has a fairly straightforward explanation. As the alloy is cooled from 220°C, a $\alpha \rightarrow \beta$ transformation is observed (Fig. 5) in accordance with the state diagram [5, 6]. The β phase which is formed (V₂H) possesses a high tetragonality ($c/a \simeq 1.1$) which is due to the ordered arrangement of hydrogen atoms in octahedral interstices [7, 8]. The application of a load during cooling leads to an oriented growth of β-phase domains such that one direction of the axis of tetragonality becomes predominant, and this leads to deformation. In a single crystal with the axis of tension oriented in the $\langle 100 \rangle$ direction 10% deformation can apparently be attained if the tetragonality axis of all the domains coincide with the axis of tension. In a polycrystal the maximum possible deformation will be smaller by the Taylor factor, i.e., about 3.3%. In estimating the stored deformation it is necessary to consider that the transformation is accompanied by volume changes [1], which amount to about 0.5% during cooling from 240 to 20°; this is several times the usual thermal contraction of volume. Taking this effect into account, in the experiment we obtained a stored deformation of 2.8%, which is close to the limiting value.

The differences in the behavior of alloys of different hydrogen concentrations can be explained on the basis of the distinctive features of the state diagram. For a concentration of 0.2 during cooling precipitation of the β-phase should be observed over the entire range of temperatures below 120°C, down to room temperature, according to the solubility curve. In this case, the alloy has a two-phase $\alpha + \beta$ structure at 20°C. In the case of alloys with a concentration of nearly 0.5, under cooling from the temperature of the α-solid solution the alloy passes through the region of the two-phase state, i.e., a transition of the first kind is observed. It is natural to assume that the greatest deformation during cooling under a load is observed in the temperature range in which β-phase domains are formed and grow. The appearance of stored deformation under an isothermal load in this temperature range indicates that the domain boundaries possess good mobility and, conse-

quently, one domains can grow at the expense of other, less advantageously oriented, domains. In the one-phase β-region, however, the possibility of rearrangement of the domain structure decreases substantially; it may be that this requires considerable stresses, which cannot be attained during tension.

Heating of specimens which had been cooled under load is accompanied by the reverse $\alpha \rightleftarrows \beta$ transformation and the disappearance of the stored deformation. The thermal hysteresis observed in this case is related essentially to the hysteresis of the $\alpha \rightleftarrows \beta$ transformation as transformation of the first kind. The existence of hysteresis is also observed from the volume effects in the absence of a load. The incomplete recovery of the deformation during heating to the temperature of the α-solid solution is due to plastic deformation which is caused by the relaxation of internal stresses accompanying the $\alpha \rightleftarrows \beta$ transformation. The magnitude of the plastic deformation and, consequently, the degree of shape recovery depend essentially on both the size of the load during cooling and the geometric dimensions of the specimen, particularly its thickness. This permits the assumption that internal stresses arise between variously oriented grains of the polycrystal while the relaxation of these stresses is probably due to the existence of intergrain slippage. This is indicated by such facts at the existence of a threshold stress σ_{cr}, above which irreversible deformation appears, as well as by the higher σ_{cr} in thick specimens in which intergrain slippage is hindered.

Evidently, the existence of unrelaxed internal stresses can be explained by the appearance of a reversible SME during recooling without a load. Relaxation of the internal stresses significantly decreases the magnitude of this deformation.

The distinctive features of SME in the V-H system, which we have considered here, are in general typical of alloys which undergo a thermoelastic martensite transformation. The only difference is the absence of noticeable effects of superelasticity, this being due to the lack of any influence by the stress on the temperature at which the $\alpha \rightarrow \beta$ transformation begins. The $\alpha \rightarrow \beta$ transformation closest to the martensitic type occurs in alloys which are close to the stoichiometric composition V_2H since in this case the concentration of α- and β-phases is practically identical and ordering of hydrogen in the β-phase occurs with the displacement of hydrogen atoms to the nearest octahedral interstices. The process of the $\alpha \rightarrow \beta$ transformation is somewhat different in alloys which are far from stoichiometry (0.2 (H/V). In this case the concentration of α- and β-phases, according to the state diagram, differs markedly and this requires hydrogen diffusion over large distances. The high rate of hydrogen diffusion [8], however, as well as the absence of diffusion processes in the vanadium lattice make the process of the transformation martensitic in this case as well. This is what is responsible for the occurrence of SME over a wide range of concentrations.

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