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Surface modification of V and its H absorption properties

M.-Q. Lü, H.-F. Zhang, Y.-L. Wang and W.-D. Wei
State Key Laboratory of RSA, International Centre for Materials Physics, Academia Sinica, Shenyang 110015 (China)

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Abstract

Through mechanical alloying treatment of vanadium and a little $LaNi_5$, a great number of fine particles composed of $LaNi_5$ and a little vanadium formed on the surface of metal vanadium particles, which resulted in an improvement in the properties of the vanadium particles. For example, the modified V can be activated at room temperature, it possesses much better resistance to oxygen poisoning than unmodified metal vanadium, and after repeated H absorption–desorption cycles no severe pulverization occurred. All these characteristics are favourable for the practical application of vanadium.

1. Introduction

Vanadium can absorb a large amount of hydrogen: the saturation density of hydrogen in vanadium hydride can be high, up to 10.3×10^{22} H atom cm^{-3}, *i.e.* twice as much as that of liquid hydrogen [1], and half of which can be absorbed and desorbed reversibly, so it can be used as a hydrogen storage material. Although the activated metal vanadium can absorb H rather fast, *e.g.* it will be half-saturated within decades of seconds, it is very difficult to complete the first H absorption in vanadium: so-called "activation". A troublesome activation procedure, *e.g.* heating to 300–500 °C can carrying out several absorption–desorption cycles or heating to a very high temperature in ultrahigh vacuum, is required to make vanadium react with hydrogen at an appreciable rate.

Several attempts have been made to activate vanadium at room temperature. A coating method in which a thin layer of noble metal such as Pd or Pt is deposited onto the surface of V has been used [2] to prevent the formation of a stable oxide layer and to lower the activation temperature. Maeland *et al.* [3] reported $V_{1-x}M_x$ alloys which can form VH monohydrides at room temperature and ambient pressure, if the metal element M possesses an atomic radius 5% smaller than that of the V atom, but no further report on the formation of the dihydride VH_2 and reversible hydrogen absorption was given. The activation of hydrogen storage materials is greatly dependent on the surface state, and therefore the surface modification of V metal is a way to improve its activation properties. Generally hydrogen absorption materials are used in powder form. Through mechanical alloying new alloys can be synthesized, so we consider that, if we select properly the kind and amount of the second component, as well as technological parameters, all changes that occur in the mechanical alloying procedure take place only on the surface of the major component. Room temperature activation of TiFe, Nb etc., that are generally difficult to activate, was also achieved by this approach.

In this paper we report the results on mechanical alloying of V with a little $LaNi_5$. The surfaces of V particles were modified by this procedure and exhibited better characteristics. The modified V has come into use in ultrahigh pressure H_2 compressors. The activation of TiFe, Nd etc. at room temperature was also achieved by this approach.

2. Experimental details

Commercial V metal (purity, 99%) was cleaned with 50% HCl aqueous solution. $LaNi_5$ was obtained by melting La metal (99%) and Ni (99.9%) with a chemical stoichiometry of 1:5 in a vacuum induction furnace. The mechanical alloying of V metal and $LaNi_5$ with a composition of pseudobinary alloy $V_{0.99}(LaNi_5)_{0.01}$ was performed in a planetary ball mill. During milling, the sample was under the protection of Ar. About 10 g of mechanical alloyed sample was put in a reactor and then activated at room temperature (17 °C) in pure H_2 with a pressure of 4.0 MPa. The equilibrium characteristics (*P–T–C* curves) were determined by means of H desorption. Each time a small amount of H was desorbed and the amount of desorbed H_2 and the

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change in H_2 pressure in the system was recorded. The property of resistance to O_2 poisoning was determined by means of kinetics measurements after exposure in air, namely determining the change in pressure with time in the H absorption or desorption procedure. The composition, structure, morphology and size distribution of particles were determined by means of an electron microprobe, X-ray diffraction, scanning electron microscopy (SEM) and a particle size analyser respectively. As a comparison, the H absorption properties of V metal activated at high temperature were also measured.

3. Results and discussion

3.1. Morphology and structure

Unactivated V metal does not react readily with H_2 gas at room temperature to form hydride despite the negative free energy change associated with the reaction and the large diffusion rate in the bulk V. The reason for this behaviour is generally believed to be the presence of an oxide layer on the surface of V [4]. The aim of mechanical alloying treatment of V and $LaNi_5$ is to remove the oxide on the surface and to provide a "window" and "path" for H from the surface to the inner region of V particles. Therefore it is important to control the technological parameters of mechanical alloying so that all changes occur only on the surfaces of V particles. Since V metal is tough and $LaNi_5$ is very brittle, during the mechanical alloying the former will become particles of size 0.3–2.0 mm, whereas the latter will become fine particles and bed on the surfaces of the former. This structure can be seen clearly by SEM (Fig. 1(a)). Figure 1(b) shows the morphology after 300 absorption–desorption cycles. No obvious difference between them was observed.

The element composition profile of the mechanically alloyed V particles was determined by an electron microprobe (Fig. 2). Obviously, the surface is composed of La–Ni alloy with a small amount of V, while the inner region is pure V. This means that only the surface states of the V particles were changed and the composition in the inner region remained unaltered. This composition distribution was confirmed further by the energy-dispersive spectrum of the particle profile. In this paper, the mechanically alloyed V is referred to as modified V. The unmodified V is called V metal.

Figure 3 shows the X-ray diffraction patterns of the modified V, $V_{0.09}(LaNi_5)_{0.01}$. The diffraction lines located at $2\theta = 40°$, 60° and 76°, which come from the surface layer of the modified V, correspond to those of V metal. These lines, being not sharp but rather broad, indicate a nanocrystalline structure of this surface layer. The other weaker and broader diffraction peaks correspond to those of $LaNi_5$, indicating a nanostructure of $LaNi_5$.

The above-mentioned structure was observed when the amount x of $LaNi_5$ decreased to 0.003 or increased to 0.03.

3.2. Activation

H_2 gas at 4.0 MPa was introduced into sample chamber at room temperature after the reactor was evacuated (about 1 Pa). The sample absorbed hydrogen slowly and was saturated approximately within *ca.* 20 h; the x value does not have an obvious effect on this procedure. After undergoing 3–5 absorption-desorption cycles the sample can absorb and desorb hydrogen more rapidly; for example, half-saturation was reached within *ca.* 60 s. This means that the sample had been activated. No difference in equilibrium properties and kinetic characteristics between the modified V activated at room temperatures and V metal activated at high temperature was found (see Sections 3.3 and 3.4); the amount of H absorption in both situations reaches the same value, 196 ml g^{-1}.

$LaNi_5$ reduces greatly the energy barrier for dissociation of H_2. Through the mechanical alloying of V and $LaNi_5$ a great number of fine particles of $LaNi_5$ containing a little V form on the surface of the modified V, which provide the necessary catalytic activity for dissociation of H_2 and act as window and path for the entrance of H from the surface to the inner region of

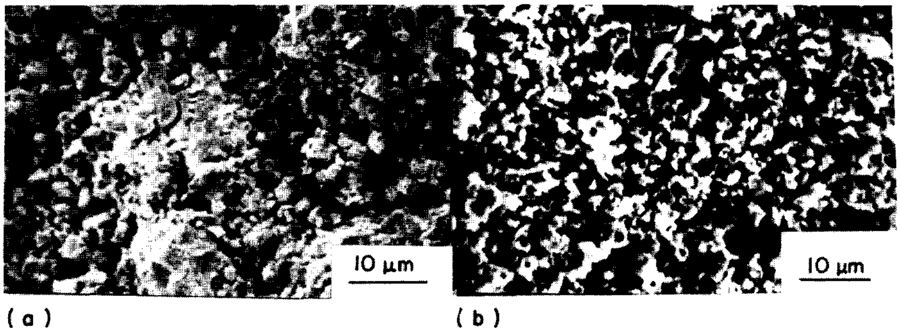

Fig. 1. The morphology of modified V: (a) before activation; (b) after 300 cycles.

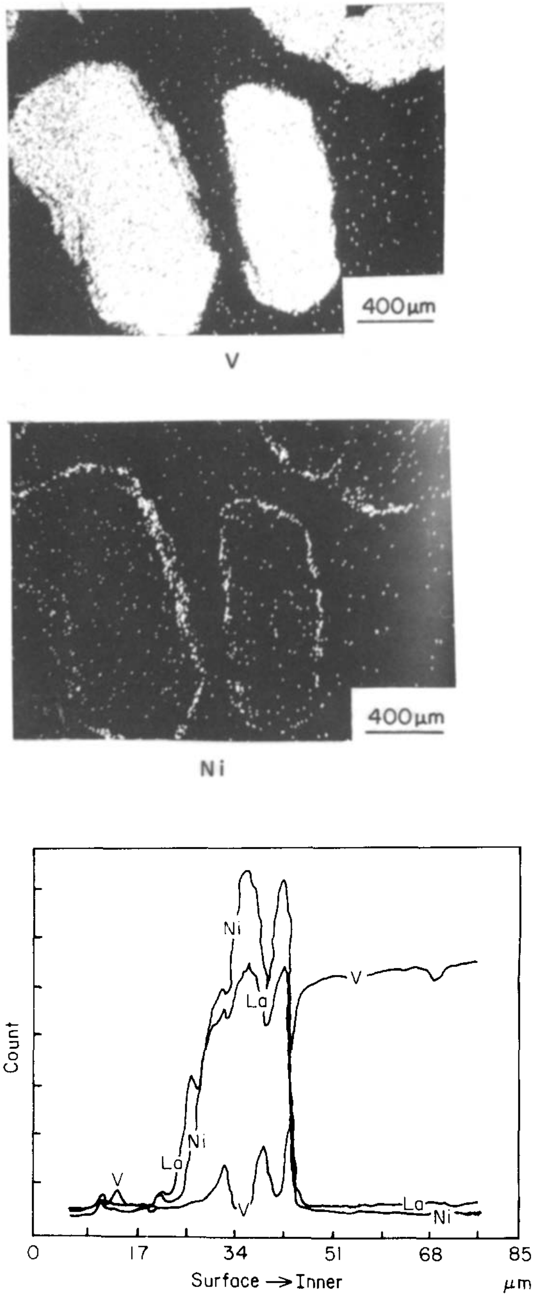

Fig. 2. Electron microprobe element distribution from surface to inner region of modified V.

V. This explains why the modified V can be activated at room temperature.

3.3. Equilibrium properties

The H desorption curves of the equilibrium state (*P–T–C* curves) of both modified V and V metal are shown in Fig. 4. There is no obvious difference between them. This means that the surface modification treatment does not change the equilibrium properties of H absorption in V. A van 't Hoff relation exists between equilibrium pressure and temperature (Fig. 5):

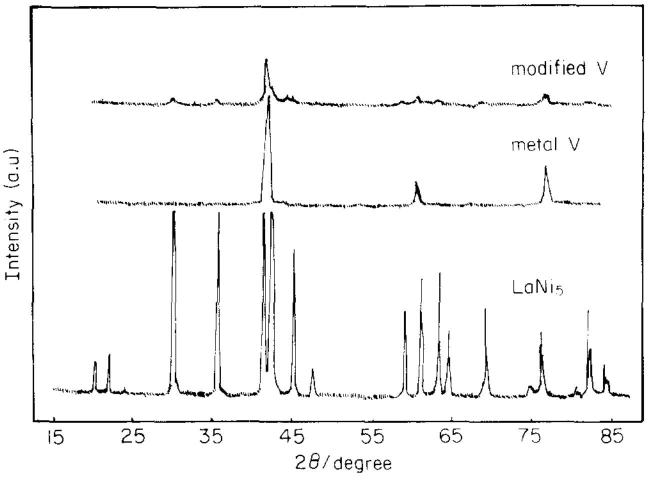

Fig. 3. X-ray diffraction patterns of modified V particles.

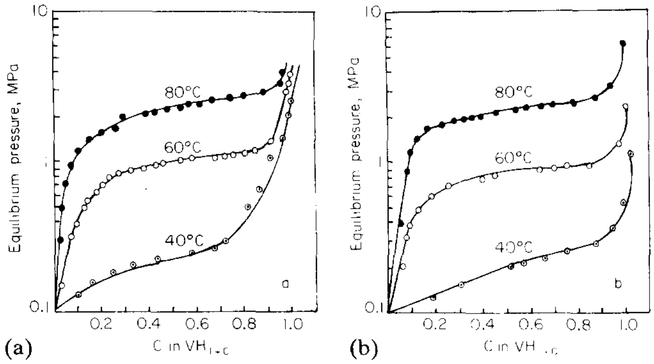

Fig. 4. Desorption isotherms of V (*P–T–C* curves): (a) modified V; (b) V metal.

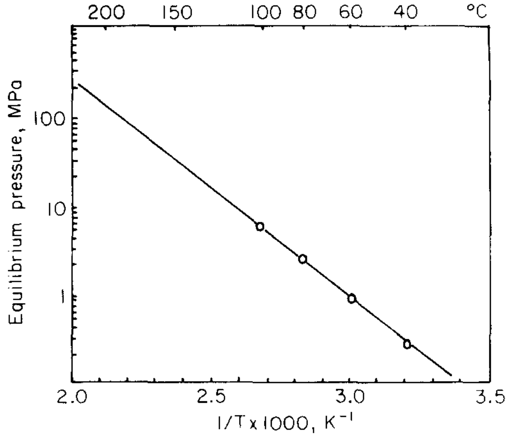

Fig. 5. van 't Hoff relation of modified V.

$$\ln P_{\mathrm{eg}_i} = \Delta S/\mathrm{R}\text{-}\Delta H/RT$$

where ΔS, ΔH and R are reaction entropy, enthalpy and gas constant respectively. From Fig. 6 we have $\Delta H = -9.6$ kcal $(\mathrm{mol}\ H_2)^{-1}$ the same value as in ref. 5. The equilibrium pressure rises sharply with increase in temperature. For example, the equilibrium pressure

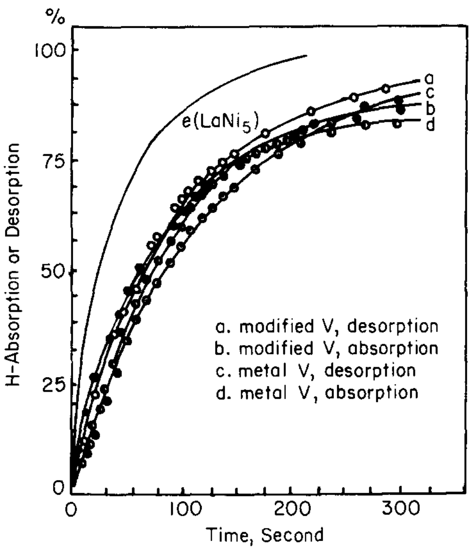

Fig. 6. Kinetics curves of modified V and V metal.

reaches more than 100 MPa at $T = 200$ °C. Thus the modified V is very suitable for producing ultrahigh pressure H_2 with ultrahigh purity.

3.4. Kinetic characteristics

After the activated sample was saturated at room temperature in H_2 under a pressure of 4.0 MPa, the H_2 pressure in the system was quickly reduced to 0.3 MPa. As the equilibrium pressure at this temperature was 0.15 MPa the hydride did not decompose. When the reactor was put in boiling water, the H_2 pressure in the system was raised owing to the enhancement of equilibrium pressure and the decomposition of the dihydride. The relation of pressure and time reflects the change in hydride decomposition with time, which is called the H desorption kinetics curve. Figure 6 shows these curves for modified V (curve a) and unmodified V metal (curve c); the amount of decomposition is given as a percentage. When the reactor was moved from boiling water into cold water, it absorbed H and the pressure of the system was lowered; thus the H absorption kinetics curves were determined (Fig. 6, curves b and d). When the amount of H absorption or desorption was less than 70%, no difference was observed between the absorption and desorption curves for both V materials. Beyond 70%, the absorption rate decreased more obviously than the desorption rate owing to the expansion of the lattice, which needs extra energy to overcome distortion. As a comparison, Fig. 6, curve e, shows the absorption kinetics curve of $LaNi_5$. It is obvious that the surface modification does not change either the absorption curve or the desorption curve of V metal. Although the surface state, *i.e.* the condition of dissociation of H_2 on the surface of unmodified V, was changed by mechanical alloying, the H absorption characteristics were not affected (Fig. 6, curves a and b). In other words, the dissociation of H_2 was not a rate-limiting step during H absorption. This point is further supported by comparison with the H absorption curve of $LaNi_5$. Although the fine particles on the surface of the modified V provide catalytic activity for the dissociation of H_2, the H absorption kinetics of modified V is far inferior to that of $LaNi_5$ (Fig. 6, curves b and e).

As will be described below, after 30 or even 300 cycles of repeated absorption–desorption. the modified V particles do not pulverize obviously, but the activated V metal (unmodified V) pulverizes markedly. This means that a distinct difference in the average size of the particles exists between these two V samples, and therefore the lengths of the diffusion paths of H in these samples would be very different. So it can be deduced that diffusion of H from the surface to the inner region is not the rate-limiting step of H absorption of V. In fact, the rate of H diffusion in the b.c.c. metals is extremely high (about 10^{-5} cm^2 s^{-1} at room temperature) and exceeds the diffusion rates in the f.c.c. and hexagonal metals by several orders of magnitude [6]. Therefore the phase transformation from VH to VH_2 must be the rate-limiting step in the process of H absorption of V, which determines the rate of H absorption in V.

3.5. Resistance to O_2 poisoning

The sample of activated modified V, after several absorption–desorption cycles, was exposed in air for 5 min, and then the H absorption and desorption kinetics curves were determined (Fig. 7), where curve d is that for before the exposure. It is clear that after the exposure

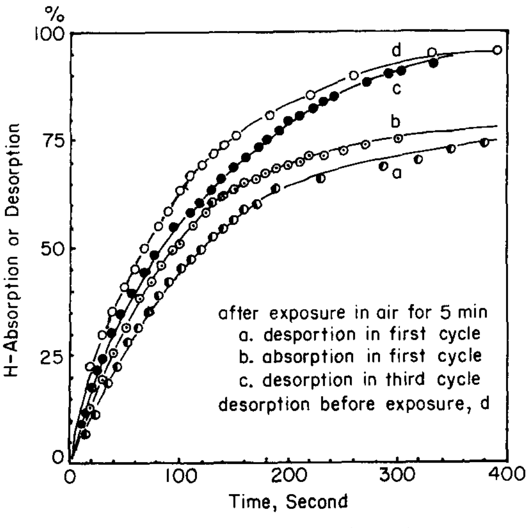

Fig. 7. Kinetics curves of modified V after exposure in air for 5 min.

the rate of H absorption or desorption of the sample decreases significantly, especially in the later stage of H absorption or desorption. Even so, the modified V can still absorb a lot of H at an appreciable rate. This is analogous to the result for $LaNi_5$ exposed to air [7], and much better than that of both V metal and commonly used TiFe. V metal or TiFe, when exposed to air for several minutes, cannot absorb hydrogen unless a reactivation process is used. This inactivation is due to the effect of O_2 on the surface of H-absorbing materials [7, 8].

The difference in resistance to O_2 poisoning results from different surface states. The H absorption of the activated H absorption materials, including both modified V and unmodified V metal, is closely related to the catalytic activity of the surface. The activity of $LaNi_5$ remains to a certain extent after exposure to air for a short time and can be easily restored [7], and thus the modified V maintains its H absorption properties to a certain extent after exposure in air. The catalytic activity of the surface of activated V metal originates from V itself; it loses this activity after exposure to air because of its oxidation and has to be reactivated.

The difference in resistance to O_2 poisoning can also be explained by the so-called "surface segregation" [8].

The kinetic characteristics of the exposed modified V can be approximately restored in several absorption–desorption cycles. Good resistance to exposure in air is of great advantage for the application of modified V.

3.6. *Resistance to pulverization*

The size distributions of modified V, before and after 30 and 300 absorption–desorption cycles, were determined (Fig. 8); here the vertical coordinate indicates the amount (weight per cent) of particles with a diameter equal to or smaller than the value corresponding to the horizontal coordinate. No significant difference was observed for the modified V, but a distinct pulverization occurred in the sample of modified V metal after 30 cycles, which possesses the same initial particle size distribution as that of modified V before mechanical milling. In the sample of modified V, more than 95% of the particles are larger than 0.3 mm in diameter, and *ca.* 25% of them are larger than 1 mm in diameter after 30 cycles. Even after 300 cycles, modified V does not pulverize severely. However, for unmodified V metal, despite its large original size, after 30 cycles only *ca.* 50% of its particles are larger than 0.3 mm, 3% are larger than 1.0 mm, 27% are smaller than 0.1 mm and 10% are smaller than 0.05 mm (Fig. 8). The difference between the modified V and V metal is distinct. As to $LaNi_5$, after about 10 absorption-desorption cycles, 85% of the particles are smaller than 10 μm and 50% are smaller than 1 μm. The average size of $LaNi_5$ particles is two orders of magnitude smaller than that of modified V. So the resistance of modified V to pulverization is better than that of unmodified V metal and much better than that of $LaNi_5$. Despite cracks that occured in the particles of modified V after many cycles, their shape is approximately maintained and they did not break up severely.

The reason for the good resistance of modified V to pulverization is not clear now, but it should be related to the surface state. As is known, progressive pulverization is a common phenomenon for H absorption materials when the number of cycles increases. In the application of H absorption materials, overpulverization leads to some problems with the purity of H_2, sealing of the system and so on. When an H absorption material is used in the form of bonded bulk, it would break up owing to severe pulverization. Good resistance of the modified V to pulverization is another of its advantages.

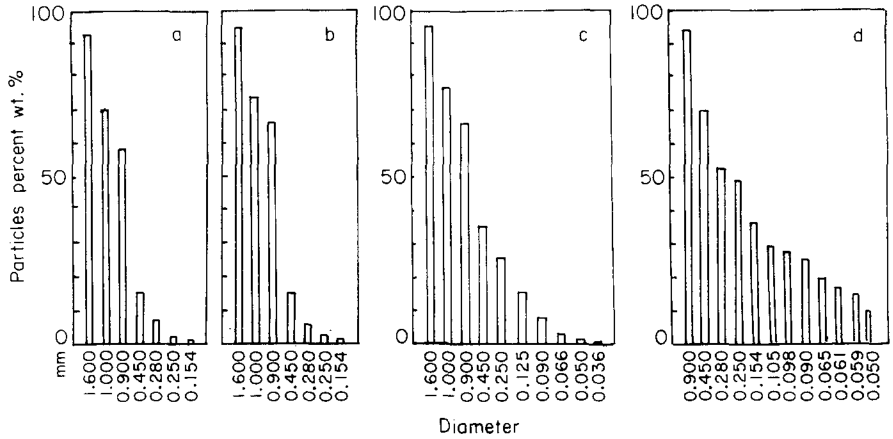

Fig. 8. Size distributions of modified V: (a) 0, (b) 30 and (c) 300 cycles and (d) unmodified metal V after 30 cycles.

4. Conclusion

Mechanical alloying of V and $LaNi_5$ leads to the surface modification of V. The modified V can be activated at room temperature. Its resistance to O_2 poisoning is better than that of V metal, FeTi etc. After repeated H absorption–desorption cycles no significant pulverization occurred. All these characteristics are favourable for the practical application of V. The modification treatment of the surface has no obvious effect on the equilibrium behaviour of the $V–H_2$ system. The rate-limiting step in the H absorption process of both activated modified V and V metal is the phase transformation from VH to VH_2.

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