International Journal of Engineering, Mathematical and Physical Sciences
ISSN: 2517-9934
Vol:6, No:11, 2012

Preparation of Vanadium Powder by Hydrogenation and Dehydrogenation

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***Abstract*—**Low oxygen content vanadium powder was prepared by hydrogenation dehydrogenization (HDH). The effect of purification treatment on hydrogen absorption kinetics of dendritic vanadium was tested, and the effects of milling technique on powder yield and grain size were studied. The crystal phase, oxygen and nitrgen content, and grain size of prepared powder were characterized and analyzed by X-ray diffraction (XRD), oxygen and nitrogen analyzer and grain size analyzer. The results show that the alkaline cleaning can improve the hydrogen absorption of vanadium. The yield of vanadium hydride powder can reach as high as 90% by 4h ball-milling, The resultant product also have an oxygen content less than 600μg/g, and the grain size is smaller than 37μm. Meanwhile, the XRD results show that the phase of hydride vanadium powder is mainly $VH_{0.81}$. After a hydrogen desorption treatment in vacuum at 700℃, the phase of the powder converts into V and a little of V_2H.

***Keywords*—**V-5Cr-5Ti alloy, HDH, microstructures, mechanical properties.

I. Introduction

MUCH more attention have been paid on vanadium and vanadium alloy in the design of the first wall, blanket and divertor in fusion reactor for the excellent low activation performance[1]-[3], high temperature strength[4]-[6], bearing corrosion of melt metal[7]-[11] and neutron irradiation swelling[12]-[16], so the preparation of vanadium and vanadium alloy has been the one focus in researching of materials for fusion reactor structure. As one powder near-net-shape technique, the parts with no segregation composition, stable and superior performance and homogeneous microstructure can be obtained through the powder metallurgy technology [17]. However, the chemical property of vanadium is active, it is easily solidly dissolved with the impurities in environment such as oxygen, nitrogen, carbon and so on, or forms brittle compound. The finer vanadium powder has a larger the surface area, and it is more difficult to control the content of O and N. The impurities content in vanadium powder supplied in market is high and, especially the oxygen content is usually more than 3000μg/g, which leads to high oxygen content in vanadium powder prepared by powder metallurgy technology and poor mechanical properties of vanadium alloy prepared from them, the small elongation and reduction of area particularly. So the vanadium alloy performance produced with powder metallurgy technology is worse than that produced with melting-casting method. To obtain the powder metallurgical vanadium alloy with low impurity content, it is the essential to adopt high pure raw powder. Thus, in virtue of the hydrogen absorption properties of vanadium, the high-purity dendrite vanadium absorbs large number of hydrogen to form brittle hydrogenated vanadium. Hydrogenated vanadium powder is prepared by ball milling of the brittle hydrogenated vanadium, and then the Hydrogenated vanadium powder is dehydrogenated at suitable temperature and vacuum. Therefore the hypoxic vanadium powder is obtained, which provides necessary technology for the preparation of high-performance powder metallurgical vanadium alloy.

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II. Experimental

A. Preparation of Powder

Firstly, the dendritic vanadium is cleaned with saturated sodium hydroxide solution to remove the oxide and nitrided layer on the surface, then the alkali washed dendritic vanadium is washed clean with distilled water. Secondly, the dendritic vanadium is washed with acetone and put into hydrogenator to be dried and degassed at 700 ℃ and 1×10^{-3}Pa. The hydrogenation of dendritic vanadium is finished in the pressured system. In this experiment, the hydrogen is purified through $LaNi_5$ bed and it is got through the high temperature analysis of $LaNi_5$ bed to ensure the purity of gas. The hydrogenated vanadium is filled in ball mill tank containing argon atmosphere to be high-energy ball milled. The weight ratio of ball and powder is 6:1, and the grinding ball material is tungsten ball. The dehydrogenation of hydrogenated vanadium is completed at 700℃ and 1×10^{-2}Pa. The specification and composition of dendrite vanadium are shown in Table I.

TABLE I
Specification and Composition of Dendritic Vanadium

Material	Size (mm)	Oxygen (μg/g)	Nitrogen (μg/g)
vanadium (dendrite)	3-15	246	23

B. Test of Vanadium Hydrogenation Dynamics

The hydrogen absorbing speed of dendritic vanadium is expressed with the relationship between the volumes of H2 stored in unit mass of vanadium atom and the reaction time.

And the hydrogen storage capacity is tested with constant volume method, which means to observe the change △P of hydrogen pressure in system over time. Then, the state equation of ideal gas is illustrated:

$$PV = nRT \quad (1)$$

the hydrogen storage capacity △n of sample is:

$$\Delta n = \Delta PV / RT = (P_0 - P)V / RT \quad (2)$$

Next, the hydrogen in unit mass of vanadium atom is obtained and it is:

$$w = (2\Delta n / m) \times 100\% \quad (3)$$

where m is the mass of dendritic vanadium and 2 is the molar mass of H_2.

Combining formula (1) and (2), the following formula can be got:

$$w = (2(P_0 - P)V / mRT) \times 100\% \quad (4)$$

The decline of the hydrogen pressure and the increase of hydrogen storage capacity in constant volume system are contacted together; by recording time and testing decline speed of P, consequently, the hydrogen absorbing speed can be converted.

C. Characterization of Powder Properties

By using the LS13-320 type: the grain size of powder is analyzed with laser diffraction particle size analyzer; the content of oxygen element is measured with nitrogen/oxygen analyzer; and the phase of hydrogenated and dehydrogenated powder is analyzed by adopting the D/Max-2500PC type X-ray diffractometer (Japan Rigaku). The main parameters of instruments are as follows: target at anodic: Cu; K α 1 is 0.154056nm; The scope of scanning angle is $30^o \sim 90^o$.

III. Results and Discussion

A. The Dynamics Influence of Purification Treatment on Hydrogen Absorption of Dendritic Vanadiums

Fig. 1 shows the dynamic isotherms of hydrogen absorption of alkali-washing dendritic vanadium and non alkali-washing dendritic vanadium after the cold and heat degassing, and the dynamic isotherms of secondary hydrogen absorption of alkali-washing dendritic vanadium after heat degassing, hydrogenation and then heating dehydrogenation. Seen from Fig. 1, the untreated dendritic vanadium nearly does not absorb hydrogen, but the hydrogen absorbing speed of alkali-washing dendritic vanadium is apparently higher than that of the non-alkali-washing dendritic vanadium, because one compact oxide film on the surface of pure metal vanadium prevent from the reaction between vanadium and H_2. The NaOH can be reacted with the oxide film on the surface of dendritic vanadium to form the Na_2VO_3 which is dissolved in water easily, then the cold degassing and ultrahigh vacuum degassing treatment increase the fresh surface and improve the activation effect of dendritic vanadium. The alkali-washing dendritic vanadium at the secondary hydrogenation only absorbs hydrogen after one incubation period, and the speed is slightly higher than the primary hydrogenation. Additionally, because the activation property of pure metal vanadium is poor and there are two hydrogen absorption platforms and the time of hydrogen absorption is long, the dendritic vanadiums treated with different methods can not obtain saturated hydrogenated vanadium.

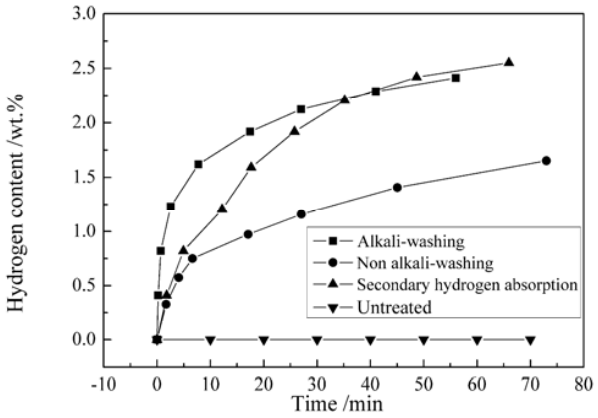

Fig. 1 The dynamic isotherms of hydrogen absorption of dendritic vanadium treated by different methods

B. Effects of Ball Milling Parameters on Pulverization Yield and Powder Sizes

Fig. 2 describes the pulverization yield curves of hydrides treated by different modes and milled with different time. The pulverization yield in this paper is defined as the ration between the sieved hydride powder and total hydride after the hydride is milled and sieved with 80 mesh screen. As shown in the Fig. 2, the ratio of fine powder increases rapidly with the increase of milling time in the prophase of milling, but the pulverization yield is maintained at about 93% with the gradually increase of milling time, which means that there is still a certain amount of hydrogenated vanadium can not be grinded down. Since the hydrogen absorbing speed is fast after alkali washing and the hydrogen storage capacity is larger at the same time, it is more likely to be grinded down in short time, the 90% of hydrogenated vanadium can be grinded down in 3 hours.

Fig. 3 demonstrates the average particle size and oxygen content curves of powder after the hydride absorbs hydrogen with different treatment and milled in different time. Fig. 3 shows that the average particle size of powder from alkali-washing dendritic vanadium is grinded from 80μm to 37μm, and the average particle size of powder from non alkali-washing dendritic vanadium is grinded from 155μm to 88μm. It is suggested that the influence of hydrogen storage capacity on pulverization yield and particle size of powder after milling is remarkable. If the hydrogen absorption is full, the needed milling time will decrease apparently. Fig. 4 indicates that the change of oxygen content in powder after ball milling with the time is not obvious, which shows that the ball mill tank is well sealed and the oxygen content do not increase apparently with the extension of milling time. The oxygen content of powder after treating with alkali washing is about 600 μg/g.

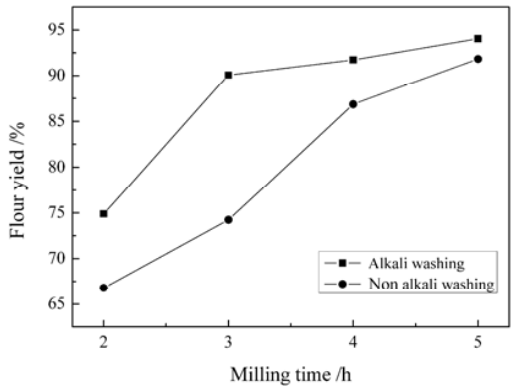

Fig. 2 The pulverization yield curves of hydrides treated by different modes and milled with different time

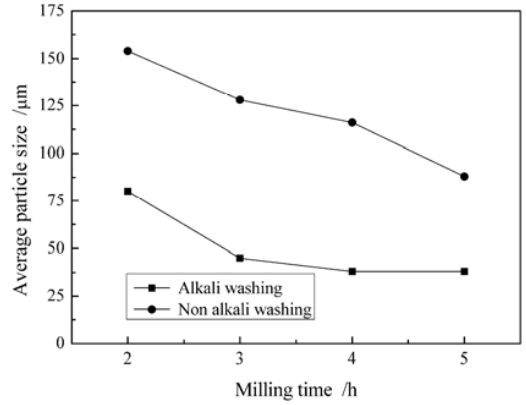

Fig. 3 The average particle size curves of powder after the hydride absorbs hydrogen with different treatment and milled in different time

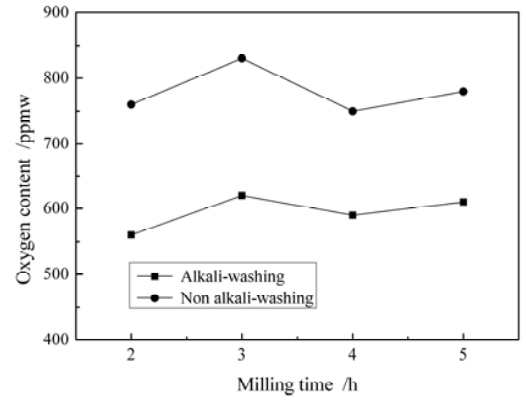

Fig. 4 The oxygen content curves of powder after the hydride absorbs hydrogen with different treatment and milled in different time

C. XRD Analysis

Fig. 5 describes the X-ray diffraction patterns of powder in different states. It can be seen from Fig. 5 that the phase composition of hydrogenated vanadium powder is unsaturated VH_2 but the $VH_{0.81}$; after dehydrogenation at 700℃, the phase composition of vanadium powder is V and V_2H, which indicates that there is still a certain amount H in vanadium.

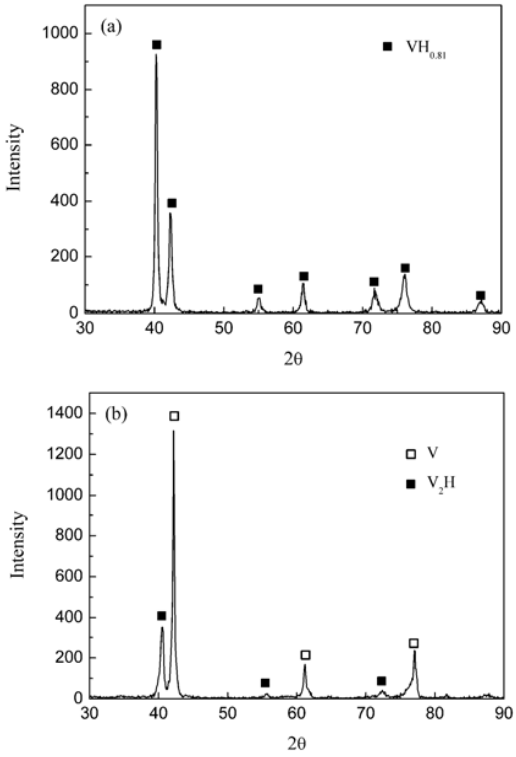

Fig. 5 X-ray diffraction patterns of powder in different states (a) Hydrogenated Powder (b) Dehydrogenated powder

When absorbing hydrogen, the metal vanadium forms firstly the β1 phase (V_2H low temperature phase), then β1 phase converts into β2 phase (high temperature phase or VH phase) when it goes on absorbing hydrogen. It will form phase of hydride VH_2 after hydrogen absorption saturation. Therefore there are two platforms on the PCT curve in the process of hydrogen absorption and hydrogen desorption, as shown in Fig. 6. The first platform is corresponding to the solid solution hydride (α phase) and β1 phase, reacted as the following formula (5):

$$2V(\alpha) + H \leftrightarrow V_2H(\beta_1) \quad (5)$$

However the β1 phase is quite stable and its balanced decomposition pressure at room temperature is only 0.1Pa, so it will not be decomposed at room temperature. The second platform is corresponding to β2 phase and phase γ, the reaction formula is as the following (6):

$$VH(\beta_2) + H \leftrightarrow VH_2(\gamma) \quad (6)$$

If the phase is not stable and it can be decomposed at room temperature with the plat decomposition pressure reaching 0.3 MPa. So, there are only stable VH or V_2H after the pure vanadium absorbing hydrogen and then placing for some time.

Therefore, the vanadium hydride tested in this experiment is the relative stable $VH_{0.81}$. Because the β1 phase is stable enough, the mixed powder can not dehydrogenate completely as well as a small amount of V_2H.

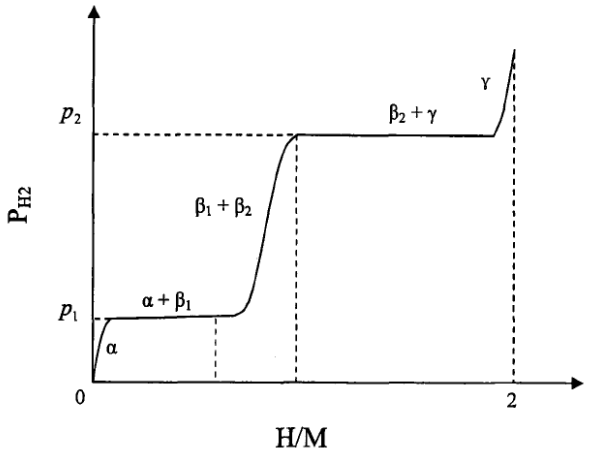

Fig. 6 The PCT schematic diagram of the V - H system

D. Powder Properties

Table II displays the data of different powder sizes and the contents of oxygen and nitrogen. In Table II, the steps for preparation of hydrogenated vanadium powder is as follows: the alkali washing of dendritic vanadium→ cold and heat degassing→ hydrogenation →ball milling for four hours; the process of producing the dehydrogenated vanadium powder is described as the followings: firstly the hydrogenated vanadium powder is heated by 700℃ step by step, and then the hydrogenated vanadium powder is cooled in vacuum with ≤ 1×10^{-3}Pa. It is suggested in Table II that the hydrogenated vanadium powder with the 38μm of average particle size can be obtained after 4 hours of ball milling and the oxygen content and nitrogen content in this powder are 500 μg/g and 1700 μg/g, respectively. After dehydrogenation, vanadium powder with 570 μg/g of oxygen content and 256 μg/g of nitrogen content can be got.

TABLE II
DATA OF DIFFERENT POWDER SIZES AND THE CONTENTS OF OXYGEN AND NITROGEN

Material	Particle Size (μm)	Oxygen (μg/g)	Nitrogen (μg/g)
Hydrogenated powder	38	500	1700
Dehydrogenated powder	38	570	256

IV. CONCLUSION

The purification treatment contributes to improve the effect of hydrogen absorption. For the poor activation property of vanadium, the saturated hydrogenated vanadium cannot be obtained ; with the extension of milling time, the pulverization yield and particle size of powder firstly increase remarkably and then maintain at a certain value; if the ball mill tank is sealed well, the change of oxygen content is not apparent over time. The XRD results indicate that the composition of hydrogenated vanadium phase is $VH_{0.81}$; the compositions of vanadium powder phase are V and a small amount of V_2H.

The vanadium powder with 570μg/g of oxygen content and 38μm of particle size can be produced by adopting the hydrogenation dehydrogenation method.

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