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Mechanical alloys in the Ti–B–H system: Influence of dispersion and alloying by boron upon thermal stability of hydride phases

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ABSTRACT

Influence of dispersion and alloying by boron upon thermal stability and decomposition temperature of hydride phases of mechanical alloys of the Ti–B–H system that were derived in the conditions of high-energy ball milling either of ($TiH_{1.9}$ + 9 wt.% B + 13 wt.% Ti) and ($TiH_{1.9}$ + 50 wt.% TiB_2) mixtures (50 h milling, rotation speed 1000 rpm) or of ($TiH_{1.9}$ + 40 wt.% B) and ($TiH_{1.9}$ + 50 wt.% TiB_2) mixtures (20 milling, rotational speed 1630 rpm) has been studied employing scanning electron microscopy, X-ray diffraction analysis, and thermal desorption spectroscopy. It has been established that, dispersion and boron additives to the $TiH_{1.9}$ powder followed by mechanical treatment influence thermal stability of the hydride. Mechanical milling the ($TiH_{1.9}$ + 9 wt.% B + 13 wt.% Ti) mixture for 50 h in argon causes decreasing the decomposition temperature of a $Ti(B,H)_x$ hydride phase by more than 300° compared with that of the initial $TiH_{1.9}$ hydride. Mechanisms of influence of both dispersion and boron alloying upon thermal stability of the $TiH_{1.9}$ hydride have been studied.

1. Introduction

In recent years, a great attention is devoted to a synthesis of hydrides by methods that differ from the method of direct hydrogenation with molecular hydrogen. Among methods that are widely used for a synthesis of magnesium, transition metal and rare-earth metal hydrides, the method of mechanical alloying is rather famous and gives a good account of itself. However, literature data regarding an application of this method for deriving transition metal hydride derivatives, e.g., binary boron-containing hydrides, are scarce. Elaboration of new methods for a synthesis of such kinds of compounds (e.g., aluminum hydride-based materials) and studies of their physical and chemical properties allow to increase our knowledge regarding a nature of hydrides as well as interstitial alloys [1–3]. Titanium-boron hydride $Ti(BH_4)_3$ is known to be a rather prospective hydrogen capacitor (ca. 17 wt.%), however, it is unstable and decomposes at room temperature [4]. Theses disadvantages, as well as toxicity of products of its decomposition and irreversibility of the hydrogenation process, restrict the application of $Ti(BH_4)_3$ even in close systems of energy transformation and accumulation. Zhang and Kisi [5] have applied the thermogravimetric method for studies of thermal decomposition of nanocrystalline titanium dihydride derived by reactive mechanical alloying (RMA) in hydrogen atmosphere, and, for comparison, of standard (commercial) TiH_2. It has been established that, nanocrystalline TiH_2 synthesized by the RMA method starts to decompose and completes its full decomposition at significantly lower temperatures compared with titanium dihydride obtained employing traditional methods. Additionally, the dehydrogenation process occurs in a narrower range in the case of TiH_2 synthesized by RMA in comparison with commercial titanium dihydride. Zhang and Kisi [5] attribute the dehydrogenation differences to extremely small particle sizes and high specific surface of TiH_2 powder obtained by the RMA method. Additionally, a great number of defects formed when milling titanium dihydride influences the above differences.

The influence of size upon dehydration of 40 μm commercial TiH_2, which has been undergone by high-energy mechanical treatment at irregular intervals in order to obtain hydride powder with different particle sizes, was studied in Ref. [6] employing methods of differential thermal analysis (DTA) and thermogravimetric analysis (TGA) and adopting also X-ray diffraction and transmission electron microscopy. It has been established that, with increasing milling intervals (and, accordingly, with decreasing particle sizes of TiH_2 powder) the distance between two peaks on the DTA curve increases and the curve shifts towards lower temperatures. Like in Ref. [5], Bhosle et al. [6] explain a decrease of temperature of the $TiH_2 \rightarrow TiH_x$ phase transition by decreasing particle sizes of titanium hydride powder, increasing its specific surface and a quantity of defects caused by milling the powder.

The aim of the present work was to verify a possibility of synthesis of new hydride phases in the Ti–B–H system by mechanical alloying as well as to study the influence of boron and its

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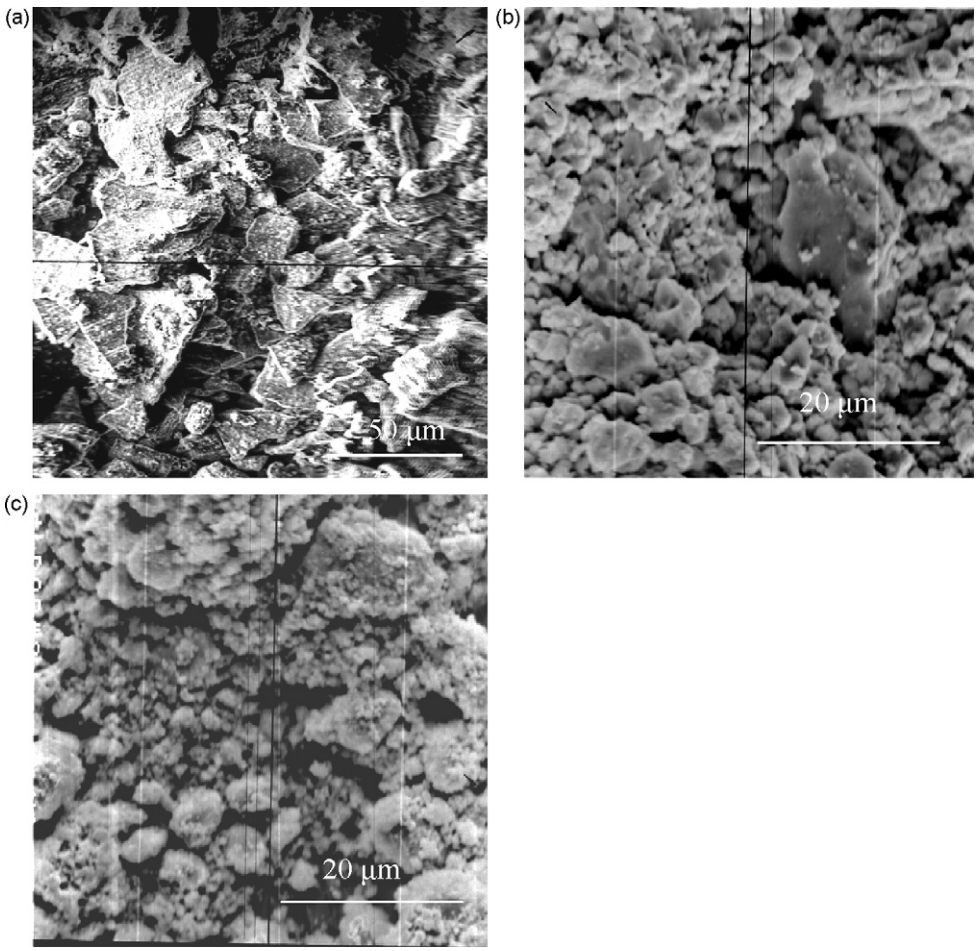

Fig. 1. SEM images of (a) the initial (Ti $H_{1.9}$ + 9 wt.% B + 13 wt.% Ti) mixture and the (b) MA1 and (c) MA2 mechanical alloys.

alloys with titanium upon thermal stability of TiH_2 decomposing at relatively high temperature. This dihydride is widely used when synthesizing different materials and in many applications the decreasing temperature of its decomposition plays an important role. With this aim, we have used possibilities of X-ray diffraction analysis, transmission electron microscopy and thermal desorption spectroscopy (TDS) methods to study hydride phases in the Ti–B–H system for mechanical alloys obtained using treatment of different mixture powders in a ball planetary mill and in Ar atmosphere.

2. Experimental

Mechanical alloys (MAs) that have been derived by treatment of ($TiH_{1.9}$ + 9 wt.% B + 13 wt.% Ti) and ($TiH_{1.9}$ + 50 wt.% TiB_2) mixtures, for clarity, we shall refer to MA1 and MA2, respectively. These alloys were obtained by 50 h treatment of the mixtures in a spherical planetary mill (rotation speed 1000 rpm). The ratio of steal balls weight to initial burden's weight was equal to 20:1. Average grain sizes of initial $TiH_{1.9}$, Ti, B and TiB_2 powders were 12, 10, 2 and 10 μm, respectively. MAs obtained by treatment of ($TiH_{1.9}$ + 40 wt.% B) and ($TiH_{1.9}$ + 50 wt.% TiB_2) mixtures we shall refer to MA3 and MA4, for clarity. The latter alloys were derived by 20 min treatment of the mentioned mixtures at rotation speed 1630 rpm. In this case, the ratio of steal balls weight to initial burden's weight was equal to 10:1. Titanium hydride $TiH_{1.9}$, a component of all the mixtures treated, was synthesized by direct hydrogenation of iodine titanium with molecular hydrogen.

Microstructures of MAs powders under consideration were studied using a CAMEBAX SX-50 scanning electron microscope-analyzer. An X-ray diffraction analysis of hydrides obtained was carried out using a computerized DRON-3M diffractometer equipped with CuKα source with a graphite monochromator on the diffracted beam. To determine the level of the hydride thermal stability and the decomposition temperature, thermal decomposition of hydrides was carried out using a computerized installation allowing measurements of a volume of hydrogen desorbed from the sample heated at a rate of 20°/min in hydrogen atmosphere under constant normal pressure (1 bar). TDS spectra of hydrides were obtained by measuring isobar–volumetric curves using the above-mentioned installation.

Changes of particle sizes of titanium hydride powder as a result of its mechanical dispersion were evaluated taking into account values of specific surfaces of initial and disperse TiH_2. The specific surfaces were determined by measuring a quantity of nitrogen adsorbed on the particles (in a stream of nitrogen–helium mixture at the temperature of liquid nitrogen) and an amount of nitrogen desorbed with increasing temperature up to 20 °C. The calculations were made adopting the BET method.

3. Results and discussion

From a TEM image presented in Fig. 1a, it is evident that the presence of asymmetric particles is characteristic of the initial $TiH_{1.9}$ + 9 wt.% B + 13 wt.% Ti mixture. After its mechanical 50 h treatment, a disperse material MA1 was obtained (Fig. 1b). The similar microstructure is characteristic of the MA2 material, obtained by 50 h treatment of the initial $TiH_{1.9}$ + 50 wt.% TiB_2 mixture (Fig. 1c).

The XRD pattern of the MA1 sample reveals a broad line, which resembles a halo of an amorphous material, containing a number of rather broad and low-intensive reflexes (Fig. 2a, curve 2). The XRD pattern of the MA1 sample differs significantly from that of the initial mixture (Fig. 2a, curve 1) and represents a pattern typical for ultrafine powder that contains a great number of rather broad diffraction reflexes superposing each other. From Fig. 2a (curve 2), it is apparent that the MA1 sample is a multiphase material: high-energy treatment of Ti and B leads to the formation of TiB, TiB_2, Ti_3B_4, and Ti_2B_5 compounds. These compounds, due to the diffusive XRD pattern, were identified taking into account one or two diffraction lines corresponding to the above-mentioned