PECULIARITIES OF LOW-TEMPERATURE INTERACTION OF MECHANICALLY ACTIVATED TITANIUM HYDRIDE WITH NITROGEN

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Introduction

Hardness of titanium hydride is determined to a great extent by grain size, therefore it can be increased by formation of an ultrafine structure. One of the ways to obtaining of high dispersivity of heterogeneous or solid state interaction products is creation of conditions for low-temperature interaction [1] through formation of defected structure and active surfaces.

In order to intensify chemical processes with participation of solid substances, mechanical treatment of the latter is often used. The total energy accumulated by a solid body, which determines its reactivity, is connected rather with accumulation of defects in crystals than with an increase in the surface area [2].

Paper [3] describes in detail various methods for production of titanium nitride and points to the fact that optimal condition is annealing of titanium in a nitrogen atmosphere; herein nitration of titanium takes place in the temperature range 500-1200°C and the transformation into TiN is over at 1200 °C. The use of titanium hydride results in slowing down nitrogen diffusion by hydrogen introduced into the titanium lattice at 500-800 °C when titanium hydride is stable enough. Nitrogen is known to be very active for disperse titanium; thus in the absence of oxygen fine titanium reacts with nitrogen even at room temperature. Decomposition of titanium hydride at low temperatures promotes remaining of the large specific surface area resulted from milling in the presence of nitrogen. Titanium obtained after low-temperature dehydrogenation of hydride can form nitrides at low temperatures. Addition of urea and salmiac stimulates titanium activity and decrease in the temperature of nitrides formation.
The task of this work is to reduce the temperature of TiH_2 dissociation in order to obtain TiN at low temperatures. We have also studied the effect of intense mechanical treatment of TiH_2 on decreasing the temperatures of its decomposition and subsequent nitration of active titanium.

Experimental

Titanium hydride with a specific surface area of 0.1 m^2/g underwent mechanochemical treatment in a planetary mill under a nitrogen atmosphere for 15 and 45 min. The obtained titanium hydride powder was heated in nitrogen. The initial materials and products were examined by chemical analysis for the contents of bound nitrogen, oxygen, and hydrogen and X-ray analysis on a DRON unit in Cu radiation for phase composition. Specific surface area was determined by nitrogen desorption method. Thermal stability of titanium hydride was determined using a differential thermal analysis in argon flow. The effect of urea and salmiac addition on nitration acceleration was studied as well.

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Results

The carried out investigations have shown that in the course of milling titanium hydride in the planetary mill its specific surface area increases from 0.1 m^2/g for the initial powder to 7 m^2/g for the powder milled for 15 min. Further milling for 1h does not cause further increase this value any more. The hydrogen content corresponding to the stechiometric composition of titanium hydride TiH_2 is equal to 3.8 mass %. Under milling hydrogen content in titanium hydride decreases down to 3.6 mass % after 15 min milling and to 3.4 mass % after 1h whereas oxygen content increases up to 3.04 mass % after 15 min and to 3.8 mass % after 1h.
It should be noticed that during milling contamination with iron occurs: iron content is 1 mass %, which, in its turn, catalyses dehydrogenation of titanium hydride.

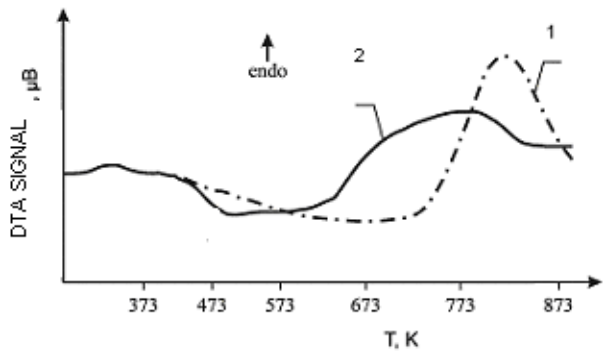

Fig.1. DTA curves for dehydrogenation of $TiH_{1.89}$: 1-initial, 2-after mechanical treatment in a hydrogen atmosphere.

Fig. 1 compares the DTA curves for initial conventional titanium hydride with a specific surface area of 0.1 m^2/g and titanium hydride/ milled for 1h in a hydrogen media. An endothermic effect for the initial titanium hydride is observed above 500 ^oC whereas it significantly decreases and shifts by 150 ^oC towards lower temperatures upon milling in . hydrogen. ADTA signal corresponding to an endothermic process of dehydrogenation is not observed at all upon milling for 1h in nitrogen. This absence of the thermal effect on the DTA curve can be attributed to the high activity of milled powder and the formation of surface oxide films during discharge. The XRD patterns showed very blurred lines of titanium hydride for the milled powder.

Nitration of titanium hydride at 500 ^oC in nitrogen after intense mechanical treatment yields titanium nitride; however, it contains oxygen in the form of Ti_2O. In the presence of oxygen titanium, which is sensitive rather to oxygen than to nitrogen, forms oxide compounds. The data of the chemical analysis indicate that after nitration of titanium hydride at 500 ^oC the contents of oxygen and bound nitrogen are equal to 4 and 19 mass %, respectively. containing 4 mass% oxygen at 500 ^oC, the content of bound nitrogen equals 19 mass%. Taking into account the XRD data, it is easy to calculate that the amount of formed titanium nitride is 80% and Ti_2O −20%.

Conclusions

It has been shown that intense initial powder milling is very efficient for chemical activation of titanium hydride: it reduces the temperatures of its decomposition and subsequent low-temperature nitration. To further intensify and improve milling and nitration conditions, the presence of oxygen should be excluded.

References

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