

Fabrication of TiH_2 Powders from Titanium Tuning Chip by Mechanical Milling

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Abstract

In present work, manufacturing technologies of titanium hydride powder were studied for recycling of titanium tuning chip and for this, attrition ball milling was carried out under H_2 pressure of 0.5 MPa. Ti chips were completely transformed into TiH_2 within several hundred seconds. Dehydrogenation process TiH_2 powders is consist of two reactions: one is reaction of TiH_2 to TiH_x and the other decomposition of TiH_x to Ti and H_2 . The former reaction shows relatively low activation energy and it is suggested that the reaction is caused by introduction of defects due to milling.

Keywords : Ti hydride, Titanium tuning chip, mechanical milling, activation energy

1. Introduction

Titanium and its alloys have a large range of applications due to the combination of high mechanical and corrosion resistance and low density [1]. At the same time, quantity of by-products like Ti chip obtained in machining process has also been rapidly increasing, but technologies for their recycling have been limited yet due to its activity at high temperature and cost of process.

One of the useful processes for recycling of Ti by-products is hydrogenation. Conventional procedures for hydrogenation of Ti are i) exposure to H_2 gas at elevated temperature and/or pressure for several hours, and ii) slow cooling in order to maintain maximum hydrogen content [2].

On the other hand, the mechanical milling has been used to produce metal hydrides and nitrides at room temperature. Chen et al. [3] reported that the $TiH_{1.9}$ could be synthesized after milling of about 5.5 hrs in H_2 gas using Ti powder and planetary ball mill, suggesting that mechanical milling probably could be a simple and economical method to produce metal hydride powders.

In this work, manufacturing technologies of Ti hydride powders by mechanical milling were studied for recycling of titanium tuning chip at room temperature. Also, the effects of milling time on dehydrogenation of hydrides were investigated.

2. Experimental and Results

Elemental Ti powders and Ti tuning chips were used to produce Ti hydride. They were mechanically milled by an attrition ball mill with stainless steel canister and balls.

The canister was evacuated to about 10^{-2} torr prior to filling with hydrogen gas of 0.5 MPa. The mechanical milling was conducted for specific times from 80s to 600s in 320rpm, followed by maintenance for 2 hrs for enough hydrogenation. An absorbed amount of hydrogen by Ti sample was calculated using pressures of H_2 monitored during milling.

Fig. 1 shows the variations of the number of hydrogen atoms absorbed per Ti atom with milling time. The number of hydrogen atoms increased quickly after milling time of 80s (STP) and 330s (STC) in Ti powders and chips, and saturated after 180s and 800s, respectively.

The crystalline structure was analyzed to cubic TiH_2 phase in all samples, implying that Ti powders and chips were completely transformed into Ti hydrides within several hundred seconds. These results are very important and surprising because TiH_2 phase was obtained after milling of about 5.5 hrs in the previous report [3].

Dehydrogenation behaviors were investigated by DTA with the TiH_2 powders obtained in each milling condition of Fig. 1. The results are shown in Fig. 2 and each peak temperature is summarized in Table 1. The DTA curves of STC and commercial TiH_2 powders reveal only one peak at relatively high temperature and that of STP very small 1st peak and large 2nd peak. However, in cases of samples milled continuously during formation of TiH_2 , two endothermic peaks are obviously observed and shifted toward low temperature with increase of milling time. Also, as can be seen in Table 1, the shift of the 2nd peak with milling time is much larger than that of the 1st peak. These results indicate that appearance and temperature of the 1st peak depend strongly on milling time. According to Ref. [4], the 1st peak means transformation reaction of TiH_2 into TiH_x ($X=0.7\sim 1.1$) and the 2nd peak TiH_x into Ti and H_2 .

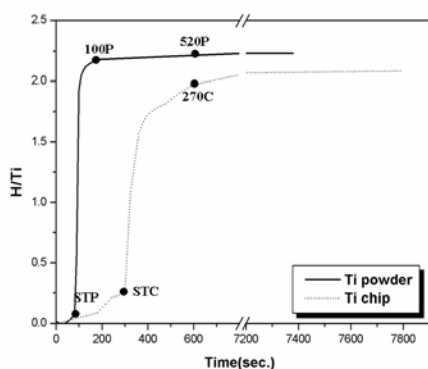


Fig. 1. Variations of the number of hydrogen atoms absorbed per Ti atom with milling time.

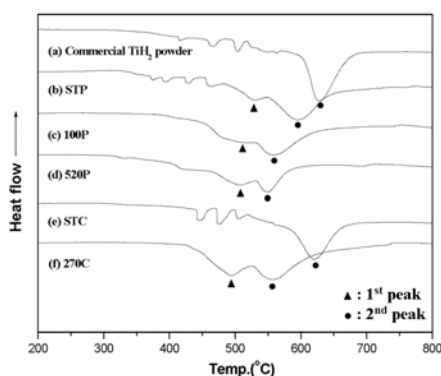


Fig. 2. DTA curves of as-milled powders with size ranging from 38 μm to 45 μm (heating rate 10 °C/min).

Also in the report, the peaks were shifted toward low temperature as milling time increase and then, X value was decreased. These results are very consistent with those in this work, indicating that the 1st peak infers transformation of TiH₂ into TiH_x and the TiH₂ powders in STC are decomposed directly to Ti and H₂ without formation of TiH_x. Nevertheless, two questions remain still: i) why occurrence of the 1st peak is affected by milling and ii) why STC powder is decomposed directly to Ti and H₂. For approach in point of view of kinetics, activation energies, energy barriers, for dehydrogenation reaction were evaluated using Kissinger relation [5] and the results are summarized in Table 2. As can be seen in Table 2, activation energy (energy barrier) for the direct reaction of TiH₂ to Ti and H₂ in STC is very large as much as 929 KJ/mole, which means that the reaction is very difficult.

Table 1. Peak temperatures in DTA curves.

	Commercial TiH ₂	STP	100P	520P	STC	270C
1 st peak(°C)		530	520	519		495
2 nd Peak(°C)	628	594	559	550	620	558

Thus, the reaction of TiH₂ to TiH_x with relatively very low energy barrier will occur preferentially when requirement for the reaction is met. Milling brings about formation of defects such as vacancy in TiH₂ phase and the number of defects increase as milling time increases. In this work, TiH₂ powders in STC hardly contains defects while the many number of defects exist in milled TiH₂ powders. As a results, it is suggested carefully that the existence of defects is the requirement for the reaction of TiH₂ to TiH_x and thus, defects in TiH₂ introduced by milling lead to the reaction. This seems to be supported very well from the fact that the activation energy decreases as milling time increases.

Table 2. Activation energies of dehydrogenation process.

	STP	100P	520P	STC	270C
1 st Peak(KJ/mol)	242	148	124		104
2 nd Peak(KJ/mol)	643	185	152	929	201

3. Summary

In present work, manufacturing technologies of Ti hydride powder by mechanical milling were studied for recycling of titanium turning chip. Ti powders and chips were attrition milled in H₂ atmosphere.

Ti powders and chips were completely transformed into TiH₂ within several hundred seconds and this shows a large difference in milling time comparing to the previous report where TiH₂ phase was obtained after milling of about 5.5 hrs. Dehydrogenation process is consist of two reactions: one is reaction of TiH₂ to TiH_x and the other decomposition of TiH_x to Ti and H₂. As milling time increases, peaks for both reactions in DTA are shifted toward low temperature and activation energies for the reactions are smaller. In case of TiH₂ powders which were not milled, the reaction of TiH₂ to TiH_x does not occur and activation energy for decomposition of TiH₂ to Ti and H₂ is very large as much as 929 KJ/mol.

Consequently, it is suggested carefully that defects in TiH₂ introduced by milling lead to reaction of TiH₂ to TiH_x.

4. References

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