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상온에서 RMG법에 의한 타이타늄 수소화분말의 제조

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Synthesis of nano-size titanium hydride powder at room temperature with RMG

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ABSTRACT

볼밀링법을 이용하여 타이타늄 스펀지와 칩 또는 스크랩으로부터 상온에서 직접 타이타늄 수소화 분말을 제조하는 실험을 행하였다. 실험결과 진공중에서 볼링을 행한 타이타늄 스펀지와 칩의 경우 24시간의 후 합금분말의 크기는 약 20 um 정도의 크기를 갖는 것을 확인하였다. 그러나 수소화 분위기에서 볼밀링을 행한 경우에 12시간 후 수소화분말의 입도는 0.1-0.2 um로 극히 미세한 합금 분말이 제조되었다. 수소분위기에서의 볼밀링에 의한 타이타늄 분말제조는 기존의 방법에 비해 열을 가하지 않고 타이타늄 수소화 분말을 얻을 수 있다는 장점과 나노크기의 미세한 수소화 분말을 얻을 수 있음을 알 수 있었다.

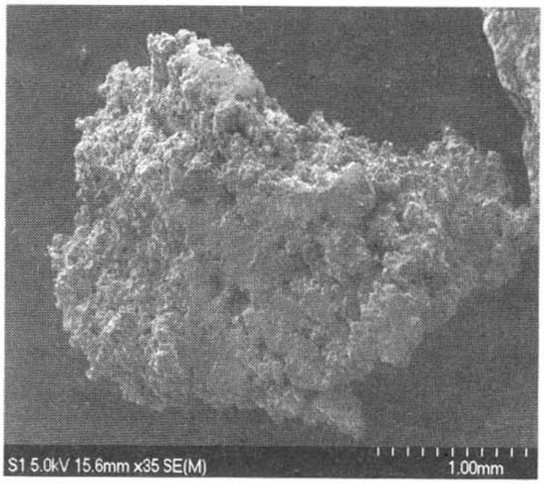
주요기술용어: Reactive mechanical grinding (RMG)(활성 기계적 분쇄법), Titanium powder (타이타늄분말), Amorphous structure(아모퍼스 구조), Titanium hydride(타이타늄수소화물)

1. Introduction

Titanium powder has been used for processing carbon fibers reinforced titanium matrix composites (TMC) and synthesizing various titanium alloys [1].

To produce titanium powder, Ti hydride should be prepared before. The approach commonly used for preparing titanium hydride is a solid-gas reaction about 5000C and a milling of the resulting hydride [2]. Another method was also introduced to reduce the cost. It is called reactive mechanical grinding (RMG) of titanium at room temperature under hydrogen atmosphere [3-4]. However, in order to apply RMG method for producing titanium hydride, titanium powder should be prepared as a starting material because increase the surface for interaction with hydrogen. It takes a cost and time for preparing coarse titanium powder.

Therefore, in this study, we intend to reduce a procedure for preparing titanium hydride and cost of starting material. We adopted the titanium sponge and chips which were produced as a by-product during mechanical process and melting process as starting materials. RMG method was introduced to these cheap materials under hydrogen atmosphere and the results were discussed in this study.



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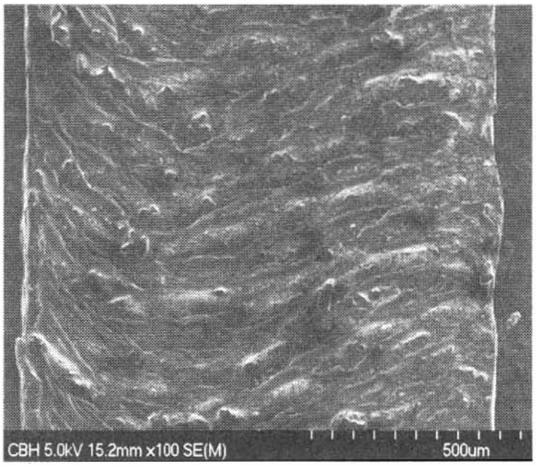


(b)

Fig. 1. shape and size of titanium sponge and chip. (a) sponge (b) chip

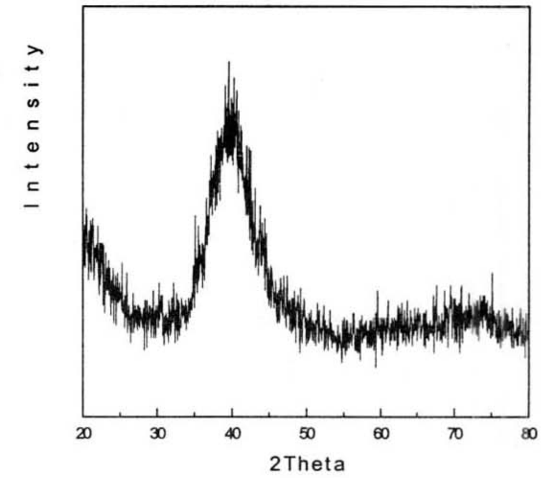
2. Experimental

Titanium sponge with purity 99% was purchased in domestic and titanium chip was a by-product during titanium cutting. The size and shape of sponge and chip was shown in Fig. 1. Before milling procedure, Ti sponge and chips were immersed in acid in order to clean the surface from organic contamination and cutting oil. Ball milling was carried out at 200 ml size ball milling stainless jar of planetary ball miller with 200 rpm rotation speed under vacuum or 10 atm. hydrogen atmosphere. The purity of hydrogen was 99.99% and titanium sponge and chip (4g) to ball(diameter, 10mm) weight ratio was 1:30 or 1:60. Titanium chips were cut with size of 1 cm to increase surface which was contacted to ball. Ball milling time was chosen at 1, 3, 6, 12 and 24 hour. After finishing ball milling, milled specimen was subjected to XRD (Rigaku, D-1000) and SEM (JEOL, JSM-5200) measurement to classify the structure of milled powder and size.

3. Results and discussions

The X-ray diffraction patterns before and after ball milling was shown in Fig. 2, 3. In Fig. 3, after ball milling under hydrogen atmosphere, titanium hydride (TiH1.92) peak was identified. This result explains the fact that during ball milling, titanium sponge and chip absorbed hydrogen and transformed its structure to titanium hydride. In the shape of sponge and chip, it is difficult to absorb hydrogen at room temperature due to a dense oxide film at surface. But mechanical energy transfer with stainless ball to Ti sponge and chip pulverized Ti sponge and chip, provide oxide-free surface and make easy to absorb the hydrogen. If the titanium absorbs hydrogen and transformed to Ti hydride, it become brittle and it is easily crushed with ball milling..

After ball milling, titanium sponge and chip have a two different shape, one is powder and the other is remained sponge or chips. It is certain that crushed powder is Ti hydride and remained sponge and chip is a metal, because Ti hydride is so brittle and easily crushed with low energy impact. Therefore pulverization rate is directly related to hydrogenation rate. Fig. 4 shows the crushed ratio of titanium sponge and chips with ball milling time. Under hydrogen atmosphere, 100% sponge and chips became powder with ball milling time, 24 hour and 12 hour, respectively. It can be explained that fast powdering ratio of chip, compared to sponge, is due to a wider contact surface to ball. From the X-ray diffraction patterns, it was found that the powder which was produced during ball milling is not a metallic titanium but titanium hydride in Fig. 5. It also show very small contamination



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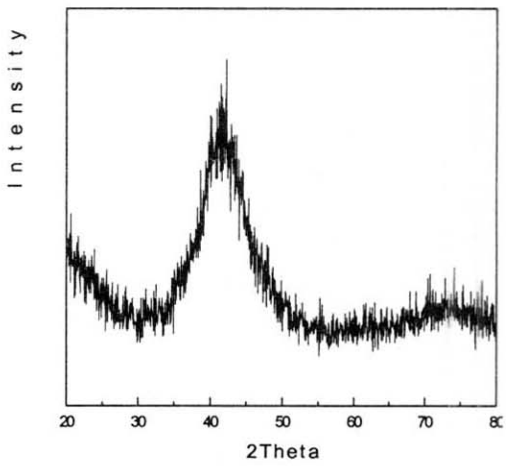
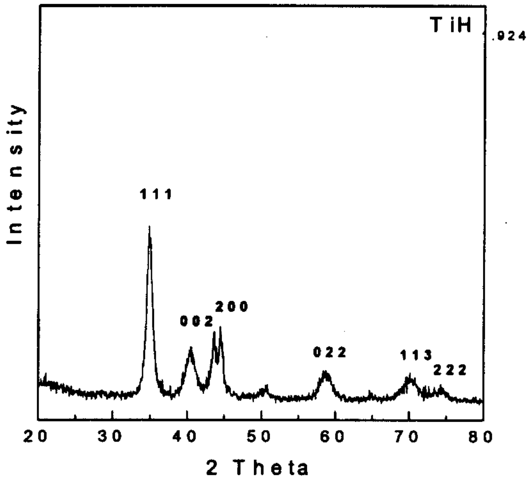


(b)

Fig. 2. X-ray diffraction patterns of starting materials. (a) sponge, (b) chip

with Fe which cannot be identified by X-ray diffraction patterns even after 24 hour ball milling. It is thinkable that the ball milling energy is too low to make contamination from the ball or wall of ball milling pot.

However ball milling in vacuum condition shows different results. Over 50% titanium sponge and chip did not transform to powder



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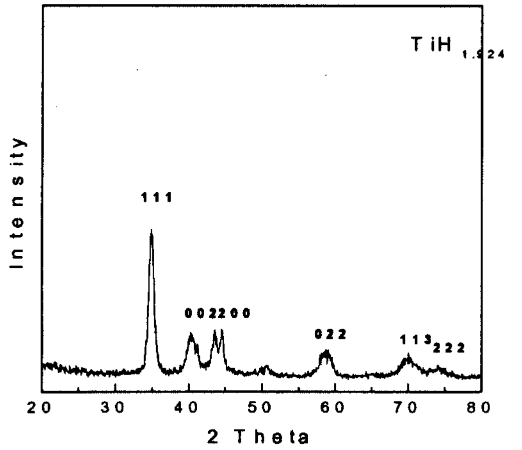

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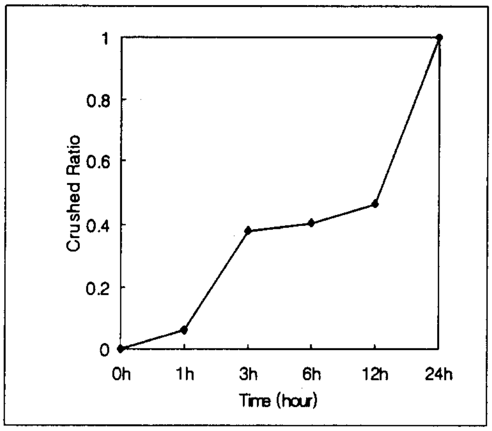
Fig. 3. X-ray diffraction patterns after 1 hour ball milling under 5 bar hydrogen atmosphere ((a) sponge, (b) chip))



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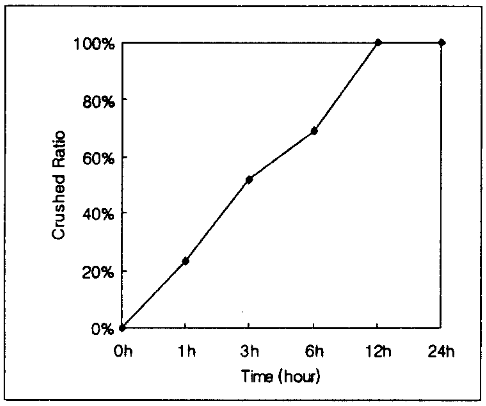
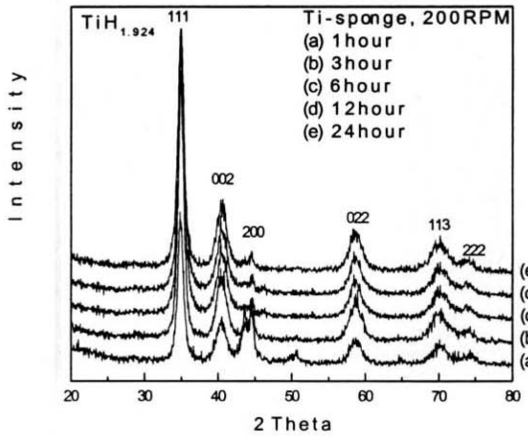


(b)

Fig. 4. Crushed ratio of Ti sponge and chip after ball milling under hydrogen

even after 12 h ball milling wherever 100% chip transformed to powder at 12 hour under hydrogen atmosphere.(Fig. 6), In case of Ti sponge, pulverization rate is below 20% even after 12H ball milling under vacuum condition. Therefore resulted titanium powder have amorphous structure due to higher shock energy from ball to powder. This result explains the fact that hydrogen absorption helps the process of crashing from bulk to powder with hydrogen embrittlement. Also ball milling accelerated hydrogenation of titanium.

The particle size of titanium hydride became smaller and more uniform increasing ball milling time. (Fig. 7) After 24 hour ball milling, the particle size of titanium powder were



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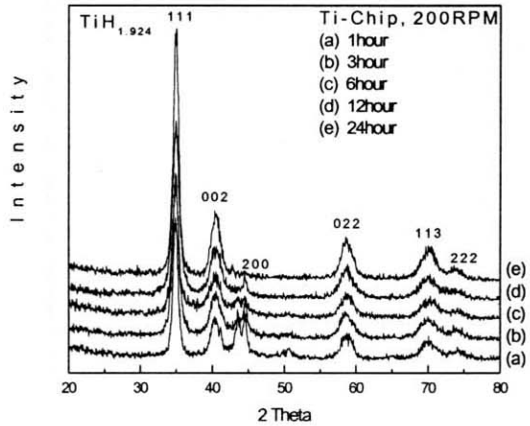


(b)

Fig. 5. X-ray diffraction patterns of titanium after ball milling under hydrogen ((a) sponge, (b) chip)

sub-micron where conventional titanium hydride production method(hydrogenation and ball milling at argon atmosphere) have a particle size around 10 um. It means that if the ball milling time become longer, particle size will be smaller around nano size. However, the particle size(around 100 um, 12 H) after ball milling at vacuum condition was much larger

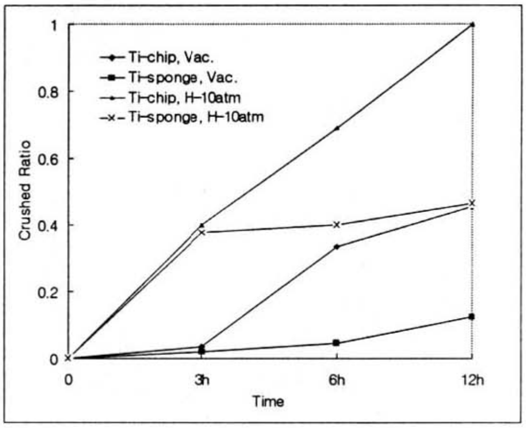
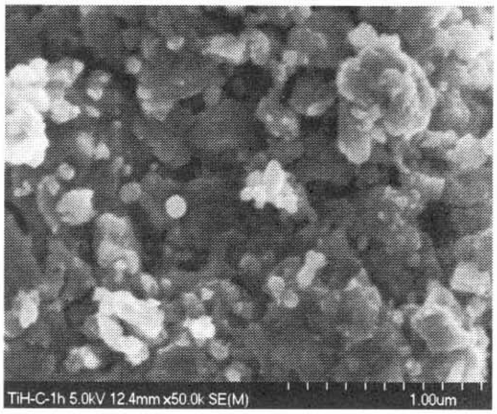


Fig. 6. The crushed ratio of Ti sponge and chips after balling under vacuum or hydrogen atmosphere



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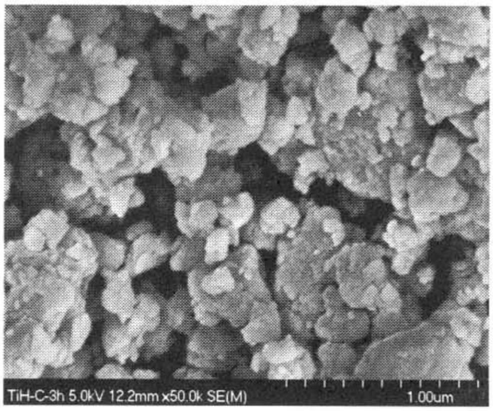

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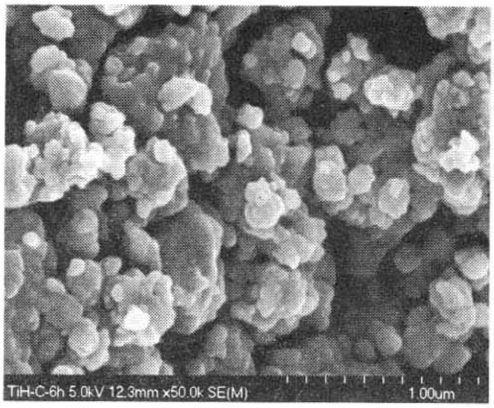

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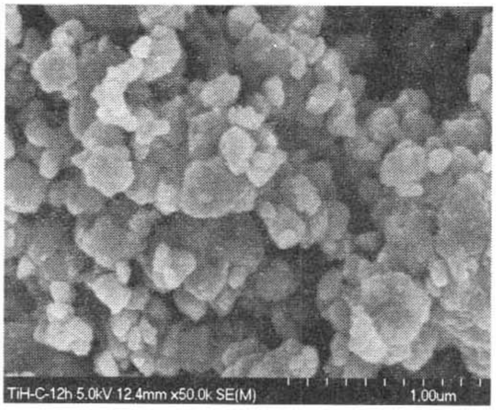

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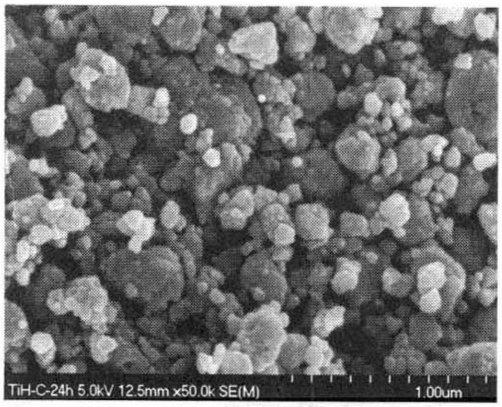


(e)

Fig. 7. The particle size of titanium hydride after ball milling (X50,000, (a) 1H, (b) 3H, (c) 6 H, (d) 12 H, (e) 24H)

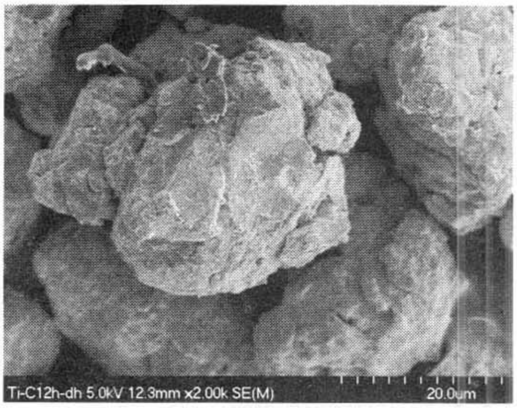


Fig. 8. Titanium powder after 12 hour ball milling at vacuum (X2,000)

than hydride one(Fig 8). It means that hydrogen accelerated the crushing of titanium sponge and chip.

In order to investigate milling energy effect to crushing rate, ball to titanium ration was changed from 30: 1 to 60: 1. After 6 hour and 12 hour ball milling, it was shown that the change from 30: 1 to 60: 1 resulted in increasing crushing ratio in Fig. 9. And the resulting

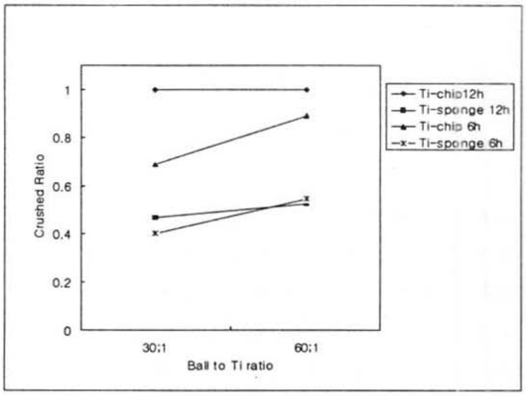
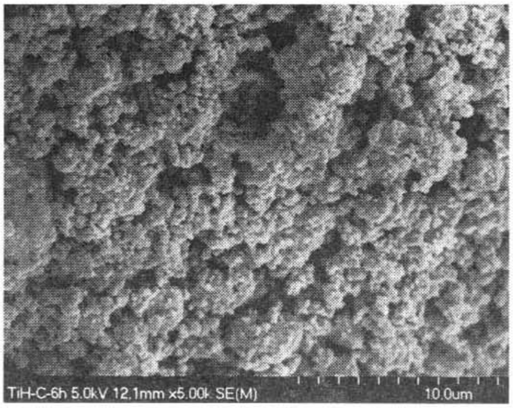
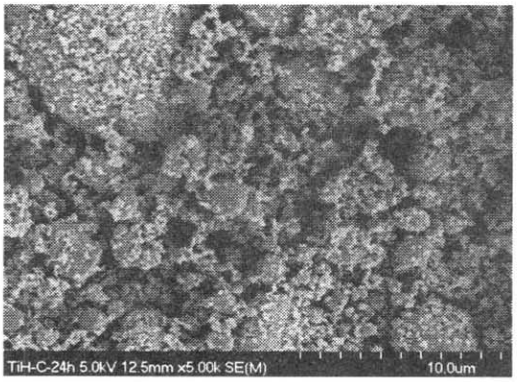


Fig. 9. The crushed ratio of Ti sponge and chip with change of ball titanium ratio



(a)



(b)

Fig. 10. SEM photographs of Ti hydride powder after ball milling ((a) 30:1, (b) 60:1)

powder in case of 60:1is much smaller than in case of 30:1, as shown in Fig. 10. It explains the fact that higher ball energy means higher pulverization rate. It is thinkable that if the high energy ball milling is applied, hydrogenation rate and pulverization rate will be much higher, therefore producing Ti hydride powder will be finished within an hour.

It was confirmed that RMG is very effective way to produce Ti hydride with low cost. Also it can be applicable in case of producing other hydride powder, such as zirconium hydride, magnesium hydride and so on.

4. Conclusion

The simple titanium powder production method was developed for the first time. Titanium hydride (TiH1.92) was produced at room temperature by mechanical grinding of titanium sponge and chips in a reactive atmosphere of hydrogen (RMG). Hydrogenation of titanium was accelerated with ball milling and helped pulverization of titanium through hydrogen embrittlement. That is, RMG accelerated the pulverization rate of titanium and made particles smaller with same ball milling time. The resulted particle size after ball milling was sub-micron and higher ball energy resulted in a higher pulverization rate and smaller particle size. With these results, usually waste titanium chip become useful to produce a titanium powder and RMG appears as a simple and inexpensive route for fine titanium and titanium hydride powder.

Acknowledgements

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