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A study on Titanium Hydride Formation of Used Titanium Aircraft Scrap for Metal Foaming Agents

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Aircraft industry is developed very fast so titanium scrap was generated to manufacture. Titanium scrap was wasted and used to deoxidize cast iron so we are study recycling of it. In this research were studied that metal hydride of reacted in hydrogen chamber of AMS4900, 4901, return scrap titanium alloy and sponge titanium granule. The temperature of hydrogenation was 400℃ in the case of pure sponge titanium, but return scrap titanium alloy were step reaction temperature at 400℃ and 500℃, and after the hydride of titanium alloy were crushed by ball mill for 5h. Titanium hydride contains to 4wt.% of hydrogen theoretically as theory. It was determined by heating and cooling curve in reaction chamber. The result of XRD was titanium hydride peak only that it was similar to pure titanium. Titanium hydride Powder particle size was about 45㎛, and recovery ratio was 95w% compared with scrap weight for a aluminum foam agent.

Introduction

As a new ultra-light-strength material, titanium is widely used in chemical, aerocraft, medical and food industry and sports machine. Although the quantity of titanium scrap is growing, It is difficult to cast and manufacture due to its activity at high temperature and hardness of processing. In consideration of shortage of resource and environmental protect, the primary task is titanium recycling. Titanium react actively in high temperature, it must be operated in inert atmosphere and control the effect of impurities. So the essential factor in reduction manufacturing cost is the simplification of recycling process. The common recycling process contains collection, classification, composition examination, washing and melt and then flew to secondary production. To control the mechanical and chemical properties it is important to consider the effect of impurities. The waste titanium have 5 grades and what we can obtain is mixed ones, so the classification and composition examination is the necessary technique. If the importance of recycling is recognized and the classification is performed in factory, the recycling will be more easily processed.

In this study the recycling was accomplished after collection, classification and washing without the secondary process. The raw material is the titanium scrap (AMS4900 titanium plate, another 4 kinds of titanium chip) and 99.6% sponge titanium. Return scrap was putt in a reaction chamber, which was made by Laboratory, and treated in hydrogen, milled and checked the possibility as foaming agent.

Experimental procedure

1) Hydrogen treatment of titanium scrap for hydride

In this study were used sponge titanium and industrial return scrap titanium. Table.1 is chemical composition offormation sponge titanium and return titanium scrap. One kind of plate(AMS4900) and another four kinds of chip(Grade 3) were used in the test and the specimens of 0.7mm thickness titanium plate were cut into 3×8cm as well as sponge titanium and chip titanium were used without cutting.

Table.1. Chemical composition of Ti sponge and Ti scrap

Comp(%) / Makers	Ti	N	C	H	Fe	O
Sponge Ti	99.6	0.02	0.01	0.015	0.1	0.09
Plate Ti	99.1	0.05	0.08	0.015	0.5	0.3
Chip Ti Ⅰ	99.3	0.03	0.1	0.015	0.3	0.25
Chip Ti Ⅱ	99.3	0.03	0.1	0.015	0.3	0.25
Chip Ti Ⅲ	99.3	0.03	0.1	0.015	0.3	0.25
Chip Ti Ⅳ	99.3	0.03	0.1	0.015	0.3	0.25

When washing was carried out by ultrasonic cleaner (Branson 2210) with alcohol for 30minutes. Then 100g titanium was put into the chamber, purged with Ar and injected the hydrogen. The pressure of chamber was maintained at 1~2.5atm and the hydrogen was injected until under the temperature of reaction to avoid the inverse reaction. Then cooled down in Ar atmosphere and checked the change of temperature and weight to certify the absorption of hydrogen. Because one titanium atom combined with about two H atoms, 4wt% of hydrogen absorption will occur per chamber. The schematic diagram of hydrogen treatment apparatus is shown in Fig.1.

2) Milling and sieving

Mechanical method was chosen to make powder. Titanium hydride were crushed and milled in ball miller for 5 hours and after the particle grading was performed on 140mesh~325mesh by standard sieve. After sieving the specimens were observed with SEM(JSM-6400) for particle foam and size measuring. Phase analysis was performed on XRD (Rigaku 2,Cu target, 25kV) between 20 to 80 degree.

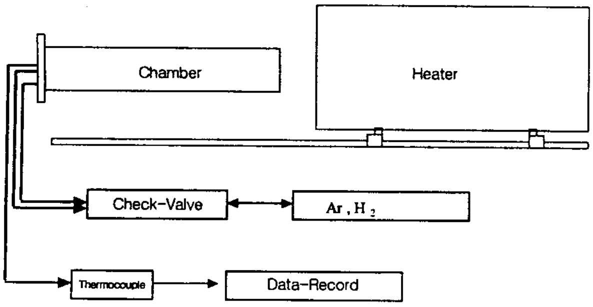

Fig. 1. The schematic diagram of hydrogen treatment apparatus

RESULTS AND DISCUSSION

1) Results of hydride treatment

Fig.2 is shown the picture of surface shape of each specimen after titanium hydride treatment. It can be observed that all kinds of titanium have many cracks. Titanium with different shapes have shown the excellent hydrogen absorption capability but different reaction temperature.

Time dependent reaction temperature was shown in Fig3. a is the starting point of rapidly reaction. During the reaction, the temperature acceleration showed the increasing tendency. The reason is that it is the exothermic reaction. After reached the peak of temperature, the remaining reactions occurred and cooled down. Hydride process is shown in equation

$$Ti + H_2 \rightarrow TiH_2 + \Delta H$$

The emission of heat per mol Ti at 400℃ is

$$\Delta H_T = H_{298} + \int_{298}^{T} \Delta C_p dT$$

$$\Delta C_P = C_{P,TiH2(S)} - C_{P,Ti(S)} - C_{P,H2}$$

$$\Delta H_T = - 144.348 + [-41.21T + 0.06T^2 - 72376.6]_{298}^{673}$$

$$\Delta H_T = -41.21T^2 + 72376.6T - 78826$$

So the heat is

$$\Delta H_T = 29965421.7 \text{ J/mole-673K}$$

The peak of temperature is in proportion to the quantity of titanium. The reaction temperature is about 400℃. Plate titanium and chip titanium reacted at higher temperature than pure sponge titanium. It may be resulted by the small surface area and the oxide layer. We also found the surface effect from the different reaction temperature of chip titanium and plate titanium. The absorption of hydrogen resulted in the change of cubic structure of titanium and the cracks occurs that made the following milling easier.

Cubic rearrangement during the reaction resulted from the cracks along the boundary. The cracks enlarged the surface and stimulated the velocity of reaction. The instant reaction followed by the broken of oxide layer. Because the hydrogen absorption related to the width of the layer, the removal of the layer will decrease the reaction temperature.

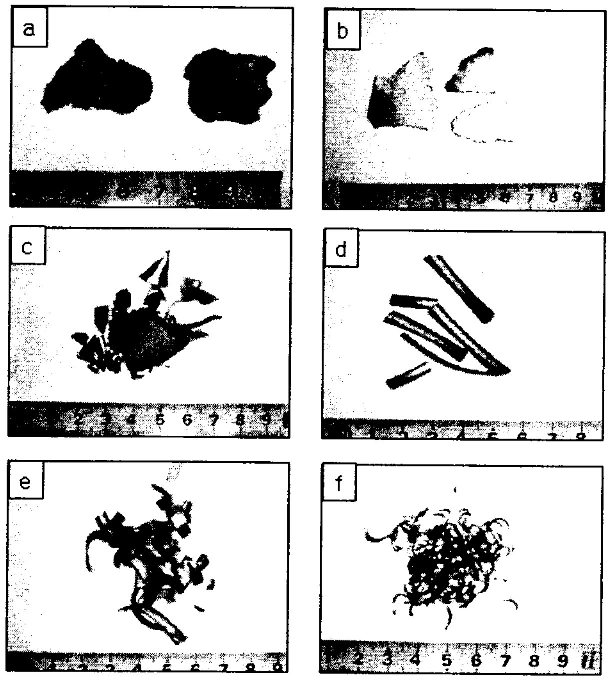

Fig. 2. The surface of titanium hydride shape
(a) Sponge Ti (b) Plate Ti (c) Chip Ⅰ (d) Chip Ⅱ
(e) ChipⅢ (f) ChipⅣ

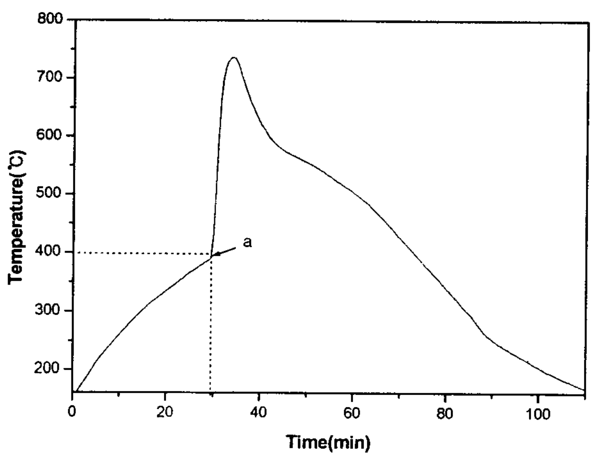

Fig.3. The variation of reaction temperature and time

Plate titanium absorbed the most hydrogen but never reached the theoretical value 4w%. The absorption restricted by the oxide layer and impurities and we can concluded that hydrogen absorption of the chip titanium restricted by this reason

Surface shape of titanium after hydrogen treatment showed in Fig2. It can be observed that sponge titanium and plate titanium generated many cracks.

Titanium with Different shapes showed excellent hydrogen absorption but different reaction temperature.

2) Particle shape and size of titanium hydride

Titanium hydride were milled during 5hours by ball mill

Fig. 5 shows the size distribution after 3 hours sieving. Absorption of moisture must be considered in this process. It showed in SEM that the particle size is below 10μm, but it never passed the 45μm - 150μm sieve.

Foaming agent need the size of 100μm, TiH2 powder can be used without the sieving.

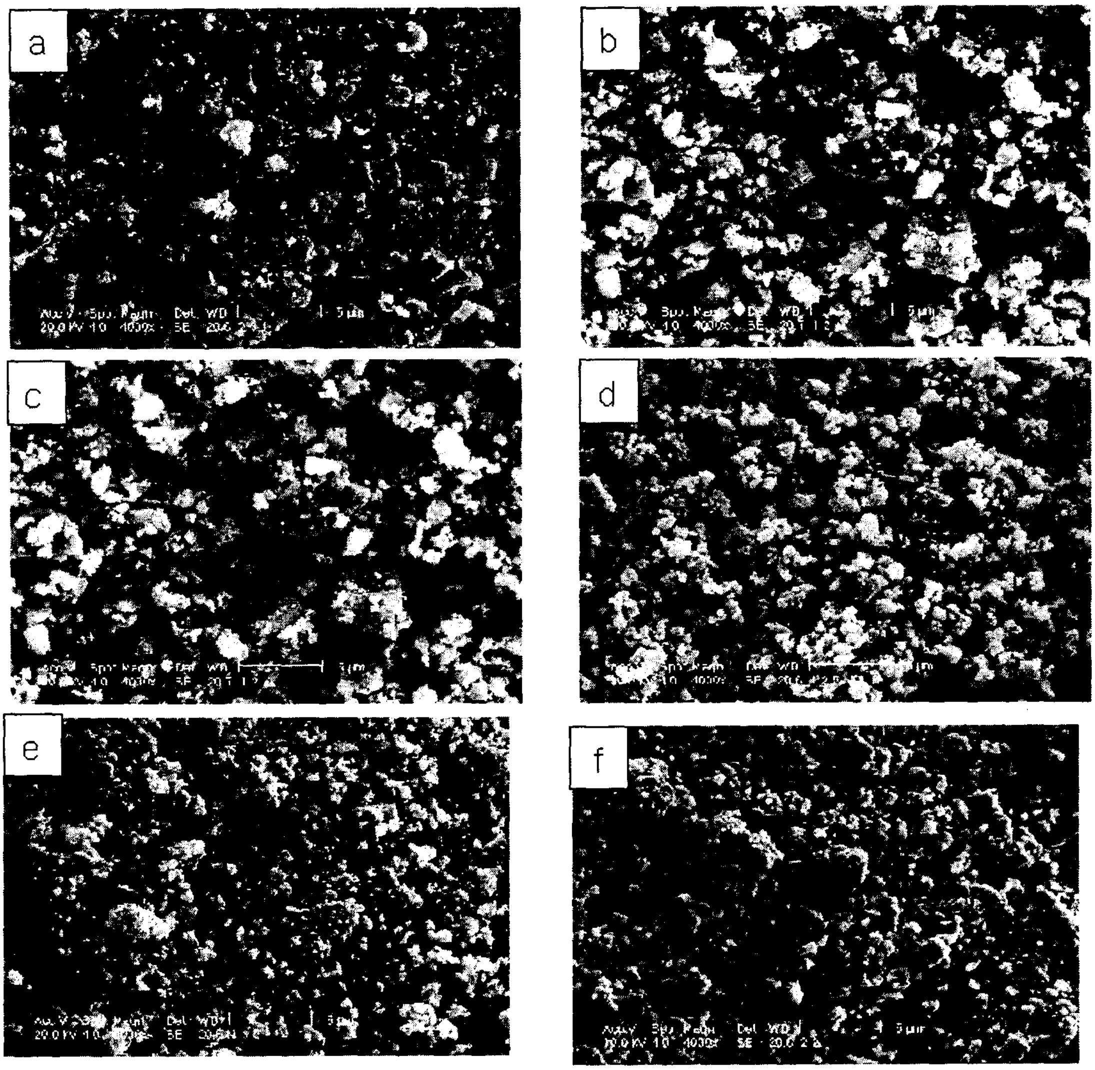

Fig. 4. SEM micrographs of titanium hydride
(a)Sponge Ti (b) Plate Ti (c) Chip Ⅰ (d) Chip Ⅱ (e) Chip Ⅲ (f) Chip Ⅳ

and sieved 3hours. The SEM micrographs of titanium hydride powder(below 230Mesh) showed in Fig4. Compared with the sponge titanium, the chip titanium and plate titanium have smaller sizes and less triangular shapes. Hydride titanium is brittle and easy to mill. titanium hydride powder can be used as foaming agent.

Fig. 5 shows the size distribution after 3 hours sieving. Absorption of moisture must be considered in this process. It showed in SEM that the particle size is below 10μm, but it never passed the 45μm - 150μm sieve. Foaming agent need the size of 100μm, TiH_2 powder can be used without the sieving.

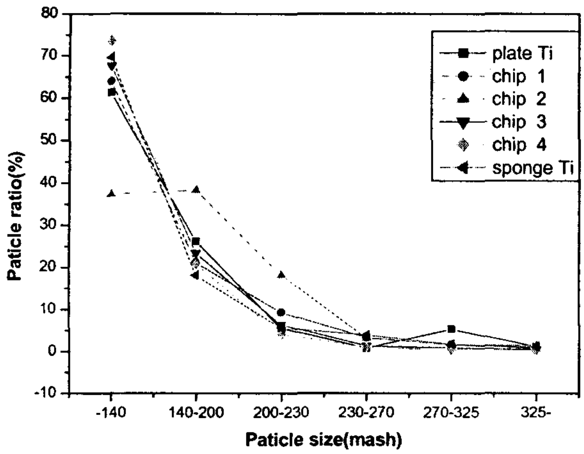

Fig.5 The relation of particle ratio and size after sieving

Fig.6 shows the X-ray diffraction result. TiH_2 made by Sponge titanium and Scrap titanium showed single α phase without TiO_2 and decomposition. It means the powder stored the hydrogen that needed in foaming process.

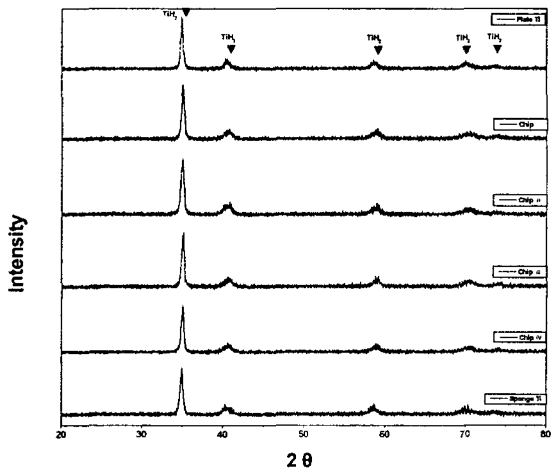

Fig.6 X-ray diffraction patterns of titanium hydride

CONCLUSION

In this study, the purpose is the possibility of substitution of sponge titanium for return scrap titanium for manufacturing Aluminum foaming agent. It can be concluded that

1. If control the surface and oxide layer effect of titanium, it is possible to use the return scrap titanium.
2. The hydride formation temperature of return scrap titanium were increased more than pure titanium.
3. XRD showed that the powder have single phase without second one.
4. The effect of oxide layer and impurities in foaming agent must be considered and controlling the powder size will benefit the equality of foaming properties.

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