Pulsed Current Sintering of Amorphous Titanium Alloy Powder Synthesized by Mechanical Alloying Process

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Ti–2 at%Fe–10 at%Si, Ti–4 at%Fe–10 at%Si and Ti–6 at%Fe–10 at%Si powders were synthesized by mechanical alloying (MA) of pure Ti, Fe and Si powders using a planetary ball milling for 720 ks. The amount of collectable powder milled for 720 ks decreased with increasing Fe content in the MA powder. An amorphous phase was generated for all of the powders milled for 720 ks. The crystallization temperature of Ti–2 at%Fe–10 at%Si powder synthesized by MA for 720 ks was higher than that of the other MA powders. Ti–2 at%Fe–10 at%Si powder prepared by milling for 720 ks, which contained amorphous phase, was consolidated using a pulsed current sintering apparatus under a high pressure. The compact consolidated at 673 K under a pressure of 1500 MPa was almost densified with the retention of amorphous phase. The pulsed current sintering under a high pressure is a powerful technique to consolidate amorphous powder into a bulk material.

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1. Introduction

Titanium alloys are widely used as structural materials in the aerospace and chemical industries because of their superior specific strength and corrosion resistance. If their strength is improved, the area of industrial application is expanding. To improve the strength, an addition of various alloying elements1,2 and ceramic powders3 have been performed so far. It would be desirable if expensive alloying elements such as V, Zr, Mo and ceramic powders could be replaced with cheaper elements without sacrificing desirable mechanical and chemical properties. A new technique controlling constituent phases of the alloy is desirable to develop a highly strengthened titanium alloys. Especially, the materials containing amorphous phase and nano crystalline4 are expected as a new approach to improve their mechanical properties.

Authors have reported that an amorphous Ti–37.5 at%Si powder was synthesized by mechanical alloying (Hereafter, described as MA) of elementary Ti and Si powder as starting materials.5 In the mechanically alloying of titanium alloys, the amount of the collectable powders is generally small because of their adhesion to the MA vessel and balls. However, the addition of Si powder to titanium powder was effective to prevent the adhesion phenomenon during MA. The MAed Ti–37.5 at%Si powder is difficult to consolidate into a dense compact because it has a very high hardness. We have found an amorphous Ti–10 at%Si powder was synthesized by MA.6 However, it was difficult to prepare a dense sintered Ti–10 at%Si compact because the crystallization temperature was low. On the other hand, we have also found an addition of Fe element to Ti–37.5 at%Si powder in MA resulted in higher crystallization temperature.7

In this study, the effect of Fe addition on the formation of amorphous phase in MAed Ti–10 at%Si alloy powder was investigated. Moreover, an attempt was made to fabricate amorphous Ti–Si–Fe compacts by a pulsed current sintering (Hereafter, described as PCS) process under a high pressure. Since the air oxidation resistance of Ti–4 mass%Fe–(0.5–2)mass%Si alloys prepared by a vacuum arc melting was much better than that of Ti–6 mass%Al–4 mass%V alloy,8 Ti–Fe–Si alloys are expected as a new low-cost titanium alloys.

2. Experimental Procedure

Ti–2 at%Fe–10 at%Si, Ti–4 at%Fe–10 at%Si and Ti–6 at%Fe–10 at%Si alloy powders were synthesized as starting materials of elementary Ti powder (99.5 mass%Ti), Fe powder (99.85 mass%Fe) and Si powder (99.9 mass%Si) using a planetary ball mill for 720 ks. The vessel (5 × 10−4 m3) and the balls (0.01 m in diameter) for MA were made of chromium steels (84.1 mass%Fe, 11 mass%Cr). The mechanically alloyed powder was 5% of the MA balls by weight. The rotational speed of MA was 2.83 s−1. To prevent oxidizing and nitriding of the milled powders, MA was performed under an argon gas atmosphere of reduced pressure 66 kPa. The structure of the obtained MA powder was identified by X-ray diffractmeter, and the thermal analyses by differential scanning calorimeter (DSC) and the microstructural observation by transmission electron microscope (TEM) were performed to clarify the generation of an amorphous phase. DSC was measured at the heating rate of 0.33 K/s under an argon gas flow in an alumina pan.

The mechanically alloyed Ti–2 at%Fe–10 at%Si powder for 720 ks was filled in a pipe made of stainless steel (SUS304) of 3.8 mm in the inside diameter, 6.4 mm in the outside diameter and 3 mm in height. This pipe was put in a die set of hard metal of 10 mm in the inside diameter, 30 mm in the outside diameter and 30 mm in height. The MAed powder was consolidated by a PCS under a high pressure. The shape and dimensions of punches, made of hard metal are shown in Fig. 1. The pressure given to the powder in the pipe is four times as much as that applied to the electrode. The sintering temperature (Hereafter, described as a die temperature) was measured by alumel-chromel type thermo-couple inserted in the hard metal by 3 mm. To suppress the
radiation heat, the carbon wool of 5 mm thickness was wrapped around the die. The initial pressure of 64 MPa was applied. When the die temperature reached 673 K, the compaction pressure increased to the target pressure. After that, the current 500 A was maintained constantly for 120 s. The target pressure 392 MPa (The compaction pressure is 98 MPa), 600 MPa (150 MPa), and 1500 MPa (375 MPa) was applied to the powder in the pipe. The amount of the amorphous phase included in the obtained compact was evaluated by DSC. Moreover, porosity of the compact was determined by the observation of the sectional microstructure.

3. Experimental Result and Discussion

3.1 Effect of Fe addition on formation of amorphous phase in MA

The amounts of the collectable MA powders has decreased with increasing Fe content of MA powder milled for 720 ks. They were 83.2 mass% for Ti–2 at%Fe–10 at%Si and 34.4 mass% for Ti–6 at%Fe–10 at%Si. In a small amount of the collectable MA powder, the content of Fe has decreased compared with the composition of the starting materials. The X-ray diffraction patterns of the obtained MA powders, the content of Fe has decreased compared with the composition of the starting materials. The X-ray diffraction patterns of the obtained MA powders were shown in Fig. 2. MA powders were fixed using a double-faced tape on the glass in X-ray diffraction measurements, because all of the obtained MA powders were coarse of 20 μm or more. The X-ray diffraction patterns were sharpened according to an increase in Fe content of MA powders. It can be speculated that an increase in the Fe content of the MA powders enlarges the crystalline size of the MA powder.

DSC curves of the obtained MA powders are shown in Fig. 3. In each MA powder, a sharp exothermic reaction was observed at about 850 K just like Ti–10 at%Si MA powder reported previously. This exothermic reaction suggests the crystallization of an amorphous phase synthesized by MA. The amorphous phase was generated in all of the MA powders for 720 ks in this study. DSC was measured by almost the same weight, and the calorie was evaluated by each unit weight. The gradual exothermic reaction was observed at the lower temperature than the crystallization temperature in all of DSC curves. This suggests the structural relaxation. This gradual exothermic reaction decreased with increasing Fe content. Moreover, the peak temperature of the exothermic reaction caused by the crystallization has lowering according to an increase in the Fe content. The crystallization temperature of Ti–2 at%Fe–10 at%Si powder was about 10 K higher than that of Ti–4 at%Fe–10 at%Si and Ti–6 at%Fe–10 at%Si powders, and about 25 K higher than that of Ti–10 at%Si powder. It is concluded that Ti–2 at%Fe–10 at%Si powder synthesized by MA contained a stable amorphous phase and was suitable for the consolidation below the crystallization temperature.

Bright field image and the corresponding selected area diffraction pattern of Ti–2 at%Fe–10 at%Si powder synthesized by MA milled for 720 ks are shown in Fig. 4. This figure shows the powder is composed of nano-sized crystalline and amorphous phase.
In DSC curves of Fig. 3, the profile of Ti–4 at%Fe–10 at%Si is almost the same as that of Ti–6 at%Fe–10 at%Si. To investigate this cause, the composition of the MA powder milled for 720 ks was analyzed by X-ray fluorescence. The Fe contents of Ti–4 at%Fe–10 at%Si powder and Ti–6 at%Fe–10 at%Si powder were 3 at% and 3.5 at% respectively. When the amount of Fe included in the MA powder increased, the composition of the MA powder deviated from the initial composition of starting materials. This is because the adhesion to the MA balls and the vessel increased. Therefore, when the Ti–Fe–10 at%Si powders containing more than 3 at%Fe were mechanically alloyed, the obtained powder contained less Fe content than initial blended powder. In addition, the agglomerated particles of about 1 mm were observed in MA powders of high Fe content alloy. This coarse powder is unsuitable for the consolidation at a low sintering temperature. It is concluded that Ti–2 at%Fe–10 at%Si composition is desirable to synthesize an amorphous phase with a high crystallization temperature by MA.

3.2 Consolidation of Ti–2 at%Fe–10 at%Si MA powder by a pulsed current sintering

Ti–2 at%Fe–10 at%Si alloy powder synthesized by the MA for 720 ks was consolidated by a PCS under a very high pressure. It was difficult to consolidate the obtained MA powder using an ordinary PCS process because of its high hardness of 441 Hv (it was measured with 10 g load). Then, the MA powder was packed into a stainless steel (SUS304) pipe, and consolidated by a PCS process under a high pressure using a novel die as shown in Fig. 1. This technique can generated a shear stress between MA powder particles accompanied with a transformation of the pipe. The compact was embedded in and easily taken out of pipe. The compact was fully densified at the center but not around the part just near the pipe.

Figure 5 shows the change of a die temperature and the amount of shrinkage against the sintering time when the high pressure of 1500 MPa was applied to the MA powder. When the die temperature reached 673 K, the compacting pressure was increased from 64 MPa to 1500 MPa. The amount of shrinkage has rapidly increased with increasing the compacting pressure. A resistance heating of the die and Joule heating of the powder leads to a high-speed heating of 1.25 K/s. However, Joule heating of the powder has become small with increasing the density of compacts. As a result, the die temperature has decreased gradually by the heat transfer to the water-cooled electrode though the current value is maintained in 500 A. This means that high-speed heating is difficult when the very high pressure of 1500 MPa is given at the first stage of the pulsed current sintering. Therefore, the proposed sintering process, being energized under a low pressure without a transformation of the powder in the pipe at the first stage of sintering, a very high pressure being applied at the target sintering temperature, was effective to fabricate the bulk amorphous material. The compact fabricated by this sintering process was so dense that it had a metallic luster though it still included the pore of 10.8 vol%.

Figure 6 shows the change in the die temperature and the amount of shrinkage during the pulsed current sintering against the sintering time when the pressure of 352 MPa was applied to the powder. Because the compacting pressure was small, the amount of total shrinkage became small. The pressurizing and heating condition were the same as the case of 1500 MPa. However, the die temperature increased gradually after it had reached a target sintering temperature. This is probably because the obtained compact was porous due to low compacting pressure and Joule heating of the powders in the pipe continued while the current was constantly held. The amorphous phase included in the compact has crystallized easily since the compact in the pipe was heated up to more than the die temperature by Joule heating. The porosity of compacts decreased with increasing the compacting pressure, and showed 58.1 vol% in the case of 392 MPa, 38.1 vol% in the case of 600 MPa.
DSC curves of Ti–2 at%Fe–10 at%Si milled for 720 ks and the compact prepared at 673 K under 1500 MPa were shown in Fig. 6. In the MA powder, a gradual exothermic reaction was recognized at about 720 K like the one reported in the previous study. This reaction suggests a primary precipitation of $\alpha$-Ti nanocrystals from the amorphous phase. This reaction was not observed in the compact because it had ended while sintering. The sharp exothermic reaction at about 860 K in both DSC curves reveals the crystallization of the amorphous phase. The calorific value of the compact was 81.6% of that of the MA powder. It is speculated that a part of the amorphous phase in the MA powder crystallized at the contact part between powder particles while sintering. This is verified by the fact a lot of amorphous phase remained in a compact since generation of heat in the contact part becomes small when the compacting pressure is high. Actually, it was confirmed that the calorific value of the crystallization of the compact prepared under a pressure of 600 MPa was above 5% less than that of the compact prepared under a pressure of 1500 MPa. Therefore, it is effective to consolidate the amorphous powder synthesized by MA using the pulsed current sintering under the very high pressure at the high temperature as much as possible. It will be necessary to examine the influence of the coexistent crystalline on a mechanical characteristic of a bulk amorphous material in the future.

4. Conclusion

Ti–2 at%Fe–10 at%Si, Ti–4 at%Fe–10 at%Si and Ti–6 at%Fe–10 at%Si powder were synthesized by mechanical alloying for 720 ks of elementary Ti, Fe and Si powders. The effect of Fe content on the formation of an amorphous phase was investigated. In addition, the obtained amorphous powder was consolidated by a pulsed current sintering with a very high pressure below the crystallization temperature. As a result, the following are drawn.

(1) The alloy powder including an amorphous phase is obtained by mechanical alloying for 720 ks at all composition in this study. Especially, the Ti–2 at%Fe–10 at%Si powder reveals the highest crystallization temperature.

(2) The amount of the collectable powder decreased with increasing Fe content in the MA. Therefore, the Ti–2 at%Fe–10 at%Si powder is the most suitable to fabricate a bulk amorphous material.

(3) Ti–2 at%Fe–10 at%Si amorphous powder synthesized by mechanical alloying for 720 ks can be consolidated by the pulsed current sintering under a very high pressure below the crystallization temperature. The compact consolidated at 673 K under a pressure of 1500 MPa contains the pore of about 10%, and maintains about 82% of the amorphous phase included in the MA powder.

(4) The proposed process that gives a very high pressure at the sintering temperature after heating under a low pressure is effective to fabricate a dense bulk amorphous material.

REFERENCES