Preparation and Characterization of Nano-Crystalline Ti-2 at%Fe-10 at%Si Alloy by Mechanical Alloying and Pulsed Current Sintering Process*

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Ti-2 at%Fe-10 at%Si amorphous powder was synthesized by mechanical alloying (MA) of elemental Ti, Fe and Si powders using planetary ball milling for 1440 ks. Crystallization temperature of the obtained amorphous powder was ca. 830 K. Ti-2 at%Fe-10 at%Si amorphous powder was consolidated using a pulsed current sintering (PCS) process at a die temperature of 773 K under a pressure of 372 MPa. Then the compact was densified at a die temperature between 743 K and 763 K, which is around the crystallization temperature of the amorphous phase. The obtained Ti-2 at%Fe-10 at%Si alloy consists mainly of nanocrystalline α-Ti phase. The compressive strength of the nano-crystalline compact at room temperature was more than 1.7 GPa, much higher than that of a commercial Ti-6 mass%Al-4 mass%V alloy.

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1. Introduction

Titanium based alloys have been used as high temperature structural materials for aerospace applications because they offer low density and excellent corrosion resistance. However, the activity under a melting state and high melting temperature over 1600 K increases their manufacturing cost. Generally, to improve the strength of titanium alloys, the addition of rare metallic elements has been accomplished. But the use of rare resources results in the high cost of starting materials.1,2)

On the other hand, it is well known that a fine matrix structure improves the specific strength. Therefore, a number of studies of nano-crystalline structure have been continued. It has been reported that an amorphous-like Ti-2 at%Fe-10 at%Si alloy powder was synthesized by mechanical alloying (MA) method of elemental powder blends, and the corresponding bulk-amorphous materials was provided when pulsed current sintering was applied under a high pressure over than 1.5 GPa.3) We infer that the bulk-amorphous material may offer high strength since it is consisting of an ultra fine structure. Unfortunately the intrinsic characteristics have not been evaluated due to some remained pores in the bulk materials. But Ti-Fe-Si alloy consists only of abundant resource elements. This material might be an answer to demands for a low cost titanium alloy that offers superior oxidation resistance.4,5)

In this study, amorphous Ti-2 at%Fe-10 at%Si alloy powder synthesized by MA for 1440 ks was consolidated to a high density compact by pulsed current sintering process (following PCS) at above its crystallization temperature.6) The structure and mechanical properties of Ti-2 at%Fe-10 at%Si nano-crystalline bulk compact were investigated.

2. Experimental Procedures

Ti-2 at%Fe-10 at%Si powder mixture of elemental Ti (99.5 mass%) and Si (99.9 mass%) powders, was mechanically alloyed for 1440 ks using planetary ball mill. The vial 5 × 10⁻⁴ m³ in volume and balls of 0.01 m in diameter, made of hardened steel were used for MA. A ball-to-powder weight ratio was 20:1. The vial was filled with an argon gas atmosphere of 66 kPa to prevent oxidation and nitriding in MA.

The phases of synthesized powder after MA were characterized by X-ray diffraction measurement (XRD); the crystallization temperature of the amorphous phase was measured by differential scanning calorimeter (DSC). In DSC, the sample was settled into an alumina cell and heated at a rate of 0.33 K/s under an argon gas flowing condition. Mechanical alloyed Ti-2 at%Fe-10 at%Si powder was poured into a 20-mm-high hard metal die (WC-Co) with 6 mm interior and 20 mm exterior diameter, and sintered using pulsed current sintering equipment. Furthermore, a 5-mm-thick carbon cloth was wound laterally around the hard metal die to prevent heat radiation. The die temperature was measured with a K-type thermocouple inserted to 3 mm inside from the outer surface of the die. The target pressure was applied in tow steps. At first, a relatively low pressure of about 120 MPa was applied until a die temperature reached at 573 K to remove some adsorbed gases or adherent moisture on the surface of MA powder. Then, the pressure was increased to 392 MPa. The structure of the obtained compact was observed by TEM. The synthesized phase was characterized by X-ray diffraction method. Furthermore, a larger compact was prepared by PCS method using a 30-mm-high hard metal die with 15 mm interior and 30 mm exterior diameter under the same sintering conditions mentioned above. The compact was cut into 1.6 mm² square and 8 mm length for the compression testing. The compressive test was carried out under the crosshead speed 0.2 mm/min.

3. Results and Discussion

3.1 Characteristic of Ti-2 at%Fe-10 at%Si alloy powder synthesized by MA

SEM image of Ti-2 at%Fe-10 at%Si alloy powder prepared
by MA for 1440 ks is shown in Fig. 1. The particle size was about 30 μm in diameter. It has been already reported that a Ti-2 at%Fe-10 at%Si amorphous powder was successfully synthesized by MA for 720 ks. However, the collective of MA powder up to 720 Ks was largely varied. This is probably due to the variation of nitrogen and oxygen content. Therefore the MA time was determined to be 1440 ks that can constantly yield 70% powder by weight. The obtained powder contained 0.38 mass% of oxygen and 0.16 mass% of nitrogen. The composition of MA powder did not change when MA time was longer than 720 ks, but the ratio of millimeter order agglomerated powder was increased when time was longer. It is inferred that amorphous powder was welded with each other when the MA balls collided. The agglomerated powder by MA for 1440 ks was less than 10% of the collected powder by weight.

X-ray diffraction patterns of the MA powder are shown in Fig. 2. There is no clear peak revealing a crystal. This indicates that the MA powder became amorphous phase. Subsequent DSC analysis of this powder revealed a large exothermic reaction peak around 830 K, as shown in Fig. 3. The exothermic reaction is caused by crystallization of amorphous phase. Therefore, it is surmised that the amorphous Ti-2 at%Fe-10 at%Si alloy powder synthesized in this study was crystallized by heating above 830 K.

3.2 Pulsed current sintering of Ti-2 at%Fe-10 at%Si powder synthesized by MA

To make a bulk amorphous, it is effective to consolidate an amorphous powder synthesized by MA under a high pressure and low temperature less than crystallization temperature. If a compact can be formed between the glass transition temperature and the crystallization temperature of amorphous powder, the compact should be consolidated under a low compressive pressure with the help of viscous fluid of amorphous phase. But a clear glass transition temperature is not observed in the DSC curve of MA alloy powder as shown in Fig. 3. A high compacting pressure is necessary to produce a bulk amorphous in a low temperature, which is less than glass transition temperature. This indicates that the densification of amorphous powder is difficult. Therefore, consolidation was carried out just above the crystallization temperature, which did not damage the hard metal die. Our experience in sintering by PCS process demonstrates that a pressure of about 400 MPa and sintering temperature below 973 K does not induce any damage to the hard metal die. Therefore, we tried to produce a high dense compact at the maximum die temperature of 773 K by PCS. Die temperature and shrinkage for mechanically alloyed Ti-2 at%Fe-10 at%Si powder in sintering plotted against time is shown in Fig. 4. The positive change of the thickness of compact demonstrates shrinkage. The compact seems to expand apparently due to thermal expansion of the die punch up to 573 K. Subsequently, the compact thickness decreased when the compaction pressure increased up to 392 MPa. When the die temperature exceeds 743 K, an abrupt shrinking is observed. When the die temperature becomes 763 K, shrinking stops and sintering would be completed. The density of the provided compact is 4.49 g/m$^3$ and pores were not observed in the cross section of the specimen by optical microscope observation.

X-ray diffraction patterns of Ti-2 at%Fe-10 at%Si consolidated at (a) 723 K and (b) 773 K under 392 MPa are shown in Fig. 5. Broad peaks suggesting indicating an α-Ti was recognized in the X-ray diffraction pattern of the compact
sintered at 723 K, but there is no clear peak of crystal. This reveals that it might include a large amount of amorphous phase. On the other hand, sharp $\alpha$-Ti peaks and small Ti-Si compound peaks were observed in the compact sintered at 773 K. This demonstrates no existence of amorphous phase. Actually, no exothermic reaction was observed in the DSC analysis of this compact. This result reveals the compact sintered at 723 K consist of mainly amorphous phase and that at 773 K consist of some kinds of crystalline. Therefore, large shrinkage at 743 to 763 K is probably due to crystallization of amorphous phase. It has been reported that Joule heating, when the electric current passes in a specimen in the PCS sintering, engenders necking between powder particles and consequently sintering was promoted at lower temperature.\textsuperscript{6,7} Therefore, the sintering rapidly proceeded with accompanying heat generation due to crystallization. A densification might be caused by super plasticity of fine grains in this sintering. But the deformation velocity is very fast and the densification proceeds in the narrow temperature range of ca. 20K. It is concluded that the prevailing mechanism for densification is the transition from amorphous phase to crystalline phase. Notwithstanding, further study for the densification mechanism is necessary in the future.

The microstructure of the compact prepared at 773 K was observed by TEM. Figure 6 shows bright field image and the corresponding selected area diffraction pattern of the nano-crystalline Ti-2 at%Fe-10 at%Si compact. It can be seen that the compact consisted of nano-sized crystalline around 50 nm. The die temperature in forming was a little lower than the crystallization temperature measured in DSC curve, but the compacting temperature might slightly exceed the crystallization temperature. It is suggested that the compacting temperature was about 80 K higher than the die temperature in this experimental condition.

The obtained compact has a homogeneous structure, so it might provide its high strength. Compression test was carried out using a test piece with the size of 3 mm diameter and 15 mm height. A compressive strength of nano-crystalline Ti-2 at%Fe-10 at%Si plotted against stroke is shown in Fig. 7, compared with the results of Ti-6 mass%Al-4 mass%V (follows Ti-6Al-4V) cast alloy. The strength of the nano-crystalline Ti-2 at%Fe-10 at%Si material demonstrates about 1.7 GPa, which is higher than the cast Ti-6Al-4V alloy. However, Ti-2 at%Fe-10 at%Si alloy demonstrated no yield phenomena and fractured without plastic deformation. This reveals that the nano-crystalline material prepared in this process offers high strength, high rigidity and few elongation.
In addition, high vickers hardness of 707Hv for this nano-crystalline compact was obtained. The synthesized amorphous Ti-2 at%Fe-10 at%Si alloy powder by MA was successfully consolidated into a high dense compact under a pressure of 392 MPa just above the crystallization temperature (773 K in die temperature). In this sintering condition, a near-net-shaped product can be produced by the use of a hard metal die. Therefore, an attempt was made to prepare a product with the shape of gear part by PCS. A nano-crystalline Ti-2 at%Fe-10 at%Si gear part is shown in Fig. 8. Large shrinkage was observed between 743 K and 763 K just the same as the sintering phenomenon of a simple columnar sample. The compact was completely formed to a part of a gear tooth. Neither cracking nor pores were observed. The proposed process in this study made it possible to form various industrial titanium alloy tools at lower temperature below 873 K. This nano-crystalline Ti-2 at%Fe-10 at%Si alloy consisted of only abundant metallic elements, leading to reducing primary material costs. Moreover, saving the energy can be attained using the good forming ability of amorphous phase.

4. Summary

Ti-2 at%Fe-10 at%Si alloy powder was synthesized by MA for 1440 ks using elemental Ti, Fe and Si powders. The provided MA powder was formed into a dense compact. Then, structure and mechanical properties of the compact were investigated.

Main results are the following.
(1) Ti-2 at%Fe-10 at%Si alloy powder by MA for 1440 ks consists of mainly amorphous phase, and its crystallization temperature is 830 K. In addition, the collective amount of the powder by MA is about 70% by weight.
(2) A high dense compact was obtained by forming an amorphous powder using PCS method under a pressure of 392 MPa at the sintering temperature of 773 K. The compact consisted of nano-crystalline around 50 nm. The transition of the amorphous phase into crystalline in sintering lead to the densification of the compact.
(3) The provided Ti-2 at%Fe-10 at%Si compact mainly consists of nanocrystalline α-Ti. It demonstrates a compressive strength 1.7 GPa and vickers hardness 707 Hv. This alloy comprises only abundant metallic elements. Therefore it offers both high strength and low cost.
(4) Pulsed current sintering of amorphous Ti-2 at%Fe-10 at%Si powder is able to produce a high dense compact with nano-crystalline structure at low temperatures below 900 K. This means a complex compact such as a gear shape can be prepared by use of a hard metal die.

We intended to develop a high-strength amorphous titanium bulk alloy using amorphous titanium alloy powder. However, we found that the high dense compact with high strength was successfully fabricated via crystallization of amorphous phase in sintering at lower temperature.

This process also makes it possible to fabricate a complicated product. It has the possibility of a novel manufacturing process to produce various industrial tools.

REFERENCES