Amorphous Phase and Compact Solid Formation of Ti–(37.5 - X) at%Si–X at%Fe (X = 0–10) Powders by Mechanical Alloying and Pulse Current Sintering

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Ti-(37.5 - X) at%Si-X at%Fe (X = 0-10) powder mixtures have been mechanically alloyed in a planetary ball mill under an argon atmosphere for 180 ks. The milled alloy powders become amorphous and crystallization temperature is 843 K for X = 5, being 90 K higher than that for X = 0. Milled powders have been consolidated using a pulse current sintering process under 1.5 GPa. The porosity of an amorphous compact solid consolidated at 813 K is estimated to be 7.5% for X = 5, being much lower than 24% for X = 0. Fe addition to Ti-37.5 at%Si powder mixtures in mechanical alloying improves the stability of an amorphous phase and forming-ability of compact solid powders.

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1. Introduction

Ti-based amorphous powder was obtained by mechanical alloying (MA) from elemental powder mixtures of titanium and silicon with the composition of Ti-37.5 at%Si, and a Ti-based amorphous compact solid was successfully consolidated by high hydrostatic pressure consolidation technique (HHPC method) under a high pressure of 5.4 GPa.^{1,2)} Its compressive strength was 2.5 GPa, which was about 20% higher than that of the crystallized solid. As Ti-37.5 at%Si amorphous alloy is light, mechanically strong and non-toxic, it is expected to use as a structural material for micro-machines and bionics. However the crystallization temperature of Ti-37.5 at%Si amorphous solid was rather low of about 750 K, probably because the volume fraction of amorphous phase was about 60% and the remained crystalline phase promotes the crystallization of amorphous phase. In the present study, Fe was added to Ti-37.5 at%Si to fabricate more stable Tibased amorphous alloy powders, and the forming-ability of the milled alloy powders was investigated using high performance pulse current sintering (PCS method) instead of a large-scaled HHPC method.

2. Experimental Procedure

Elemental powders of titanium (99.5 mass%, less than 45 μ m), silicon (99.9 mass%, less than 75 μ m) and iron (99.8 mass%, less than 75 μ m) were mixed to give the desired composition of Ti–(37.5 – X) at%Si–X at%Fe (X = 0, 1, 5, 10). The powders were milled in a planetary ball mill (Fritsch, Pulverisette-5) at the rotation speed of 170 per minute under an argon atmosphere of 66 kPa. The container (80 mm in inner diameter and 90 mm in inner length) and balls (10 mm in diameter) made of hardened steel were used for milling. A ball-to-powder weight ratio 20:1 was used for alloying 20 g batches of powders. After milling, the obtained powders were examined by X-ray diffractometer us-

ing CuK α radiation (XRD, SHIMADZU Co., XD-D1), transmission electron microscopy (TEM, JEOL Co., JEM-4000FX and JEM-2010) and differential scanning calorimeter (DSC, SHIMADZU Co., DSC-50). The oxygen and nitrogen content were determined by the inert gas fusion method (LECO Co., TC-36).

After confirming amorphous phase formation, Ti–(37.5 - X) at%Si–X at%Fe powders milled for 180 ks were consolidated using a pulse current sintering (PCS) machine (IZUMITECH Co., SPS-1050L). Milled powders of 0.5 g were filled in the hard metal die (6 mm in inner diameter and 20 mm in length) and consolidated in the temperature range between 623 K and 723 K under a high pressure of 1.5 GPa for 120 s within the strength limit of the hard metal die. The structure of the obtained compact solid was characterized using XRD and TEM. Their porosity was estimated by measuring the area of pores on the optical micrographs using a commercial imaging software.

Rectangular specimens in $1.5 \times 1.5 \times 3 \text{ mm}^3$ size were cut from the compacts using a cutting saw, followed by mechanical polishing. They were deformed in compression at room temperature between two hard metal platens using an Instrontype testing machine (SHIMADZU Co., AG-25TC) at a strain rate of $1.67 \times 10^{-4} \text{ s}^{-1}$.

3. Results and Discussion

Figure 1 shows X-ray diffraction patterns of Ti–(37.5 - X) at%Si–X at%Fe (X = 0, 1, 5, 10) powders milled for 180 ks. There are broad peaks at around $2\theta = 41$ degrees. With increasing X, the profiles become broader, suggesting that Fe addition to Ti–37.5 at%Si powders in MA promotes the amorphization. Oxygen and nitrogen contamination from the atmosphere was measured to be 0.38–0.51 mass% and 0.05–0.09 mass% respectively using the inert gas fusion method.

Figure 2 shows thermal analyses by DSC measurement for



Fig. 1 X-ray diffraction patterns of Ti–(37.5 - X) at%–X at%Fe powders milled for 180 ks.



Fig. 2 DSC curves of Ti–(37.5 - X) at%-X at%Fe powders milled for 180 ks.



Fig. 3 Bright field images and corresponding selected area diffraction patterns of (a) Ti-37.5 at%Si and (b) Ti-32.5 at%Si-5 at%Fe powders milled for 180 ks.

milled Ti-(37.5 - X) at%Si-X at%Fe (X = 0, 1, 5, 10) powders. The crystallization temperature of X = 5 is 843 K, which is about 90 K higher than that of X = 0. The crystallization temperature is not increased for X > 5.

Figure 3 shows bright field (BF) images and the corresponding selected area diffraction (SAD) patterns for X = 0 and 5. These images are featureless and the corresponding SAD patterns show a halo characteristic of an amorphous phase. The SAD patterns, however, show some diffraction spots that reveal the presence of retained titanium and/or silicon elements. The volume fraction of an amorphous phase is higher in the Ti-32.5 at%Si-5 at%Fe powders (85%) than that in the Ti-37.5 at%Si powders (60%).

The criteria to promote the amorphization in rapid quenched materials was proposed by Inoue *et al.*: (i) constitution of multi-component systems consisting of more than three elements, (ii) negative heats of mixing, (iii) significantly different atomic size ratios above 13%.³⁾ Mizutani *et al.* also proposed the similar criteria of amorpization in mechanically alloyed materials.⁴⁾ The present Ti–Si–Fe ternary system unanimously satisfies the criteria (i). The heat of mixing $\Delta H_{\text{Ti–Fe}}$ and $\Delta H_{\text{Si–Fe}}$ are estimated to be -17 kJ/mol and -19 kJ/mol, respectively.⁵⁾ The atomic sizes of Ti, Si and Fe elements are 0.147, 0.117 and 0.124 nm, so the difference of the atomic ratios are calculated to be 25% for Ti to Si, 18% for Ti to Fe and 6% for Si to Fe, respectively. Since an Fe addition to Ti–Si binary system satisfies these criteria of amorphization, leading to the higher crystallization temperature.

Figure 4 shows X-ray diffraction patterns of (a) Ti– 37.5 at%Si and (b) Ti–32.5 at%Si–5 at%Fe specimens prepared by the PCS method under 1.5 GPa. The Ti–37.5 at%Si specimen has almost the same profile as the as-milled powder up to 713 K, being crystallized to Ti₅Si₃ intermetallic compound above 733 K, while the Ti–32.5 at%Si–5 at%Fe specimen has almost the same profile as as-milled powder up to 813 K.

Figure 5 shows an appearance of the Ti–32.5 at%Si– 5 at%Fe compact solid prepared at 813 K by the PCS method under 1.5 GPa. As shown here, the compact and crack-less specimen, 6 mm in diameter and 4 mm in thickness, was obtained. S. C. Glade *et al.* attempted to consolidate amorphous Ti–37.5%Si powders prepared by MA, using a shock consolidation technique.⁶⁾ Their specimen 10 mm in diameter and 4 mm in thickness had micro- and macro-cracks, being eas-



Fig. 4 X-ray diffraction patterns of (a) Ti-37.5 at%Si and (b) Ti-32.5 at%Si-5 at%Fe compact solids prepared by pulse current sintering under 1.5 GPa.



Fig. 5 Appearance of Ti–32.5 at%Si–5 at%Fe compact solid prepared by pulse current sintering at 813 K under 1.5 GPa.

ily separated into several smaller blocks. The XRD patterns revealed some crystalline peaks. Although the shock consolidation technique can apply high pressure of 20–40 GPa to a specimen, it is one-dimensional loading without controlling the specimen temperature. Since the static pressure can be applied and the consolidating temperature can be accurately controlled in the PCS method, compact amorphous solids were successfully obtained.

Figure 6 shows a relationship between the porosity and consolidating temperature of Ti–(37.5 - X) at%Si–X at%Fe compact solids with X = 0 and 5. The porosity is 24% at 713 K and 30% at 733 K for X = 0. While it is 7.5% at 813 K and 1.7% at 833 K for X = 5. This suggests remained titanium and/or silicon grains reacted to form Ti₅Si₃ compound by combustion synthesis combined with the crystallization of amorphous grains for X = 0. The porosity of the specimen prepared by the HHPC method was about 0.5%.²⁾

Figure 7 shows BF images and corresponding SAD patterns of (a) the Ti-37.5 at%Si compact specimen prepared at 713 K and (b) the Ti-32.5 at%Si-5 at%Fe compact specimen prepared at 813 K. Many crystallites with the size of

10 to 20 nm are clearly observed in the amorphous phase in (a), while the amorphous phase was predominant in (b). Remained Ti and Si crystallites prevent viscous fluidity and deformation of the amorphous Ti–37.5 at%Si specimen. Then, the combustion synthesis between the remained Ti and Si particles resulted in high porosity of 30% for the Ti–37.5 at%Si specimen prepared at 733 K. On the other hand, as the amorphous phase is predominant in the Ti–32.5 at%Si–5 at%Fe powder, the viscous fluidity of amorphous phase contributes to formation of the compact solid.

Figure 8 shows the compressive strength of the Ti-32.5 at%Si-5 at%Fe specimens prepared by the PCS method at (a) 813 K and (b) 833 K under 1.5 GPa. Both samples lose ductility, being broken into pieces at the maximum load. The specimen consolidated at 833 K and consisted of nano- $Ti_5(Si, Fe)_3$ grains, has the strength of about 1.4 GPa. This value is two-third of the strength of the crystallized Ti-37.5 at%Si specimen prepared by the HHPC method, being almost equal to the maximum strength of a commercial Ti-6 mass% Al-4 mass% V alloy (Fig. 8(c)). On the other hand, the specimen consolidated at 813 K and consisted of amorphous phase, has the strength of about 1 GPa, which is twofifth of the strength of amorphous-remained Ti-37.5 at%Si specimen prepared by the HHPC method. This is because that the density of specimens prepared by the PCS method is lower than that of the ones prepared by the HHPC method. In the HHPC method, hydrostatic pressure applied to the powder sample, can be transferred toward the center of the sample,⁷⁾ while uniaxial pressure applied inhomogeneously to the sample in the PCS method can not be transferred into the central portion of the sample. In the present study, the pressure of 1.5 GPa is limited by the strength of hard metal die. A higher pressure application will result in more dense specimens. Recently we also proposed another novel consolidating process using the PCS method,⁸⁾ where sample powders are inserted into a stainless pipe and consolidated with the uniaxial load accompanying deformation of the pipe. We are using this consolidation process to fabricate the amorphous Ti-32.5 at%Si-5 at%Fe compact solid.



Fig. 6 Relationship between porosity and consolidating temperature of (a) Ti-37.5 at%Si and (b) Ti-32.5 at%Si-5 at%Fe compact solids prepared by pulse current sintering under 1.5 GPa.



Fig. 7 Bright field images and corresponding selected area diffraction patterns of (a) Ti-37.5 at%Si compact solid prepared at 713 K and (b) Ti-32.5 at%Si-5 at%Fe compact solid prepared at 813 K using pulse current sintering under 1.5 GPa

4. Conclusion

We studied the effect of an Fe addition on amorphization of mechanically alloyed Ti-37.5 at%Si powder mixtures and

forming-ability of their compact solids with the pulse current sintering process under 1.5 GPa. The following results were obtained.

(1) The crystallization temperature of Ti-32.5 at%Si-



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Fig. 8 Compressive strength of Ti-32.5 at%Si-5 at%Fe compact solids prepared at (a) 813 K and (b) 833 K using pulse current sintering under 1.5 GPa, and (c) commercial Ti-6 mass%Al-4 mass%V alloy.

5 at%Fe powders milled for 180 ks is 843 K, which is about 90 K higher than that of milled Ti-37.5 at%Si powders.

(2) An Fe addition to mechanically alloyed Ti-

37.5 at%Si powders promotes the amorphization and improves the forming-ability of compact solids by the PCS method.

(3) More dense compact solid of Ti–32.5 at%Si–5 at%Fe, with the retention of the original MA powders and the porosity of 7.5%, is obtained using the PCS method at 813 K for 120 s under 1.5 GPa, while that of Ti–37.5 at%Si with the porosity of 24%.

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