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Elemental blended powders semisolid forming of Ti-Al based alloys

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Ti-6Al and Ti-6Al-4V alloys fabricated by semisolid forming are investigated with microscopic observation, density measurements, X-ray diffraction and mechanical property tests. The effects of the forming pressure, the forming temperature, and the forming loading time on the density of the green compacts are discussed. The shaped green-compact that is prepared by semisolid forming method transforms into intermetallics during the further alloying heat treatment. Pore-free green compacts are obtained under almost all the selective forming conditions. However, pores often appear after alloying heat treatment. The forming loading time has a relatively strong influence on the density of the compact. Experiments have also been carried out on various alloying treatments and the effects of the alloying treatment conditions on the mechanical properties of the compacts. It has been demonstrated that Ti-6Al-4V alloy can be fabricated by semisolid forming and the optimum alloying treatment conditions are at 1473 K treating for 7.2 ks, which can result in the best ultimate tensile strength of 1050 MPa and the elongation of 10% in excess of that of the plastic materials.

1. Introduction

Titanium alloys have been expansively used in the aerospace and chemical industrial. They are also expected as a promising material which will support the future engineering technology [1–3]. However, the machining of titanium (such as cutting and forging) is difficult and its manufacturing cost is extremely high due to its low thermal conductivity, low specific heat and high toughness. Meanwhile, casting also requires strictly controlled atmosphere and special melting technique, and refractory materials of crucibles and molds are extremely limited since the high chemical activity.

The semisolid forming processing method, which was proposed by Spencer *et al.* [4] in the early 1970's, offers not only the complicated shape forming capabilities of casting method, but also achieves the refinement of the microstructure of forging method simultaneously. On the basis of it, Young *et al.* [5] in 1980's proposed the so-called "elemental blended powders semisolid forming". In this method, thoroughly blended powders with high and low melting points are filled in a mold primarily, and then heated up to a slurry state as the powders with lower melting point melt. Thus, the compacts are formed in the mold.

The elemental blended powders semisolid forming method is not only capable of forming the complicated-shape parts and achieving excellent quality, but also enhances the freedom of the alloy design because of the capability of obtaining a partially liquid state at low temperature. For instance, regarding to Ti-6wt.%Al alloy, the liquidus temperature is 1953 K, and there are only approximately 20 K of the solid/liquid coexistence range. However, in the elemental blended powders semisolid forming method, a slurry state can be obtained if only the temperature is higher than the melting point of aluminum, i.e. 933 K. Furthermore, this liquid can be used as a process-lubricant so as to produce a good plasticity which is necessary for complicated-shape parts. Kirkwood *et al.* [6–10] made an excellent review on the present situations of the semisolid forming method. In our previous works [11, 12], investigations were carried out on the semisolid forming of Ti-Al alloy.

In the present study, the elemental blended powders semisolid forming is applied to Ti-6wt.%Al and Ti-6A1-4V alloys. The influences of the forming conditions such as forming temperature, pressure, and holding time on the densities of the green compacts and the compacts after alloying heat treatment are discussed extensively. Furthermore, the relationship between the alloying heat treatment conditions and the mechanical properties of the two kinds of alloys fabricated by semisolid forming method are studied in detail.

2. Experimental

2.1. Experimental materials

The powders used in this experiment are spherically atomized powders with an average particle sizc of 150 μm for titanium, 38 μm for aluminum, and 100 μm for vanadium, respectively.

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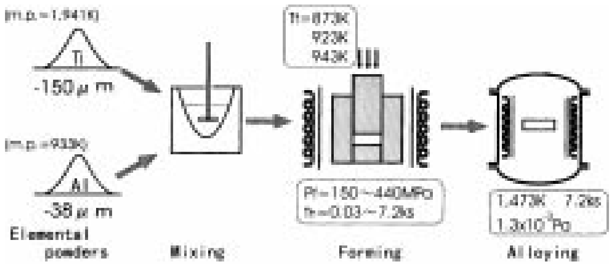

Figure 1 Ti-Al elemental blended powders semisolid processing.

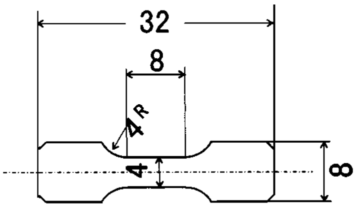

Figure 2 Tensile board specimen.

2.2. Forming process

The forming process is shown schematically in Fig. 1. The powders of titanium and aluminum were thoroughly mixed in a mortar initially. Then, 2.5–3.0 grams of the mixture was filled into a graphite-coated metal mold (Φ 16 mm) for each sample and heated up to the prescribed forming temperature (T_f). Thereafter, forming pressure was loaded and holding for about 1.8 ks to form coin-shaped specimen. The forming temperatures chosen here were just over the melting point of aluminum, i.e. 873 K, 923 K, and 943 K. The forming pressure (P_f) was in the range of 150–440 MPa, and the holding time was changed from 0.03–7.2 ks. The obtained specimens were heat treated for alloying at various temperatures of 1273 K, 1373 K, 1473 K and 1573 K in a vacuum of 1.3×10^{-3} Pa for 7.2 ks.

The fabricated compacts were characterized by density measurements by using Archimedes method, microscopic observations and X-ray diffraction analyses.

2.3. Mechanical properties tests

The geometry of tensile specimen is shown as in Fig. 2. The specimens of Ti-6Al and Ti-6Al-4V (hereafter, weight percent) were fabricated by using the elemental blended powders semisolid forming process and then machined to a sizes of 8 × 4 × 32 mm. For comparing, tensile specimens of Ti-6Al-4V were also fabricated by using conventional powders metallurgical method.

3. Results and analyses

3.1. Results of the density measurements

The relationships between the forming temperature (T_f) and the density (ρ_f) of the green compacts formed at a pressure of 400 MPa are shown in Fig. 3. The results indicate that the green density is not sensitive to the forming temperature (T_f), especially when the forming temperature (T_f) is lower than the melting point of aluminum. However, the holding time has an important influence on the green density.

The density of the pure titanium and aluminum is 4.51 and 2.70 g/cm^3, respectively. The theoretical density of elemental mixture billet of Ti-6Al can be calculated to be 4.34 g/cm^3. It can be seen that the green compact density is closed to the theoretical value under the forming conditions of $T_f = 873$ K and $t_h = 0.12$ ks, as seen in Fig. 3. Microscopic observations revealed that the green compacts formed at these conditions were free from pore. The reason that the densities of the green compacts were slightly higher than the theoretical density of elemental mixture billet is the diffusions of aluminum into titanium, and/or the transformation of intermetallics during the forming process.

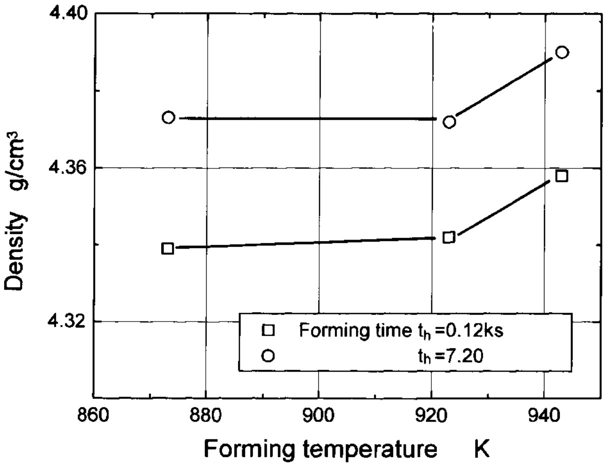

Figure 3 Effect of forming temperature on the densities of the green compacts.

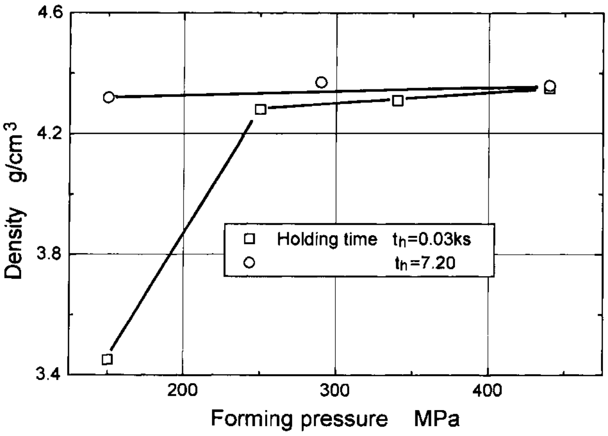

Figure 4 Effects of forming pressure on the green densities formed at various forming time.

Fig. 4 illustrates the effects of the forming pressure on the green densities under various conditions of holding time between $t_h = 0.03$ ks and 7.2 ks. The green densities, except for that the conditions of holding for $t_h = 0.03$ ks and $P_f = 150$ MPa, are in the range of 4.3–4.4 g/cm^3, which is approximately identical to the theoretical. Therefore, the pore-free green compacts can be obtained under the conditions of the forming pressure $P_f \geqq 250$ MPa and holding for 0.03 ks or 150 MPa holding for 7.2 ks.

Fig. 5 displays the relationships between the densities of green compacts and the compacts after alloying heat treatment at 1273 K, 1373 K, and 1473 K and the holding times, where the forming pressure of the green compacts is fixed at 440 MPa. The density of green compact indicated by a solid line increases gradually

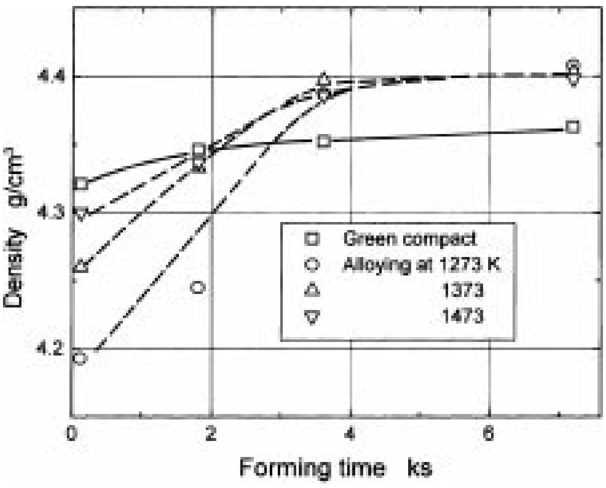

Figure 5 Effects of forming time on the densities of the green compacts and the compacts after alloying heat treatment.

with the holding time and approaches a constant as the forming time $t_h \geqq 3.6$ ks. By contrast, the density of compacts after heat treatment increases rapidly with the forming holding time. A higher density can be obtained through alloying heat treatment under the forming condition of $t_h \geqq 3.6$ ks. However, it should be noted that the densities of compacts formed under the shorter holding time of lower than 1.8 ks decrease relatively after alloying heat treatment.

As mentioned above, the holding time has an important influence on the density of the compact. Fig. 6 shows the microstructures of samples formed at 0.12 ks and 7.2 ks. A large number of pores and white α phases were observed in the microstructure of the sample formed at a holding time of 0.12 ks, as seen in Fig. 6a. X-ray diffraction analyses of the sample indicate that there are peaks of intermetallic of Ti_3Al and TiAl. The gray phases in Fig. 6 can be therefor inferred as intermetallic compounds of Ti_3Al or TiAl.

Of significance, it can be seen that the intermetallics precipitated around the pores. Fig. 6b shows the microstructure of the sample formed at a holding time of 7.2 ks. It is consisted of α and β phases without pore in it. The X-ray diffraction pattern of the sample confirmed the existence of the intermetallics.

From Fig. 5, it is clear that the decrease of the density after alloying heat treatment can be interpreted as the generation of pores, and/or intermetallics as the green compacts was formed for a shorter holding time.

The micrographs of the green compacts formed at a holding time of 0.12 ks and 7.2 ks respectively are shown in Fig. 7. It can be seen that there is no pore in the microstructures of both samples. Aluminum is distributed among the titanium particles, but the configuration of the distribution is substantially different with various holding time. Namely, the aluminum distributes massively among the titanium particles for short holding times (Fig. 7a), while the aluminum penetrates uniformly into the titanium particles and forms a network around them for long holding times (Fig. 7b).

When the green compacts are heated for alloying, the aluminum in the compact melts partially at first. The dilatation coefficient at the melting of aluminum is 6.5 percent [4], which is larger than that of the other metals.

Therefore, in the compact with the massive structure, when the massive aluminum is melted, the titanium particles are loosened by thermal expansion of the aluminum. The molten aluminum diffuses into the adjacent titanium particles resulting in the production of the intermetallics. The pores are formed at the location where massive aluminum exist. These pores grow bigger because of the volume shrinkage due to the production of the intermetallics. It is confirmed by the observation of the intermetallics around the pores (see Fig. 6).

Fig. 8 shows the differential thermal analyses on the samples with various holding times. As a reference, the elemental powder compact, which is formed at room temperature is also analyzed. As seen in Fig. 8, the elemental powder mixture created an endoergic reaction through the melting of aluminum at 933 K, an exoergic reaction around 1000 K was caused by the production of intermetallic compound. The exoergic reaction by production of intermetallic compounds was observed at a temperature above 870 K on the green compact with the holding time of $t_h - 0.12$ ks. The height of this exoergic peak decreases as holding time becomes

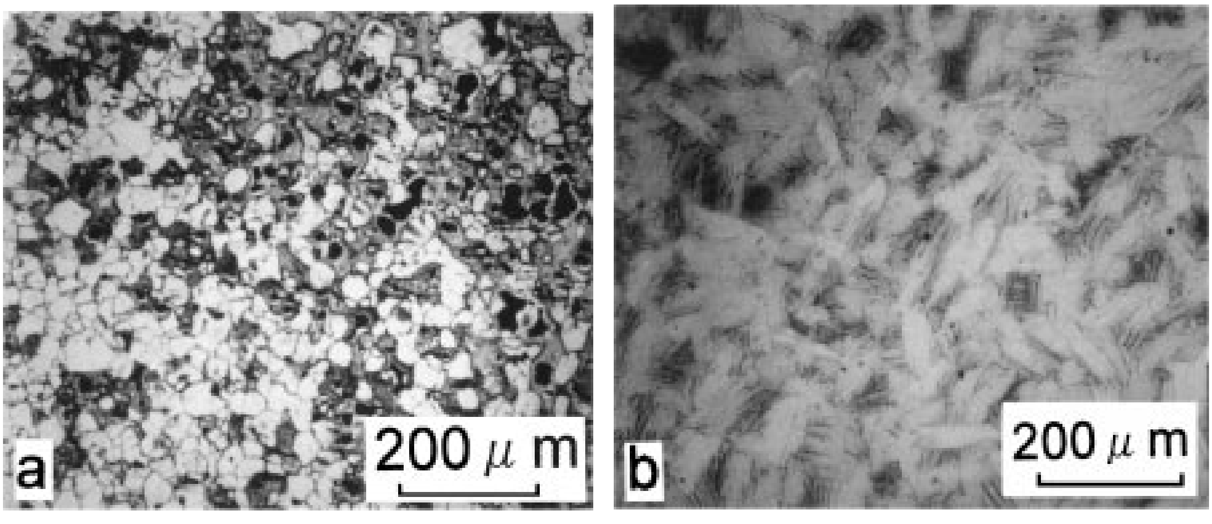

Figure 6 Optical micrographs of Ti-6Al alloy after alloying heat treatment.

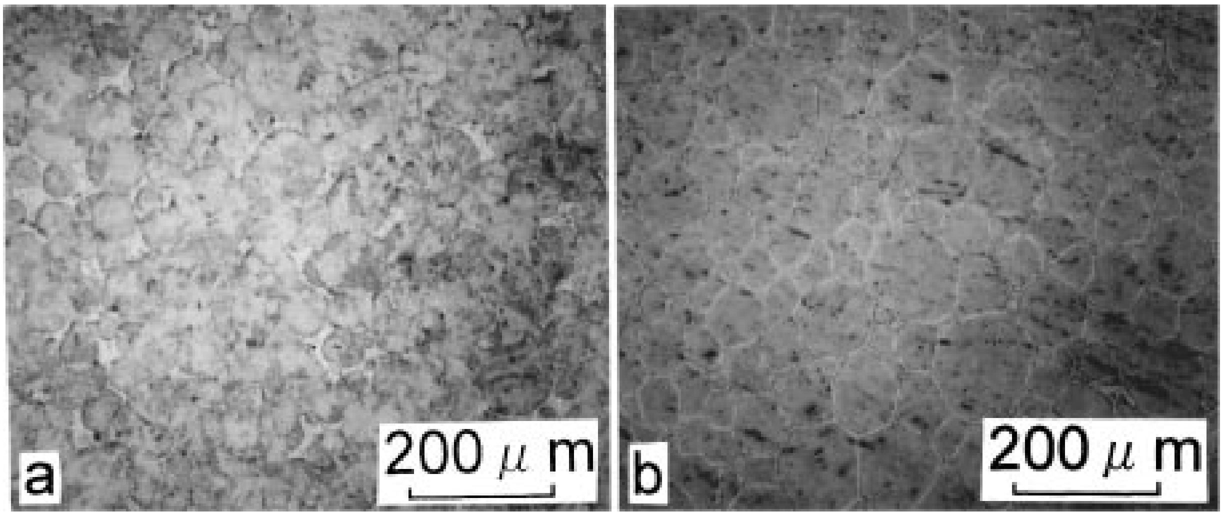

Figure 7 Optical micrographs of Ti-6Al green compact.

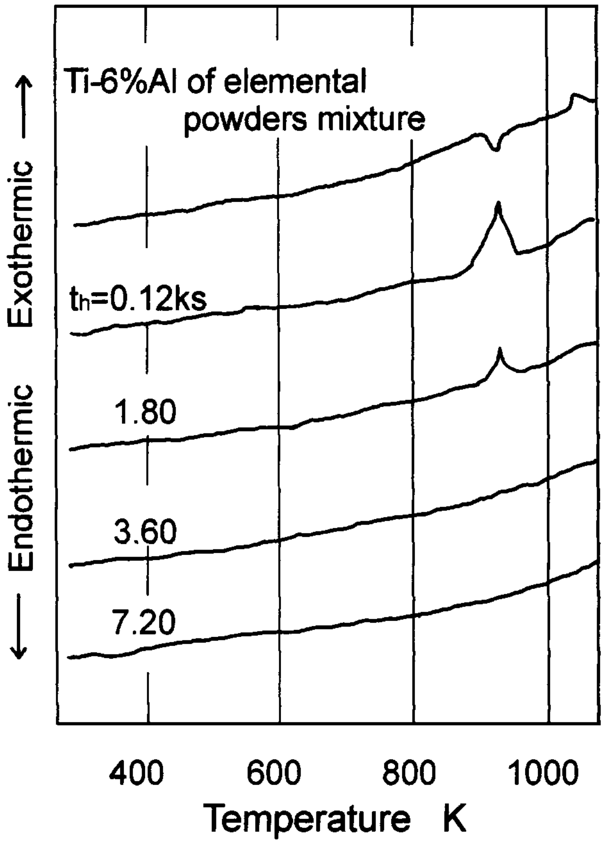

Figure 8 DTA analyses of elemental powder mixture and green compacts with various forming time.

longer and disappears completely on the green compact holding for $t_h = 3.6$ ks.

Considering the effects of the holding time on the microstructure from the results of density measurements and differential thermal analyses, the massive aluminum in the green compact which is stemmed from the short holding time may result in the generation of pores and intermetallics. Because the aluminum and its adjacent titanium react intensely at the temperature near the melting point of aluminum during the alloying heat treatment process.

On the other hand, if held for a long period, the massive aluminum penetrates uniformly into the titanium particles and forms a network around them. As the forming process progresses, aluminum reacts with its adjacent titanium and produces intermetallics. Accordingly, the density of the green compact becomes heavier than the theoretical value of the mixture billet. Since the quantity of monolithic elemental aluminum in the green compact decreases after the transformation of the intermetallics, the thermal expansion of the aluminum melting during the alloying treatment process therefore decreases. Thus, the formation of the pores is inhibited.

3.2. Oxygen analyses

Since titanium is a kind of high reactive metal, precise control of atmosphere is needed during the processes from melting to pouring into the cast in the casting method. Meanwhile, the selection of refractory materials is also a critical important point. In the semisolid forming method, the oxidization of the compacts may also supposed to be necessary since the process from mixing to forming is exposed to the air. The analyzing results of the oxygen contents is presented in Table I. The samples were formed under the forming conditions of $t_h = 3.6$ ks, $T_f = 943$ K and $P_f = 440$ MPa. The total amount of oxygen of the elemental powder mixture of Ti-6Al is determined to be 0.116 percent. In comparison, the oxygen amount of the compact is 0.171 percent. Accordingly, the increment of oxygen content during the processing is only 0.055 percent. It is obviously that the problem of the oxidization can be neglected during practical production.

In this study, it has been demonstrated that Ti-6Al alloy can be formed under the conditions of holding for a relatively long time at a temperature just above the

TABLE I Chemical analyses of the oxygen content

	O wt%
Elemental Powders	
Titanium powder (−150 micron)	0.077
Aluminum powder (−38 micron)	0.724
Green compact (Ti-6Al)	0.171

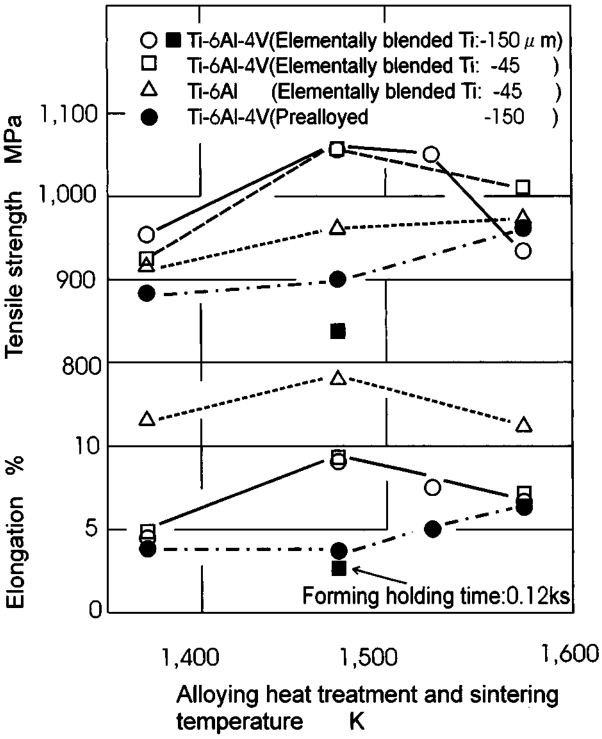

Figure 9 Mechanical properties of the two kinds of compacts fabricated by semisolid forming method and conventional powder metallurgical sintering method.

melting point of the aluminum in the air. However, further refinement of the process is required for practical applications. The long holding time in the metal mold, and the necessity of holding at a temperature above the melting point of the aluminum may result in serious problems regarding to the productivity and the choice of molding materials, respectively.

3.3. Mechanical properties

Fig. 9 shows the Ultimate tensile strength (UTS) and the elongation (EL) of the elemental blended powders semisolid forming compacts of Ti-6Al and Ti-6Al-4V after alloying heat treatment, the corresponding values of the compact formed by conventional powder metallurgical sintering method are presented here as well for comparing. The forming conditions are $T_f = 943$ K, $P_f = 440$ Mpa and $t_h = 7.2$ ks. The alloying heat treatment temperatures are selected as 1373 K, 1473 K, and 1573 K, and the alloying time is 7.2 ks. In addition, Fig. 9 also shows the results of the samples formed for a holding time of $t_h = 0.12$ ks (represented by ■); and the samples of Ti-6Al-4V fabricated by the conventional powder metallurgical sintering method (represented •).

It can be seen that, the samples with $t_h = 0.12$ ks exhibit low UTS and EL as 840 MPa and 3%, respectively. It can be contributed to the co-existence of pores and intermetallics in their microstructure.

It is noticeable that for the compacts fabricated by semisolid forming method, the UTS is improved while the EL decreases slightly after the addition of the vanadium. Meanwhile, the titanium particle size has merely effect on the UTS and the EL as here two kinds of titanium particle size of 150 μm and 45 μm were experimented at all alloying heat treatment temperatures.

Fig. 9 also shows the mechanical properties of the two kinds of the compacts and the influences of the alloying heat treatment temperature (i.e., sintering temperature of the conventional powder metallurgic sintering method). It indicates that the UTS and the EL of the compact that is fabricated by semisolid forming method are both higher than that of the compacts fabricated by the conventional powder metallurgic sintering. The UTS and the EL of the semisolid forming compact gets its best of 1050 MPa and 9% respectively under the alloying treatment temperature of 1473 K, which is in excess of the forging materials.

For the samples fabricated by the conventional powder metallurgic sintering method, the UTS and the

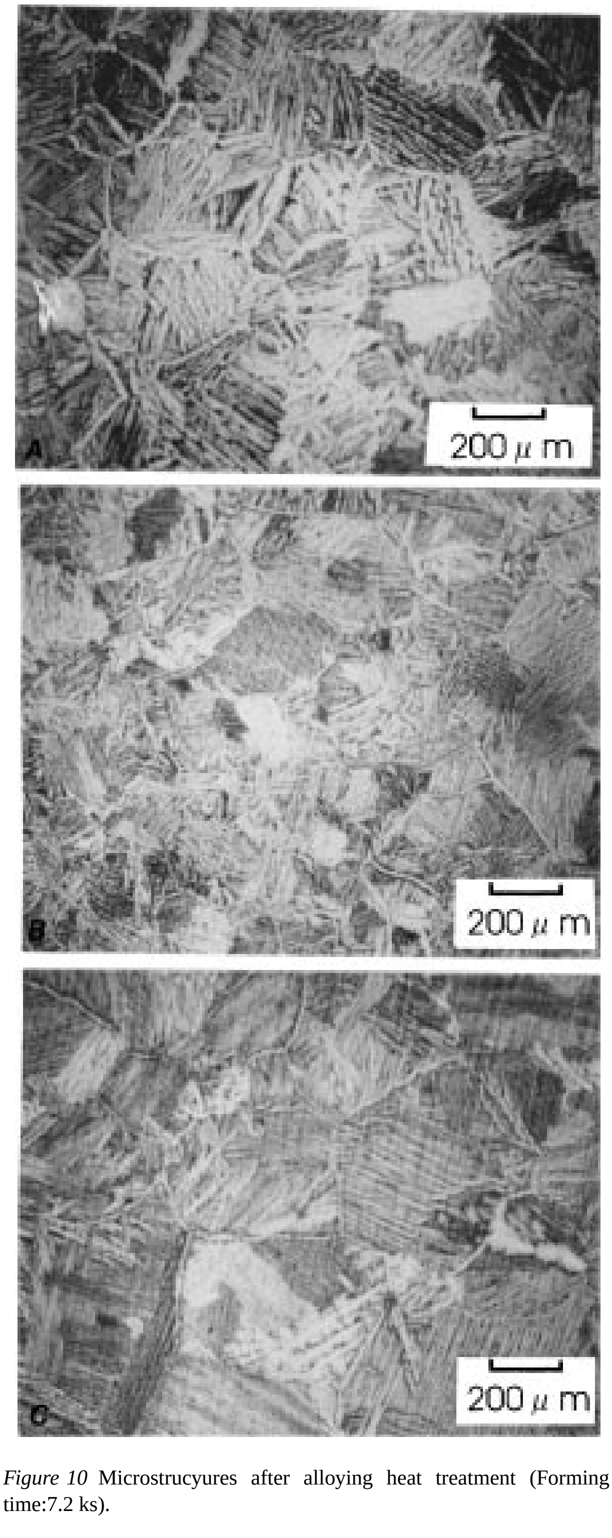

Figure 10 Microstrucyures after alloying heat treatment (Forming time:7.2 ks).

EL increases with the sintering temperature. However, in the semisolid forming method the UTS and the EL decreases after the alloying temperature surpassing 1573 K, and the peak value occurs at 1473 K, as seen in Fig. 9.

Fig. 10 shows the microstructures of Ti-6Al-4V semisolid forming compacts after alloying heat treatment. It can be seen that the grain size grows coarse at the alloying temperature of 1573 K for 7.2 ks in Fig. 10c, which may result in the damage of the UTS and EL. On the other hand, there are still dissolved vanadium distributed in the matrix heterogeneously at the alloying temperature of 1373 K holding for 7.2 ks, which give rise to the decreases of the UTS and EL. In the present study, the particle size of 100 μm of vanadium is relatively coarse. But it has dissolved completely at the alloying temperature of 1473 K. It can be deduced that the smaller the particle size, the lower alloying temperature and shorter holding time will be needed in the alloying treatment process so that the coarseness of the grain size can be avoided.

4. Summary

Titanium alloys are with high chemical activity. They are difficult to be shaped by conventional method, such as casting or forging, especially for the parts with the complicated shape. These problems can be solved by using elemental blended powders semisolid forming. In the present study, the forming conditions such as forming temperature, pressure, and holding time of the semisolid forming method were investigated by applying to the Ti-based alloys of Ti-6Al and Ti-6Al-4V. As a result, it is clear that the pore-free green compacts can be certainly obtained by using the selected conditions. However, the samples with short holding forming time will produce pores and intermetallics in the microstructure after alloying heat-treatment. Increasing the holding time, these pores disappear and the microstructure consisted of $\alpha + \beta$ phases can be obtained. The reasons of the structural difference are that the aluminum distributed massively among the titanium particles for short holding times, but formed networks after long holding times. The completely pore-free compacts with a microstructure of $\alpha + \beta$ phases can be obtained under the condition of a proper holding time.

Furthermore, results also indicate that the semisolid forming process for Ti-6Al alloys can be conducted in the air without oxidation.

Ti-6Al-4V alloys can also be fabricated at a low temperature close to the melting point of aluminum by using elemental blended powders semisolid forming. The optimum alloying treatment conditions are at 1473 K holding for 7.2 ks, which can result in the best ultimate tensile strength of 1050 MPa and the elongation of 10%. These values are identical to that of the plastic materials.

References

1. Y. M. KIM, in “High Temperature Ordered Intermetallic Alloys IV, Vol. 213,” edited by I. D. Siegler, L. A. Johnson and D. P. Pope. MRS Symp Proc, Pittsburgh, Pa, 1991.
2. II. OKAMOTO, Binary alloy phase diagram, update service, June, 1993.
3. M. B. WINNICKA and R. A. VARIN, *Metal. Trans. A* **24A** (1993) 935.
4. D. B. SPENCER, R. MEHRABIAN and M. C. FLEMINGS, *Metall. Trans.* **3** (1972) 1925.
5. R. M. K. YOUNG and T. W. CLYNE, *J. Mater. Sci.* **21** (1986) 1057.
6. D. H. KIRKWOOD, *Inter. Mater. Rev.* **39** (1994) 173.
7. E. A. BRANNDES (ed.), “Smithells Metals Reference Book,” 6th ed. (Butterworths, London, 1983) p. 1.
8. M. C. FLEMINGS, *Metall. Trans. A.* **22A** (1991) 957.
9. D. S. SHIN, J. I. LEE and H. I. LEE, in Proc. of the 4th International Conference on Semisolid Processing of Alloys and Composites, 1996, p. 92.
10. K. TAHARA, H. TEZUKA, T. SATO and A. KAMIO, in Proc. of the 6th International Conference on Aluminum Alloys, 1998, p. 303.
11. K. YASUE, G. L. YU and M. NIINOMI, “Non-Aerospace Application of Titanium,” edited by F. H. (Sam) Froes, P. G. Allen and M. Niinomi. TMS Symp. Proc. (1998) p. 81.
12. K. YASUE, G. L. YU and C. E. WEN, in Proc. of the 1998 Powder Metallurgy World Congress, Superalloys/Intermetallics, Granada, Spain, p. 495.

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