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Development of Low Cost Powder Metallurgy Process of Titanium Alloy Products

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Abstract

Methods to reduce production cost of titanium alloy products by blended elemental powder metallurgy were investigated from the various viewpoints. The cost for Cold Isostatic Pressing can be considerably reduced by replacing the conventional rubber mold to one-time use type mold made of thermo-plastic resin. Optimization of powder size distribution and an addition of small amount of B_4C or Y_2O_3 with devised means make it possible to achieve both high density ratio of more than 99.5% and refined microstructures in an as-sintered condition without detrimental increase of oxygen content, resulting in excellent mechanical properties competitive to those of Hot Isostatic Pressed materials. Furthermore, low cost Ti-Fe-Al based alloys and the reduction of machining cost are also discussed.

1. Introduction

Titanium alloys have been often used in various fields, especially in space and aircraft applications, with making good use of their light weight, high strength and high corrosion resistance. In more recent years, active moves have been made to utilize their attractive properties in consumer goods like automotive parts. Their extremely high manufacturing cost, as compared with conventional materials like steels, seriously hampers the application of titanium alloys to these consumer goods, and the manufacturing cost must be considerably reduced for titanium alloys to be used in large amounts in consumer goods. Among the reasons for the high manufacturing cost of titanium alloys, the high cost and low yield of rear processes arising from the poor workability and machinability of titanium alloys can be cited in addition to the high cost of upper processes like refining and remelting.

The fabrication of titanium alloy parts with various near net-shape technologies has been studied as solutions to their high manufacturing cost, and powder metallurgy is one of the powerful cost reduction methods. Especially, the blended elemental powder metallurgy process is relatively low-cost in which the following processes are involved; blending commercially pure titanium powder with master alloy powder in the specified proportions, filling a mold with the blended powders, pressing them at room temperature, and sintering the compacts (and hot isostatic pressing of the sintered compacts if required in the intended applications). The advantages of this method are as follows: when the blended powders are pressed, a compact with relatively high accuracy can be obtained because the soft com-

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mercially pure titanium powder accounts for the majority of the compact. In addition, during sintering, alloying can be achieved simultaneously. To ensure a large-volume supply of titanium alloy parts for consumer goods, however, it is necessary to develop more radical cost reduction technologies.

On the above-mentioned background, the authors have studied the possibility of reducing the manufacturing cost of titanium alloy parts by the blended elemental powder metallurgy process from various angles, and some of the results are reported here. This research and development work is based on the use of extra-low chlorine titanium powder produced by the hydrogenation/dehydrogenation (HDH) process as feedstock powder. In the 1980s, the Hunter process sponge fines (HSF) obtained as by-product in the titanium sponge production by the Hunter process (sodium reduction process) were frequently used[1]. Although the HSF powder was high in quality and low in cost, there were only three companies[2] then that adopted the Hunter process for refining titanium. Moreover, these companies were expected to quit the titanium industry or convert to the Kroll process (magnesium reduction process), and the supply of HSF was considered certain to run out.

The authors thought it extremely difficult to utilize the HSF diminishing in supply and excluded its use from the beginning. The authors and many other researchers have investigated the quality enhancement[3] and cost reduction[4,5] of HDH titanium powder expected to be supplied stably. Some of the study results are presented in Reference 5).

Unless otherwise specified, the compaction was conducted at 480 MPa by cold isostatic pressing (CIP), and the pressed compacts were sintered in vacuum at 1,250°C for 2 h. Some specimens were hot isostatic pressed (HIPed) at 900°C and 110 MPa.

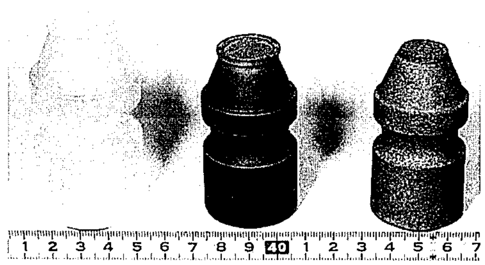
2. Low-Cost CIP Molds

The blended elemental powder metallurgy process often uses CIP as compaction method especially for relatively large parts. CIP, however, involves the problems described below and may become the second largest cost-raising factor after the above-mentioned titanium powder, depending on the shape of the parts.

In the CIP of titanium, rubber molds are usually used. Depending on the material and wall thickness, the powder compact may nibble the surface of the mold during compaction, which markedly shortens the life of the mold (the number of repeated uses), thereby increasing the manufacturing cost of sintered parts. There also occur the problems of compact breakage and surface roughening during mold release. Unless the rubber that has been nibbled in the green compact is removed before sintering, it may contaminate the compact during sintering and may reduce the mechanical properties of the sintered compact.

When a part shaped like a dumbbell, for example, is pressed in a one-piece mold, the springback of the mold may break the compact or make it difficult to remove the pressed compact from the mold. In such a case, one remedy may be to divide the mold into multiple parts, paste together these parts, and separate the mold again after pressing to remove the pressed compact from the mold. It takes a long time to paste the mold parts with high precision, which results in a marked decline in productivity. The adhesive used is also feared to degrade the rubber mold. These conditions combine to increase the manufacturing cost of the part.

To solve the problems at a stroke, the application of thermoplastic resins was studied. **Photo 1** shows a fermented lactic drink beverage container made of polystyrene and used as mold for pressing the titanium powder into a compact. The density of the compact was completely the same as that of a simple-shaped part pressed using a rubber mold. There was no mold nibble, and the surface smoothness of the compact was by far better than obtainable with the rubber mold. The pressed compact can be easily removed from the plastic mold by heating it to temperatures above the glass transition temperature of about 100 to 150°C and softening it.



Fermented lactic acid beverage container

Container and compact after CIPing

Compact removed from container by breaking container

Photo 1 Titanium powder compact CIPed using fermented lactic acid beverage container (made of polystyrene) as mold

When the pressed compact is removed from the plastic mold, there is no such springback upon unloading as experienced with a rubber mold. The plastic mold need not be divided and can be used as one-piece mold. Although the plastic molds are, of course, single-use throwaway molds, mass-production technologies of plastic products like blow molding can be utilized to sharply reduce the unit cost of sintered compacts with one-piece plastic molds as compared with multiple-piece rubber molds that are used multiple times.

When the parts are small and relatively simple in shape as shown in Photo 1, plastic molds can be used to obtain a powder compact without any problems. Longer parts may not be properly shaped in the longitudinal direction unless the material and wall thickness of the plastic mold are judiciously selected. If the plastic composition and properties are properly selected, however, relatively large parts like automobile engine connecting rods can be successfully shaped using plastic molds.

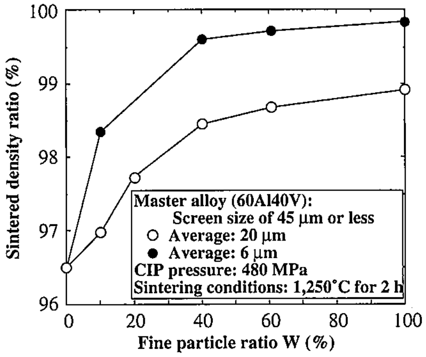
3. Technology for high sintered density

Parts in which high fatigue properties are required are sintered and hot isostatic pressed (HIPed) to achieve density ratio of nearly 100%. In recent years, HIP has been becoming able to process a large quantity of parts at a time and has significantly declined in cost per part. However, HIP still accounts for a large percentage of the manufacturing cost of sintered products and is the third largest cost factor after the titanium powder and CIP mold. If the compact possesses high density and high fatigue strength in as sintered condition, the cost can be considerably reduced.

To obtain high mechanical properties in the as sintered condition, it is necessary to achieve higher sintered density while limiting the oxygen content below the upper limit value[6], above which oxygen degrades the mechanical properties of sintered compacts. As the sintered density rises, the pores that have pinned the β grain boundaries decrease in number and the β grains can be coarsened. Therefore, it is necessary to prevent the β grain coarsening and, if possible, to achieve microstructural refinement at the same time. To counter this difficult challenge, the authors attempted to adjust the particle size distribution of the powder used and to make trace additions of Y_2O_3 and TiB reported to be effective in inhibiting grain growth in both of ingot metallurgy and powder metallurgy[7,8].

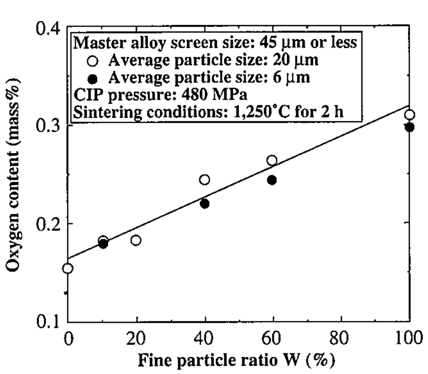
An extra-low chlorine HDH titanium powder with a screen size of 150 μm or less and a 60Al40V master alloy powder with a screen size of 45 μm or less were blended to the composition of Ti-6Al-4V. The blend was then CIPed and sintered into columnar specimens of about 15 mm in diameter and of 150 mm in length, and the effect of the powder particle size on the sintered density was examined. The results are shown in **Fig. 1**. It is natural for the sintered density to increase with increasing percentage of fine powder particles. However, it should be noticed that when the proportion of the powder with a screen size of 45 μm or less exceeds 40%, the increase in the sintered density with respect to the percentage of fine powder particles is suddenly eased. Use of the master alloy powder with a screen size of about 6 μm provides a high density of over 99.5% in the as sintered condition at a fine powder percentage of 40%.

The oxygen content of the sintered parts is 0.24 mass% at a fine particle ratio of 40% and is about 0.07 mass% higher than at a fine particle ratio of 10% (master alloy powder alone fine) as shown in **Fig. 2**. The oxygen content of the sintered parts can be fully controlled to a permissible level of 0.3 mass% or less in the presence of a powder with a somewhat high oxygen content. The 6 μm master alloy powder used here is of far smaller particle size than the titanium powder, and to obtain homogeneous material properties, it is desirable not to mix these powders directly and coarsely with a V-type mixing mill, for example, but to mix them lightly by a mechanical alloying technique, for example, to achieve homogeneous blending.



Fine particle ratio W:
Ratio of weight of particles with screen size of 45 μm or less to total weight of feedstock powder used (screen size of 150 μm or less)

Fig. 1 Effect of feedstock powder particle size distribution on sintered density of Ti-6Al-4V sintered compacts



Fine particle ratio W:
Ratio of weight of particles with screen size of 45 μm or less to total weight of feedstock powder used (screen size of 150 μm or less)

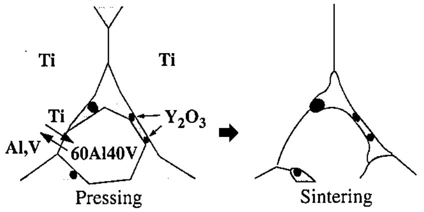
Fig. 2 Effect of feedstock powder particle size distribution on oxygen content of Ti-6Al-4V sintered compacts

The above-mentioned adjustment of the powder particle size distribution helped to produce a sintered titanium alloy with an allowable oxygen content and density ratio of over 99.5% even in the case of the use of the HDH titanium powder. As a result of the adjustment, however, the β grains coarsened to about 300 μm from about 100 μm at a fine particle ratio of 10% (screen size of 45 μm or less only for the master alloy). As method for preventing the β grain coarsening, a Y_2O_3 addition of about 0.1 mass% was attempted.

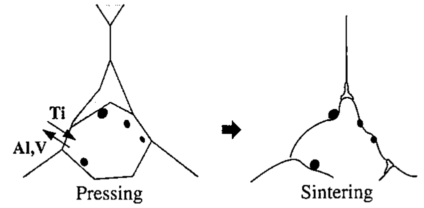
When Y_2O_3 (about 2 μm) was mixed directly with the master alloy and titanium powders, the sintered density was prevented from rising and was only about 98.5%. In other words, the Y_2O_3 addition was found to retard the progress of sintering. This phenomenon was considered to occur as the Y_2O_3 particles obstructed the surface movement of the titanium and master alloy powders in the sintering process. To avoid this phenomenon, the master alloy and an amount of Y_2O_3 equivalent to about 1% of the weight of the master alloy were melted and crushed. The resultant composite powder in which Y_2O_3 was dispersed in 60Al40V was used as master alloy powder. In this case, the Y_2O_3 particles are already incorporated in the powder as shown in **Fig. 3**, so that they are not involved in the surface phenomena and cannot inhibit the surface movement of the titanium and master alloy powders. For this reason, the β grain-boundary movement alone is expected to be inhibited. In fact, use of the composite powder (particle size of 6 μm) helped to fabricate products featuring high sintered density of 99.5% and composed of fine β grains of about 150 μm.

Next, an attempt was made to inhibit β grain growth with TiB. In overall consideration of price, crushability and other applicable factors, B_4C was selected as the boride to be added. Since B_4C is added for the purpose of inhibiting the growth of β grains, it is necessary to disperse homogeneously as many B_4C particles as possible. B_4C was thus crushed to a fine size of about 5 μm before its use. During sintering, the boron in B_4C reacts with the titanium to synthesize TiB, and the carbon in B_4C is dissolved into the matrix of titanium alloy. When B_4C is added in an amount of about 0.1 mass%, the resultant

(a) Added directly



(b) Added in the form of $(60Al40V)_{90}(Y_2O_3)_{10}$ powder*



*Produced by plasma arc remelting and crushing mixture of 60Al40V and Y_2O_3 in weight ratio of 99:1

Fig. 3 Estimated sintering mechanisms of Ti-6Al-4V with 0.1 mass% of Y_2O_3 (2 μm) added directly (a) and in the form of $(60Al40V)_{90}(Y_2O_3)_{10}$ powder (b)

increase in the carbon content is only about 0.02 mass% which is not large enough to adversely affect the mechanical properties of the titanium alloy.

Unlike Y_2O_3, B_4C is directly involved in the sintering process, does not retard the surface movement of the titanium powder, and does not lower the sintered density. Rather, it is considered possible for B_4C to accelerate the progress of sintering by local heating during the TiB synthesis reaction. Master alloy powder (6 μm), titanium powder with a screen size of 45 μm or less, and titanium powder with a screen size of 45 to 100 μm were mixed in mass proportions of 10:30:60, and 0.1 mass% B_4C (5 μm) was also added. The mixture was CIPed and sintered. The resultant Ti-6Al-4V compacts of 15 mm in diameter and 150 mm in length exhibited high density ratio of 99.7%.

The titanium alloy with dispersed TiB had a substantial proportion of equiaxed structure, which is considered to have excellent fatigue properties as shown in **Photo 2**. Although difficult to distinguish from these micrographs, the β grain size was measured to be about 60 μm by using specimens quenched from the β single-phase region. That is, there was confirmed a finer grain size than possible with the Y_2O_3 addition. The reason that the equiaxed structure partially formed is not that TiB acted as precipitation sites for the α phase, but that the grain size of the β phase was enough small.

The increase in the sintered density and the prevention of microstructural coarsening were achieved as discussed above. The mechanical properties of these materials are given in **Table 1**. The tensile properties of the microstructurally controlled materials were practically satisfactory. The rotating-bending fatigue strength (at 10^7 cycles) of no-HIPed specimens was a high 343 MPa or close to 90% of that of HIPed specimens (392 MPa).

4. Low-Cost Alloy Compositions

The research results introduced in Chapters 2 and 3 are concerned with Ti-6Al-4V. V is an expensive alloying element, although its content is a mere 4%. Substitution of Fe, a β stabilizing element of by far lower price, for V is expected to reduce the manufacturing cost, albeit to a smaller degree than achieved by the cost-saving measures discussed above.

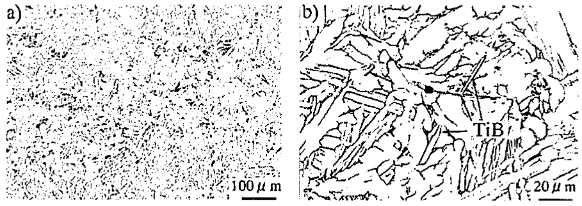


Photo 2 Microstructures of Ti-6Al-4V sintered compact with 0.2 mass% addition of B_4C

What should be first studied when fabricating the Fe-containing alloy by the blended elemental powder metallurgy process is what to use as alloy feedstock powder. When fabricating Ti-6Al-4V, it was possible to use the powder produced by crushing the 60Al40V master alloy with excellent crushability. When fabricating a Ti-Al-Fe alloy, an Fe-Al alloy powder is ductile, low in crushability and difficult to produce as pointed out by Hagiwara et al.[9] When Al and Fe elemental powders are used, such problems are likely to occur as the formation of outflow pores arising from the low melting point of Al (reduction in sintered density) and the difficulty of homogeneous mixing arising from the difference in specific gravity with titanium (occurrence of segregation).

Of binary powders with titanium, Al_3Ti and FeTi powders have excellent crushability. They are also closer to titanium in specific gravity than their individual constituents, so that they alleviate the segregation problem to some degree. Thanks to many other advantages, the Al_3Ti and FeTi binary powders are considered practicable. Use of the binary powders is particularly suited for the manufacture of many different types of parts in small lots, because various alloy compositions can be attained by appropriately changing the additions of two types of prealloyed powders. For mass-production parts, use of the Ti-Al-Fe ternary powder described next is convenient. This makes use of the composition mainly consisting of brittle and easy-to-crush intermetallic compounds $Al_{22}Fe_3Ti_8$ and $TiAl_2Fe$. When the authors studied the Ti-Al-Fe ternary powder, they found that it could be easily crushed even if it significantly deviated from its stoichiometric composition and could be used as prealloyed powder in different alloys with different Al and Fe contents. For details, refer to Reference 10).

The above binary and ternary prealloyed powders were mixed with the titanium powder, CIPed, sintered, and HIPed to a density ratio of nearly 100%. The tensile strength of the Ti-Al-Fe ternary sintered alloy specimens obtained is shown in **Fig. 4**. As the Al content exceeds 6.5 mass%, the elongation decreases to 10% or less. When the Al content is below 6.5 mass% and the Fe content is less than 5 mass% (the upper limit value in this experimental work), the ductility is high enough. Alloy systems with various levels of tensile strength in the range of 700 to 1,000 MPa are thus identified. Fig. 4 shows that total 6.5 mass% of Al and Fe must be added to attain tensile strength equal to or higher than that of Ti-6Al-4V.

High fatigue strength with respect to yield strength can be cited as one characteristic of the Ti-Fe-Al ternary sintered alloys. **Fig. 5**

Table 1 Tensile properties of Ti-6Al-4V sintered compacts produced with controlling the particle size of feedstock powder and microstructures (CIP: 480 MPa, Sintering: 1,250°C for 2 h)

		Density ratio (%)	0.2% offset yield strength (MPa)	Tensile strength (MPa)	Elongation (%)	Reduction of area (%)	Rotating-bending fatigue strength (at 10^7 cycles) (MPa)
Without control of particle size distribution	As sintered	96.5	815	919	7.1	10.8	157
	HIPed	100	862	969	15.1	36.9	392
With control of particle size distribution	Without microstructural control	99.6	859	976	14.7	35.8	225
	Y_2O_3 addition	99.6	911	1,022	11.7	22.7	284
	B_4C addition	99.7	977	1,106	12.1	17.7	343

Feedstock powder blend is Ti (screen size of 45 to 150 μm): 60Al40V (45 μm or less and average of 20 μm) = 9:1 without control of particle size distribution and Ti (45 to 150 μm and average of 80 μm): 60Al40V (45 μm or less and average of 6 μm) = 60:30:10 with control of particle size distribution. Y_2O_3 (composite powder with 60Al40V) or B_4C (average of 6 μm) is added in amount of 0.1 to 0.2 mass% to Ti-6Al-4V.

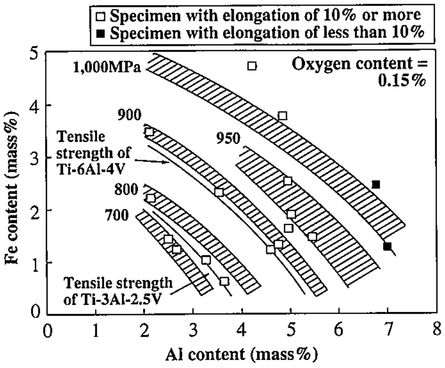


Fig. 4 Tensile strength of sintered and HIPed Ti-Al-Fe ternary titanium alloys

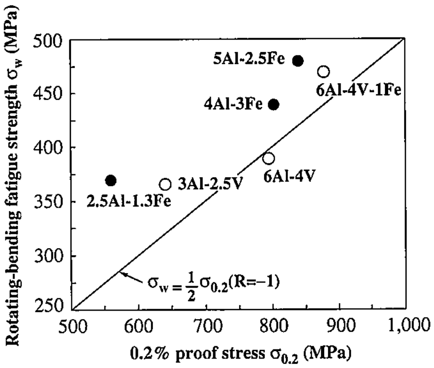


Fig. 5 Relationship between 0.2% proof stress and rotating-bending fatigue strength (at 10^7 cycles) of various sintered and HIPed titanium alloys produced by blended elemental powder metallurgy route

shows the relationship between the 0.2% proof stress and rotating-bending fatigue strength of sintered and HIPed titanium alloy specimens. Ti-5Al-2.5Fe is higher by only about 30 MPa in 0.2% proof stress than Ti-6Al-4V, but is about 100 MPa higher in fatigue strength than Ti-6Al-4V. The other Fe containing alloys have higher fatigue strength than the V containing alloys. The high fatigue strength of the Fe containing titanium alloys can be inferred from these results. This may be associated with the effects of Fe and V on the evolution of the α_2 phase (Ti_3Al phase) or short-range ordered phase and the resultant difference in the slip mode according to the study on the dislocation structure and ternary phase diagram[11].

The Ti-Al-Fe alloy is basically the same α plus β two-phase alloy as Ti-6Al-4V. This is due to the markedly retarded formation of its equilibrium phase or FeTi compound phase. When the Ti-Al-Fe alloys are used at high temperatures for long time, the FeTi phase may develop. When practically using the Ti-Al-Fe alloys, therefore, it is necessary to fully grasp their service limit. For this phenomenon, refer to another report[12].

5. Machining Load Reduction Technology

Powder metallurgy is one kind of near net-shape technologies and involves little metal removal by definition. A small reduction in the machining load makes not a small contribution to the manufacturing cost reduction of difficult-to-machine titanium alloys. From this standpoint, the results of the study on the reduction of the drilling load are introduced as an example of machining load reduction measure.

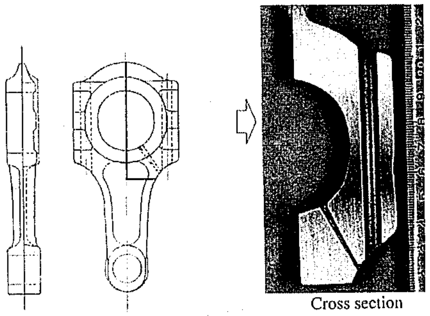


Photo 3 Example of Ti-6Al-4V sintered compact with holes provided (simulating part of automotive engine connecting rod)

Thin metal bars were installed as cores in a mold, and titanium and master alloy powders were charged into the mold and CIPed together with the cores. The pressed compact was then removed from the mold and sintered. **Photo 3** shows the cross section of the sintered compact. It is shaped to simulate part of an automotive engine connecting rod, and already has a bolt hole for connecting the large end of the connecting rod and a fine hole for supplying the lubricant oil. Any subsequent drilling operation is eliminated.

The core material and its surface call for the following cautions to be exercised. The fine hole shown in Photo 3 was made by using a stainless steel SUS 630 core aged in air and given a hard oxide film. The core was easily removed after the CIPing operation and had no effect at all on the shape and quality of the sintered compact. Depending on their materials, however, some cores deformed or galled by the titanium powder during CIPing, and could not be removed or broke the compact during its removal after CIPing.

6. Conclusions

Various measures for the cost reduction of the blended elemental powder metallurgy of titanium alloys have been discussed. The authors would like to conclude the report in expectation that the titanium alloy parts made by the powder metallurgy route with low cost and excellent properties are used in large amounts in the near future. For several cost-reduction technologies not covered in this report for lack of space, refer to References 5) and 10).

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