Self-Division Behavior of TiB Particles in TiB/Ti Composite

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The change in dispersion of TiB boride formed through the chemical reaction, $\text{Ti} + \text{CrB} \rightarrow \text{Cr} + \text{TiB}$, was investigated in the Ti-Cr system powder compact containing CrB boride particles. EPMA analysis revealed that the shape of the TiB particles was granular type at first, but they began to divide into a large number of fine plate-like TiB particles at the sintering temperature (self-division phenomenon). Although this seems to be contrary to the Ostwald ripening mechanism, the phenomenon could be reasonably explained in terms of total interfacial energy in the system: Considering the grain boundary energy within the granular TiB and the low interfacial energy of coherent plate-like TiB/matrix interface, the total interfacial energy was found to be decreased through the self-division. It was concluded that the difference in the total interfacial energy works as driving force for the self-division phenomenon.

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1. Introduction

Titanium (Ti) alloys have higher specific strength and corrosion resistance than those of steel. However, the applications of Ti alloys to structural materials are limited to special uses so far, because they have problems of poor heat and wear resistance as well as their high manufacturing cost. In order to solve these problems and to apply Ti alloys widely to general structural materials, the powder metallurgy technology, which enables the near-net-shape manufacturing, recently attracts great attention. In particular, the TiB dispersed Ti composites (TiB/Ti composites) manufactured by the blended elemental method¹⁾ can markedly raise hardness and heat resistance of Ti owing to the hard and thermally stable TiB particles without reducing fatigue strength and toughness too much. From these reasons, the TiB/Ti composites are expected as a wear-resistant or heat-resistant Ti alloy for the next generation.²⁾

In the case of the TiB/Ti composites, the boride of TiB can not be directly blended with the ingredient powder since TiB is unstable material in itself. In general, other stable boride powders such as CrB, MoB and FeB are added to the base Ti alloy powder, and then the chemical reaction of $\text{Ti} + \text{MB} \rightarrow \text{M} + \text{TiB}$ (M: metal atoms, such as Cr, Mo, and Fe) is used for dispersing TiB particles in the Ti based alloy. This process is called as 'reaction sintering'.³⁾ However, in the research field on the TiB/Ti composites produced by the reaction sintering, most of the physical or chemical phenomena caused during reaction sintering have not been sufficiently cleared although there are many investigations on the manufacturing methods or mechanical properties of produced materials.³⁻⁶⁾

We investigated the reaction process at sintering temperature in a green compact containing CrB particles,⁷⁾ and found that the reaction begins from the CrB particle surface and proceeds toward inside of the particle topochemically. Furthermore, as a result of analysis of the reaction rate using the unreacted core model, the relationship between the diameter of a blended CrB powder and the reaction finish

time was formulated theoretically. On the other hand, according to the report by Saito *et al.*,²⁾ the TiB particles change its shape from original granular type to plate-like type after finishing the reaction. Since the morphology and dispersion of TiB particles give a great influence on the mechanical properties, it is important to clear the mechanism of the change in shape of TiB particles and to establish the technology for controlling the dispersion of TiB particles.

In this study, the change in dispersion of TiB particles after finishing the reaction was investigated in a Ti-Cr based sintering alloy, and then the mechanism of 'self-division' of TiB particle was proposed on the basis of the change in total interfacial energy.

2. Experimental Procedures

HDH Ti powder and CrB boride powder were used as ingredient powders in this study. Table 1 and Fig. 1 show chemical compositions and SEM images of the powders, respectively. Both powders have a size of 45 μm (-325 mesh). These powders were blended so that the composition after the reaction sintering becomes 4 vol%TiB/Ti-4 mass%Cr matrix, and then formed into green compact by cold isostatic press (CIP) with a pressure of 196 MPa. The reason why the matrix composition was adjusted to 4%Cr is that Ti-4%Cr alloy has excellent mechanical properties⁸⁾ as well as formability at high temperature through superplastic deformation.⁹⁾ The 4%Cr alloyed to the matrix is supplied from CrB powder on the reaction sintering. The green compact obtained by CIP was heated at a rate of 0.17 to 1473 K in a vacuum and then held at this temperature for 3.6–108 ks, followed by slow cooling at a rate of 0.17 K/s. Chemical composition of sintered materials were measured by means of Electron Probe X-ray Microanalyzer (EPMA).

Table 1 Chemical compositions of Ti and CrB powders used. (mass%).

	Fe	Cl	O	N	C	H	Ti
	0.016	<0.01	0.27	0.025	0.007	0.017	bal.
CrB	Fe	Si	Mg	O	N	B	Cr
	0.066	0.006	0.017	0.32	0.008	17.3	bal.

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Fig. 1 Scanning electron micrographs showing the shape of Ti (a) and CrB (b) powders used.

3. Results and Discussion

3.1 Microstructural change during sintering

The chemical reaction occurred during sintering and the Gibbs free energy¹⁰⁾ change on the reaction, ΔG_0 , are expressed by eq. (1) and eq. (2), respectively.

$$\Delta G_0 = 0.0130T - 87.8(\text{kJ/mol}) \quad (2)$$

where, T is the absolute temperature (K). The reaction proceeds in the whole temperature range dealt in this research (room temperature to 1573 K) because the condition of $\Delta G_0 < 0$ always holds. Figure 2 represents X-ray diffraction patterns showing the reaction on heating up to 1573 K at a rate of 0.17 K/s. The specimens were water-cooled from selected temperature on heating. When the temperature reaches 1273 K, the formation of TiB starts, and peaks of bcc phase also appear in the diffraction pattern. The detected bcc phase is retained β which was stable at the heated temperature and did not undergo the phase transformation to α on cooling. The reaction almost finishes at 1473 K although some boride particles with an unreacted CrB core were found.⁷⁾ From the industrial point of view, the reaction should be completed in a short time, and besides, the density of Ti-Cr matrix must be increased as low as possible to keep sufficient ductility of the material. Thus, the sintering temperature was set at a rather high temperature of

Fig. 2 X-ray diffraction patterns of specimens heated to various temperatures (1173~1573 K) at 0.17 K/s and then water-quenched.

1473 K¹¹⁾ in the following investigations.

Figure 3 shows the dispersion and the chemical composition of TiB in the specimen which was sintered at 1473 K for 1.2 ks. The dispersion and shape of the TiB particles have hardly changed from those of original CrB powders blended in the green compact, because the reaction from CrB to TiB occurs *in-situ* during sintering and proceeds topochemically from the particle surface toward inner side as reported in the previous paper.⁷⁾ In the characteristic X-ray images, it is confirmed that Ti and B are condensed but Cr is diluted in the boride. It should be noted here that tiny plate-like precipitates are scattered within the matrix. The precipitates can be also defined as TiB boride because they have the same chemical composition as that of the granular TiB particle. To clarify the formation process of the plate-like TiB, the change in dispersion of TiB during the sintering at 1473 K was observed with back scattered electron images of EPMA (Fig. 4). The coarse granular TiB particles, which were observed in the early stage of sintering, gradually disappear and the number of plate-like TiB particles is increased. After sintering more than 97.2 ks, the granular TiB can be hardly observed. Since some groups of fine plate-like TiB particles are formed where the granular TiB have originally existed as shown by the arrows, the plate-like TiB seems to have been formed through the division of coarse granular TiB. In the 291.6 ks sintered material, uniformly dispersed fine plate-like TiB particles are observed. Figure 5 shows the change in morphology of a TiB particle during sintering at 1473 K. The initial granular TiB in the 1.2 ks sintered material has smooth TiB/matrix interface (a), but it becomes rougher with increasing sintering time (b). The division of TiB is clearly observed in the 97.2 ks sintered material (c), and the divided TiB particles grow from the original position of the initial granular TiB toward β matrix with forming plate-like precipitates. In the 291.6 ks sintered material (d), the division has almost completed, but the plate-like TiB particles increase the thickness further more. The chemical composition of the TiB is not changed during the division as

Fig. 3 EPMA images of a specimen sintered at 1473 K for 1.2 ks.

Fig. 4 Back scattered electron images showing microstructure after sintering at 1473 K for 1.2 ks (a), 10.8 ks (b), 97.2 ks (c) and 291.6 ks (d).

mentioned above. In this paper, we call such a change in morphology of TiB particle without the change of crystal structure as 'self-division'.

3.2 Total interfacial energy change with self-division of TiB particle

In general, the second phase particles dispersed in material grow at elevated temperature on the mechanism of Ostwald ripening, meaning that small particles dissolve into matrix and other larger particles grow without changing the volume fraction of the particle. The driving force for Ostwald ripening corresponds to the interfacial energy between the precipitate and matrix. Therefore, the total area of the interface decreases with Ostwald ripening. However, when a large TiB particle is divided into many fine TiB particles by the self-division, the total area of TiB/matrix interface is absolutely increased.

To understand the thermodynamic validity of the self-division phenomenon, we should consider the effect of the coherency on the interfacial energy and the contribution of grain boundary within the TiB particle. The TiB/matrix interface for the initial granular TiB can be regarded as an incoherent interface with high energy, because the granular TiB particles are formed by the transformation from the blended CrB particles which have no specific crystallographic orientation relationship with the matrix. On the other hand, it was reported that the TiB precipitated in β type Ti alloy has a coherent interface with β matrix²⁾ and grows in the $\langle 111 \rangle$ directions of the β .¹²⁾ It is generally known that interfacial energy of such a coherent interface is much lower than incoherent interfaces. Thus, the interfacial energy per unit area should be smaller in the plate-like TiB particles than that in the granular TiB particles. Figure 6 shows SEM images of the specimen sintered at 1473 K for 1.2 ks. In the magnified image of a granular TiB particle (b), it is found that grain boundaries exist within the particle, which means that the TiB is a fine-grained polycrystalline particle. The grain size is around 1 μm . On the other hand, there is no grain boundary within the plate-like TiB as found in the magnified

Fig. 5 Change in morphology of a TiB particle during sintering at 1473 K. Specimen was sintered at 1473 K for 1.2 ks (a), 10.8 ks (b), 97.2 ks (c) and 291.6 ks (d).

image (c). Takahashi reported that the plate-like TiB is a whisker.¹³⁾ Therefore, the TiB particle should be a single crystal containing few impurities and dislocations. Figure 7 represents the schematic illustrations showing the morphological change of a TiB particle at sintering temperature. The granular TiB particle before self-division (a) has an incoherent interface with the matrix and contains a large area of grain boundary because it's a fine-grained polycrystal. During sintering, the plate-like TiB particles with a coherent TiB/matrix interface begin to grow from the initial granular TiB particle in the specific directions of β matrix to expand the coherent interface (b), and then the number of the formation of plate-like TiB is gradually increased, and finally, the initial granular TiB is fully divided into a large number of plate-like TiB particles, that is, the self-division is completed.

As mentioned above, the self-division phenomenon of TiB particles seem to be contrary to Ostwald ripening mechanism.

However, both of the incoherent TiB/matrix interface and the grain boundary within TiB particle have high interfacial energy, while the coherent TiB/matrix interface has low interfacial energy. Considering these facts, we should be able to explain this phenomenon reasonably in terms of thermodynamics. To demonstrate the thermodynamic validity of the self-division, the change in total interfacial energy between before and after the self-division was estimated by using a simple model based on the experimental results. Figure 8 shows the cube approximation model on the assumption that a large cubic TiB particle, which consists of small cubic grains, is divided into n pieces of small cubic TiB without changing the total volume. The sizes of initial granular TiB and grains in the TiB are 20 μm and 1 μm , respectively. The parameters and their values needed for the estimation are listed in Table 2. It was assumed that the interfacial energy is identical between the incoherent TiB/matrix interface and

Fig. 6 SEM images of the specimen sintered at 1473 K for 1.2 ks. Photograph (b) and (c) are magnified microstructures of a granular TiB particle and a plate-like TiB particle in the Photograph (a), respectively.

the grain boundary. The total interfacial energy before self-division, E_1 , is

$$E_1 = a_1^i e_1^i + a_1^g e_1^g \tag{3}$$

while that after self-division, E_2 , is

$$E_2 = a_2^i e_2^i \tag{4}$$

When the difference of the total interfacial energies, $\Delta E (= E_2 - E_1)$, is greater than zero, the self-division is driven by the ΔE . As a result of the calculation, if the n value is smaller than 5×10^3 , the self-division was found to be possible to occur. This modeling is so rough that we can not quantitatively discuss the number or size of the divided TiB, but it has been surely confirmed that the self-division is thermodynamically reasonable phenomenon. In other words, the self-division is similar phenomenon as the Ostwald ripening, in point that the interfacial energy drives the morphological change of precipitates.

4. Conclusions

(1) The Ti-Cr system powder compact containing CrB boride particles causes the chemical reaction, $\text{Ti} + \text{CrB} \rightarrow \text{TiB} + \text{Cr}$, on heating to sintering temperature, and then the

*on the assumption that a large cubic TiB particle is divided into n pieces of small cubic TiB particles without the changing the total volume

Fig. 8 Schematic illustration of the cube approximation model of TiB particle before and after the self-division.

Fig. 7 Schematic illustration of morphological change in a TiB particle during sintering.

Table 2 The numerical values used for the calculation of ΔE .

	before division	after division
Area of TiB/matrix interface, a^i (m^2)	$a_1^i = 2.4 \times 10^{-9}$	$a_2^i = 2.4 \cdot n^{-2/3} \times 10^{-9}$
Area of grain boundary, a^g (m^2)	$a_1^g = 2 \times 10^{-8}$	—
TiB/matrix interfacial energy, e^i (J/m^2)	$e_1^i = 1.0$	$e_2 = 0.5$
Grain boundary energy, e^g (J/m^2)	$e_1^g = 1.0$	—

CrB particles are fully replaced by the granular TiB particles after sintering of 1473 K–1.2 ks.

(2) When the material is held at sintering temperature, the granular TiB particle formed through the reaction is divided into many pieces of plate-like TiB particles (self-division phenomenon).

(3) The total interfacial energy including the grain boundary energy within the TiB particle is decreased through the self-division of the granular TiB particle although the TiB/matrix interface area is increased. The difference in the total interfacial energy corresponds to the driving force for the self-division of TiB.

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