Homogenizing Analysis for Sintering of Bio-Titanium Alloy (Ti-5Al-2.5Fe) in MIM Process

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SYNOPSIS
The model suggested by Ashby and Coble was used to analyze the sintering process of pure titanium in this paper. Then based upon this result, homogenizing behavior of alloying elements of aluminum and iron during sintering was further discussed for bio-titanium alloy Ti-5Al-2.5Fe. Using this method, the concentration variation of alloying elements was calculated to indicate the effect of element diffusion on the structure transformation. It was shown that the calculated results were in agreement with the results obtained in the previous experiments.

KEY WORDS
MIM, Ti-5Al-2.5Fe alloy, sintering, homogenization, numerical analysis

1 Introduction
A series of titanium alloys for implant use have been developed due to their superior bio-compatibility, enhanced corrosion resistance and lower elastic modulus when compared to conventional stainless steels and cobalt-based alloys1,2, including the first generation (Ti-6Al-7Nb, Ti-5Al-2.5Fe) and the second generation (Ti-13Nb-13Zr, Ti-15Zr-4Nb-4Ta-0.2Pd etc.). Recently, attention has been paid to developing low cost manufacturing process because, looking at the overall cost of titanium alloy implants, manufacturing cost is much higher than that of raw material due to high activity of molten titanium alloy, machining difficulties and their delicate complex structure. For this purpose, powder metallurgy process has been developed as a feasible method of near net shape process3-5). In powder metallurgy process, finally aimed component is obtained by densifying its green compacts through sintering. Especially, control of micro-pores and structure evolution in the final products will be carried out by the optimization of sintering process. It is this porous structure that results in a combinational merit for both bio-compatibility and bio-functionality by mechanically interlocking implant with growing bone and by decreasing Young’s modulus, respectively6,8.

Although conventional press and sinter powder metallurgy process has been used in manufacturing biomedical implants, there is still a possibility to reduce manufacturing costs further by considering that press and sintering powder metallurgy process is mainly superior to other processes only when used for large and complex shape parts7. For small and complex parts to which medical implant parts are applied, MIM (Metal Powder Injection Molding) process is thought to be a most promising powder metallurgy process8. In the previous papers9,10, MIM process using blended powders has been used to the processing of titanium alloys (Ti-5Al-2.5Fe and Ti-6Al-4V) and mechanical properties of the resultant sintered compacts have been investigated. The objectives of this paper are to simulate the homogenizing process of alloying elements, Al and Fe, in the sintered compacts of Ti-5Al-2.5Fe using a model and to discuss how the phase transformation occurring during sintering is affected by homogenizing process and also to discuss the relationship between the homogenizing process and the sintering parameters.

2 Modeling the Homogenization of Alloying Elements
Homogenization is mainly dominated by mass transport of diffusing elements, but it becomes complex when considering sintering which is also a mass transport process. It becomes more complex for sintering of alloy compacts blended with elemental powders, which are usually accompanied by phase transformation. In this study, by the use of the published model representing sintering mechanism, element diffusion behavior is calculated, and determination of parameters for analysis is suggested.
according to the calculated results.

2.1 Analysis for Sintering Process of Titanium

The early analysis of sintering process was carried out in 1949 by Kuczynski\(^\text{11}\). In 1961, Coble presented Kelvin's terakaidecahedron model for describing diffusion during intermediate and final sintering\(^\text{12}\). In 1967, Rocland suggested an analytical method to compare the relative contribution of surface and volume diffusion during sintering\(^\text{13}\). Ashby further suggested an analysis method by which all the sintering mechanisms could be included. Through the study, contribution of each mechanism was compared and sintering diagram was constructed in 1974\(^\text{14}\). Here, a combination of Ashby's and Coble's models developed for pure metal powder is used in analyzing sintering process for titanium.

Ashby's model is shown in Fig. 1. The mechanisms corresponding to numbers in the figure represent (1) surface diffusion, (2) lattice diffusion (from surface), (3) evaporation and condensation, (4) boundary diffusion, (5) lattice diffusion (from grain boundary) and (6) lattice diffusion (by dislocations). Sintering is divided into 3 stages. Stage 1 is the early stage during which the individual powder particles are distinguishable. Stage 2 is the intermediate stage during which the pores are roughly cylindrical. Stage 3 is the final stage during which the pores are isolated and spherical. Stage 1 is a non-densification stage and the other two are densification ones. The equations used to describe the individual sintering mechanisms during the first stage are listed as follows\(^\text{15}\).

\[
\frac{dX}{dt} = 2D_s\delta_sFK_1^3
\]  
\[\tag{1}\]

\[
\frac{dX}{dt} = 2D_sFK_1^3
\]  
\[\tag{2}\]

\[
\frac{dX}{dt} = 4D_s\delta_sFK_1^3
\]  
\[\tag{3}\]

\[
\frac{dX}{dt} = 4D_sFK_1^3
\]  
\[\tag{4}\]

\[
\frac{dX}{dt} = 4D_sFK_1^3
\]  
\[\tag{5}\]

\[
\frac{dX}{dt} = \frac{4}{9}K_2NX^2D_sFK_1^3\left(K_2 - \frac{3\mu}{2\gamma}\right)
\]  
\[\tag{6}\]

Coble's model introduced in this paper is shown in Fig. 2 and Fig. 3 for intermediate (Stage 2) and final stage (Stage 3) of sintering. And the formulas derived are expressed as equations (7), (8) for Stage 2 and equation (9) for Stage 3\(^\text{12}\).

\[
\frac{dX}{dt} = 112D_sFK_1^3/12a
\]  
\[\tag{7}\]

\[
\frac{dX}{dt} = \frac{1}{3}D_s\delta_sFK_1^3/a^2
\]  
\[\tag{8}\]

\[
\frac{dX}{dt} = 6D_sFK_1^3
\]  
\[\tag{9}\]

Fig. 1 Sintering mechanisms suggested by Ashby.

Fig. 2 Model for intermediate sintering stage.
In the above equations (1) to (9), \( X \) is radius of neck between two particles; \( a \): particle radius; \( D_s, D_v \) and \( D_b \): surface, lattice and grain boundary diffusion coefficient; \( \delta_s \) and \( \delta_b \): effective thickness of surface and grain boundary;

\[
K_1 = \left( \frac{2(a-X)}{X^2} - \frac{1}{X} + \frac{2}{a} \right) \left( \frac{X}{a} - \left( \frac{f}{3} \right)^{1/2} \right)
\]
\[
K_2 = \left( \frac{2(a-X)}{X^2} \right) - \frac{1}{X}, \quad K_3 = \frac{2}{0.74a-X};
\]

\( f \): volume fraction of space in the compacts; \( V_0 \): theoretical density; \( P_v \): vapor pressure; \( \Omega \): atom volume; \( \gamma \): surface free energy; \( k \): Boltzmann's constant; \( F \): \( \gamma \Omega / kT \); \( \gamma \): dislocation density; \( \mu \): shear modulus.

These equations express the relationship among neck radius, sintering time and sintering temperature. The solutions of these differential equations are found by Euler method in this paper. In practical calculation, an initial value is given to the neck radius first. Then at a given temperature, the variation of neck radius with sintering time is calculated. The above process is repeated from low temperature to the desired temperature. The neck radii at different temperature for different sintering time are calculated further in order to express the relation clearly. Finally, the variations of radius with sintering temperature are illustrated as curves in the temperature-radius coordinate system. The \( X \)-axis in this system represents the dimensionless sintering temperature \( (T/T_M) \) and the \( Y \)-axis for dimensionless neck radius \( (X/a) \).

Using this procedure, the calculations are carried out for each equation separately and then for the formulation (10) in order to compare the contribution of each sintering mechanism.

\[
\frac{dX}{dt} = \sum_{i=1}^{N} \left( \frac{dX}{dt} \right)
\]  

(10)

Fig. 4 shows the results of calculation using equations (1) – (3) for 2, 3 and 5 hours, and Fig. 5 for equation (10). In Fig. 5, the time in the boxes indicate the sintering time and the curves express the size of the neck at a given sintering temperature for each sintering time. Comparing Fig. 4 and Fig. 5, the neck growth at the temperature range of \( T/T_M = \)
0.2~0.5 in Fig. 5 is comparable to the surface diffusion in Fig. 4, and hence it can be said that the sintering is mainly governed by surface diffusion mechanisms at the temperature range of $T/T_M=0.2$~0.5. This means that the surface diffusion contributes more than the other ones during initial sintering stage. Based upon this analysis and the significantly higher surface diffusion coefficients of alloying elements than titanium (listed in Table 1), it is further suggested that not only the titanium but also the alloying elements take part in surface diffusion during the sintering of stage 1 and the alloying elements mainly exist along the particle boundaries at the end of this stage.

2.2 Start Time Lag for Homogenizing Diffusion of Alloying Element

It can be easily imagined that homogenizing diffusion should begin with the start of stage 2 sintering soon after the surface diffusion finishes both for aluminum and iron. However, the diffusing sequence of alloying elements is considered to vary due to the difference of the diffusion driving force i.e. chemical potential, indicated from phase diagram indirectly. The phase diagram of Ti-5Al-Fe is shown in Fig. 6. It can be seen from the figure that the solution limits of iron is very low below $\beta$ transformation temperature ($T_\beta$). On the other hand, aluminum is $\alpha$-phase stabilizing element in titanium alloy, and so the driving force for aluminum diffusion is much stronger than for iron when the temperature is lower than $T_\beta$. Therefore, it can be reasonably suggested that the homogenizing diffusion of aluminum begins earlier than iron below $T_\beta$. Because $T_\beta$ is raised with increasing local content of aluminum, the effective $T_\beta$ may become locally higher than that indicated from the phase diagram during the sintering of stage 2. This further delays the beginning of iron diffusion until the beginning of $\beta$ transformation. As regards the diffusing sequence of alloying elements for homogenizing, it is thus suggested that aluminum diffusion begins first, continuing until just before $\beta$ transformation, then iron begin to diffuse with the start of $\beta$ transformation. According to the above discussion, the homogenizing process of alloying elements is shown schematically in Fig. 7.

3 Calculation on Homogenization Diffusion

In order to calculate the variation of alloying element concentration with time during the sintering of stage 2 and stage 3, Fick's diffusion equation is used.

$$ \frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} $$

(11)

The parameters used for calculation are determined as in 3.1 and 3.2 below.

3.1 Diffusion Distance

When sintering advances into the stage 2, densification will occur simultaneously with grain growth. Therefore, the homogenizing diffusion proceeds with the movement of grain boundary and so both the diffusing interface and diffusing distance changes continuously. With this kind of problem, several numerical analyses have been done on phase transformation process for steels during which thermo-dynamic parameters can be determined clearly. However, the detail of thermo-dynamic process in the sintering system composed of elemental powders is not clear yet.

In this paper, the maximum grain diameter of the sintered compacts is used as the diffusing distance instead of varying diffusing distance caused by moving interface. Through this treatment, calculation becomes easier. The grain size is obtained by measuring the Ti-5Al-2.5Fe sintered compacts. The results are shown in Fig. 8.

3.2 Diffusion Coefficients

Although the sintered compacts in this paper are ternary alloys, the behavior of aluminum diffusion is treated as a

![Fig. 6 Phase diagram of 5 mass% Al section in the Ti-Al-Fe system.](image-url)
4 Results and Discussion

The homogenizing process is calculated next by the use of the diffusion distance and diffusion coefficients mentioned above, the boundary conditions and initial conditions listed in Table 2. The results are shown in Fig. 9 and Fig. 10. In Fig. 9, variation of iron concentration is drawn in every 10 minutes and aluminum in Fig. 10 drawn in every 30 minutes. From the results, it can be seen that aluminum is homogenized in about 5 hours while the iron in about 1 hour. It is worth noting that the overall time for iron homogenization is about 6 hours, the total of the calculated time for aluminum and for iron considering the diffusing sequence mentioned above.

For the alloy used in this paper, the aluminum is added as an $\alpha$-phase stabilizing element and the iron is used as $\beta$ stabilizing element. The difference with vanadium used in the previous study$^{10}$ is that iron is a eutectoid type alloying...
element. When thermally processed under different conditions, this alloy exhibits a wide range of microstructure. The sintering condition may be thought as similar to solid solution above $T_\beta$, then cooling in furnace yields a microstructure of blocky and plate-like acicular $\alpha$-phase precipitated at prior $\beta$ grain boundaries.

The microstructure of the sintered compacts has been observed in the previous paper. As shown in Fig. 11, the sintered compacts exhibit two kinds of microstructures at sintering temperature 1373 K. The microstructure is mainly equiaxed $\alpha$ phase when sintering time is 5 hours, and blocky and plate-like acicular $\alpha$-phase is precipitated at prior $\beta$ grain boundaries when sintering time is 10 hours. The later one results from the $\beta$-eutectoid reaction caused by homogenization of iron. As calculated above, the time needed for iron homogenizing is about 6 hours. Therefore, when the sintering time is shorter than that needed for
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homogenizing, the homogenization is not sufficient and the resultant microstructure is a mainly equiaxed α phase. And when the sintering time is longer than that needed for homogenizing, the homogenization becomes sufficient and the blocky and plate-like acicular β-phase appears at prior β grain boundaries through β-eutectoid reaction. Like this, the difference of microstructure between the time 5 and 10 hours in the figure is attributed to the occurrence of β-eutectoid transformation governed by iron diffusion. However, although the microstructure evolution with sintering time has been explained reasonably by the calculated results, there are some assumptions made in the above analysis which may be main error source as explained below.

The model and formulas used for analyzing sintering process are based upon the first report of Ashby. After this, his second report was published in which a redistribution of matter on neck was analyzed. It was found that this redistributing process has a significant limiting effect on sintering. A more complicated geometrical model representing neck was introduced in order to calculate neck configuration. About the geometrical shape of neck, J. Svoboda et al. further calculated the equilibrium configurations of pores for three periodic structures based upon a constant mean curvature by numerical analysis method and by closed-form similarity solution and approximate analytical solution. The results showed that evolution of the pore morphology during densification is different from what has often been assumed.

On the other hand, grain growth of the sintered compacts is different from that of pore-free materials due to the pore-boundary interactions. From the analysis of this interaction, it can be seen that both grain boundary diffusion and surface diffusion contribute to the energy conservation at the pore-boundary junction and usually the cylindrical pore retards the grain growth during intermediate sintering stage (stage 2) while the closed form pore has very little retarding effect during final sintering stage (stage 3). In other words, the diffusing process is more complex than normal pore-free grain growth before the grain size reaches its final dimension. Hence, the diffusing behavior of alloying element is not clear now.

In addition, phase transformation process analysis during sintering may be more difficult because the composition of the mixed powder system is not uniform initially. The final equilibrium state can be obtained from the corresponding phase diagram, but a lot of non-equilibrium phase transformation processes may occur before the final composition is achieved, which has also a significant influence on the homogenizing diffusion.

5 Summary and Conclusion

A crude model is applied to the present study, trying to combine homogenization with sintering process for fabricating alloy compacts using elemental powders. Quantitative analysis has been carried out by numerical calculating method to show that the surface diffusion is a major factor during the first sintering stage and the alloying elements are considered to gather and distribute along the boundaries of the particles simultaneously. The aluminum element begins its homogenizing diffusion with the start of the second sintering stage until the β phase transformation. With the proceeding of this β phase transformation, iron element executes its homogenizing process. The sintering time calculated by considering the homogenizing process is in agreement with the observed structure of the sintered compacts obtained in the previous experiment.

References

8) G.Floria and L.Franchi: "Processing Titanium by


