Growth of Carbide Particles in TiC-Ni and TiC-Mo2C-Ni Cermets during Liquid Phase Sintering

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The growth behavior of carbide particles during liquid phase sintering was examined in TiC-Ni and TiC-Mo2C-Ni alloys with various Ni contents. The grain growth of TiC-Ni was markedly retarded by an addition of Mo2C. The linear relationship between the cube of mean particle size and heating time was observed in these alloys. The growth rate had a maximum near 10% Ni for TiC-Ni, but monotonously increased with increasing Ni content for TiC-Mo2C-Ni. The growth constant of these alloys was much lower by a factor of 103–104 than the rate constant expected from the diffusion-controlled growth model. The microstructural observation revealed that the growth of carbide particles took place under nearly a constant particle contact. The presence of contiguous boundaries at particle contact was considered to be an origin of sluggish grain growth in these alloys. The grain growth behavior could qualitatively be explained by assuming that the contiguous boundaries restrict the migration of solid/liquid interfaces and thus the grain growth is suppressed.

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I. Introduction

Titanium carbide (TiC) base cermets, applied to cutting tool materials, are fabricated by liquid phase sintering. The sintering condition is carefully chosen to control the size of carbide particles which strongly affects the mechanical properties and cutting performance of cermets1,2). Therefore, the information on particle growth during sintering is very important to produce highly qualified cermets tools.

In early studies on TiC base cermets, Humenik and Parikh reported that the growth of TiC particles in Ni or Co base liquid phase might be attributed to a coalescence process3,4). Warren and Woldron investigated the growth behavior of several carbides in Co liquid and concluded that the growth of VC and Mo2C could be understood by the diffusion controlled model, but of TiC, NbC, TaC and HfC took place much slower than expected from this model5,6). On the other hand, Chermant and Coster reported that the growth of TiC-Ni was controlled by the reaction at the interface between particles and liquid phase7,8). The reaction-controlled growth has also reported for TiC-Mo(W)-Ni9) and TiN-Ni10). The main basis supporting the reaction-controlled process as a rate-controlling mechanism is that the size distribution of particles is similar to that expected from the reaction-controlled model. However, the details of the interface reaction have not been clarified yet.

In the present study, the growth behavior of carbide particles was examined for TiC-Ni and TiC-Mo2C-Ni alloys with a special interest in the effect of volume frac-

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II. Experimental Procedures

Commercial powders of TiC (mean particle size, 1.5 μm), Mo2C (2.0 μm) and Ni (3.0 μm) were used for preparing TiC-Ni and TiC-Mo2C-Ni alloys in which the Ni volume fraction was changed from 2 to 60 vol% and Mo/(Mo+Ti) atomic ratio was fixed at 0.1 and carbon content was kept as high as possible in the two-phase region consisting of TiC and nickel-base liquid phase1). These powders were mixed in a nickel pot together with TiC-Ni balls and ethanol. Green compacts of the mixed powders were sintered at 1673 K for 1 h in vacuum. Sintered bodies were reheated at 1673 K for 9–29 h in Ar atmosphere. They were cooled from 1673 K to 1073 K for 3 min. The cross sections were polished with diamond powders and then examined mainly by scanning electron microscopy to measure the size (intercept length) and the contiguity of carbide particles. The particle size was estimated by the mean value of intercept length of about 1000 particles. The contiguity was evaluated from the relation G = 2N1/(N0 + 2N1), where N0 and N1 are the numbers of interceptions of solid/solid and solid/liquid interfaces per unit length of the test line, respectively. About 500 interceptions were examined on the microstructure for each heating time. The composition of Ni phase was measured by EPMA analysis.

III. Results

Figure 1 shows the microstructures of TiC-(2–60) vol%Ni heated at 1673 K for 1 and 20 h. Microstructures of 10–60 vol%Ni were obtained in as-polished state, while those of 2 vol%Ni were revealed by etching in HF-HNO3 solution. The particle size is largest around 10
Fig. 1 Scanning electron micrographs of TiC–Ni alloys with various Ni contents (vol%) heated at 1673 K for 1 and 20 h. Nickel contents are (a), (e) 2%, (b), (f) 10%, (c), (g) 30%, (d), (h) 60% and heating times are (a)–(d) 20 h, (e)–(f) 1 h.

Vol%Ni and the particle contact is observed for all alloys, even for 60 vol%Ni alloy.

Figure 2 shows the microstructures of TiC–Mo2C–(2–60) vol%Ni. The Mo2C addition results in finer particle size as has generally been known. Coring structure of carbide particles is seen in Mo2C-added alloys. The outer shell of each carbide has been called as surrounding phase which consists of (Ti, Mo)C solid solutions. The particle size of Mo2C-added alloys increases with increasing Ni content and the particle contact is seen for all alloys.

The relations between mean particle diameter, $\bar{d}$, and

Fig. 2 Scanning electron micrographs of TiC–Mo2C–Ni alloys. Nickel contents are (a), (e) 2%, (b), (f) 10%, (c), (g) 30%, (d), (h) 60% and heating times are (a)–(d) 20 h, (e)–(f) 1 h.
heating time, \( t \), for TiC–Ni and TiC–Mo\(_2\)C–Ni alloys are shown in Figs. 3 and 4, respectively. As mentioned later, the size distribution of carbide particles changed little after the heating time 1 h at 1673 K, and up to about 5\% of particles took a size larger than twice of average size. However, the average particle size can satisfactorily be expressed in the form,

\[
d^3 - d_0^3 = K t
\]

where \( K \) is the growth rate constant.

Figure 5 is a plot of growth rate constant \( K \) as a function of volume fraction of Ni in the two alloys. The \( K \) value takes a peak around 10 vol\%Ni in TiC–Ni, while \( K \) increases monotonously with increasing Ni content in TiC–Mo\(_2\)C–Ni. The Mo\(_2\)C-added alloys have a much lower growth rate than TiC–Ni alloys and the refining effect of Mo\(_2\)C is stronger at a lower Ni content.

Figure 6 is the normalized size distribution of particles for TiC–Ni heated for 1 and 20 h. These histograms are a little broader in lower Ni content alloys and shorter heating time. They seem to be more similar to the theoretical distribution for reaction-controlled process than that for diffusion-controlled process\(^{(16)-(18)}\). However, as has often been pointed out, the controlled process is not necessarily decided by the size distribution data only\(^{(17)}\).

Figure 7 shows the relation between contiguity of particles and heating time for TiC–Ni. The contiguity changes little during heating at 1673 K. A similar result was obtained in Mo\(_2\)C-added alloys. The contiguity of TiC–Ni and TiC–Mo\(_2\)C–Ni is shown as a function of Ni content in Fig. 8. The contiguity decreases with increasing Ni content in both alloys, and takes a slightly higher value in TiC–Mo\(_2\)C–Ni than in TiC–Ni.
as those in TiC-Ni alloys. In the pseudo-ternary phase diagram of TiC-Mo2C-Ni\[12\], the solubility of TiC in liquid phase decreases little by a small addition of Mo2C as the present alloys.

### IV. Discussion

The grain growth by solution/reprecipitation process has been reported in many systems of liquid phase sintering\[10\]. Grain growth kinetics by the solution/reprecipitation process is generally classified as (1) the process controlled by the diffusion of constituent solutes through liquid phase and (2) the process controlled by the reaction of solution or reprecipitation at the interface between particles and liquid phase. The relation between particle size and time in the former process is described by eq. (1).

From the theories by Lifshitz and Slyozov\[16\] and by Wagner\[17\], the rate constant in eq. (1) for spherical particles dispersed in a high volume fraction of liquid phase can be written as follows:

\[
K' = \frac{\alpha^3}{1 - (1-f)^{1/2}} K_d
\]

where $f$ is the volume fraction of liquid phase, $\alpha$ is the ratio of the average radius of particles to the critical radius. However, this theoretical constant, similarly to that of other models, decreases with increasing $f$, which cannot explain the present result of the $f$ dependency of $K$.

In TiC-Ni and TiC-Mo2C-Ni, particles were in contact during sintering and the contiguity of particles increased with decreasing Ni content. Particle contact reduces the area of solid/liquid interface where solution or reprecipitation occurs. When particles contact at a contiguity of $G$, the interface area will be reduced by a factor of $(1-G)$, and the rate constant will be

\[
K^* = (1-G)K' + GK_c
\]

where $K_c$ is the constant for contiguous boundary. In this case, however, the motion of contiguous boundary is assumed to be so small as to be neglected, because the motion occurs due to the diffusion through solid phase. Therefore, the rate constant may be approximated to be the first term of right hand side of eq. (4).

The calculated values of $K_d$, $K'$ and $K^*$ are shown as a function of $f$ in Fig. 9. In the calculation, the experimental data on $G$ for TiC-Ni was used. The $K'$ value decreases monotonously with an increment of $f$ due to the increase of effective diffusion distance of solute with increasing liquid phase, while $K^*$ has a peak around a
volume fraction 0.1. The decrease of $K^*$ with $f$ for small volume fraction range results from the reduction of solid/liquid interface. It may be said that the volume fraction dependence of growth rate constant in TiC–Ni agrees qualitatively with that of $K^*$. However, the observed growth rate constant is still much smaller than $K^*$ by a factor of 10^2 and 10^4 for TiC–Ni and TiC–Mo2C–Ni, respectively. This fact means that the growth rate of TiC–Ni and TiC–Mo2C–Ni cannot be explained by the diffusion-controlled model even by taking into account the particle contiguity.

The sluggish growth of carbides in cerments may be caused by the reaction-controlled process in TiC–Ni(5)-(10). The reaction-controlled process has been supported by various workers because of the following reasons, (1) the growth rate constant is much smaller than that expected from the diffusion-controlled growth, (2) the activation energy 150 kJ/mol is about a half of the diffusion of TiC in Co, 300 kJ/mol, (3) the grain size distribution resembles the distribution for reaction-controlled growth. Judging from the above experimental evidence, the interface reaction seems to be plausible as a rate-controlling mechanism. However, the physical meaning of the interface reaction has not been given so far. In addition, the volume fraction effect on the growth rate obtained in this study cannot fully be explained by the interface-reaction controlled model. If the interface-reaction is rate-controlling, the volume fraction dependence of growth rate will be decided by solid/liquid interface area; the growth rate will depend simply on $(1 - G)$.

On the other hand, Takajo, Kaysser and Petzow(13)(26) have proposed the kinetics of grain growth during liquid phase sintering controlled by the coalescence process, in which the particle neck growth is assumed to be controlled by the diffusion through liquid phase and an increase of the average particle size is proportional to the cube root of sintering time. The growth rate in the coalescence process is expected to decrease with the volume fraction of liquid phase because of lowering coalescence frequency. This prediction does not agree with the volume fraction dependence in present alloys. Furthermore, the coalescence process seems not to give any concrete explanation for the much smaller rate constant than that expected from diffusion-controlled model.

The present results are rather consistent with the indication by Warren and Waldron(6)(7). They have reported that the systems such as TiC–Co and TaC–Co whose growth rate is much slower than that expected from the diffusion-controlled model have a higher contiguity of particles than the systems such as VC–Co and Mo2C–Co whose growth rate constant is explained by this model, and that the rate constant of TaC–Co is not significantly affected by $f$, whereas that of VC–Co decreases with $f$. From these results and also the results on microstructural examinations, they have discussed the effects of grain contact on carbide grain growth in detail. If the contiguous boundaries have a mobility lower than that of solid/liquid interfaces, these boundaries must exert a drag on the migration of the interfaces. The drag is probably an origin of sluggish growth of the systems such as TiC–Co and TaC–Co.

Such an interpretation seems to be applicable to present alloys. Fig. 10 schematically shows the retardation of particle growth due to the drag of less mobile contiguous boundaries. When the carbide particles are impinged, the contiguous boundaries will be formed such that they are in equilibrium with the connected solid/liquid interface. A very stable configuration, probably an equilibrium configuration, must be formed between a contiguous boundary and solid/liquid interfaces. Once such a configuration is attained, the motion of contiguous boundary will further be restricted because extra energy is necessary to break the stable configuration. The drag of grain growth by less mobile contiguous boundaries must be important when the contiguity becomes a certain critical value. Above the critical value, the solid/liquid interface migration will almost completely be locked by the contiguous boundaries. In such a case,
overall growth rate is controlled by the motion of contiguous boundaries themselves. The drag by contiguous boundaries may particularly be effective for planar solid/liquid interfaces, which are less mobile than curved interfaces. The diffusion-controlled growth is essential for particles with curved boundaries, which have a slightly higher solute concentration than equilibrium value as depicted in the theory of Ostwald ripening. The TiC particles in present alloys are generally faceted and the solid/liquid interfaces are planar. It is, therefore, probable that the solid/liquid interface migration is dragged by the motion of contiguous boundaries, and thus the carbide grain growth takes place in a much slower rate than that expected from solute diffusion in liquid phase. A fairly sharp decrease in growth rate constant at small volume fraction of binder phase, below about 0.1, in Fig. 5 may reflect the low mobility contiguous boundaries in comparison with the solid/liquid interfaces. The Ni content dependency of the growth in TiC–Ni can qualitatively be understood from the two effects, viz., the decreased contiguity and the increased diffusion distance with an increase of Ni content.

The grain growth inhibition by the addition of Mo2C in TiC–Ni alloys may also be understood by the retarding effect of Mo2C on the solid/solid boundary mobility of TiC. The retarding effect of solute on the grain growth has commonly been found in ceramics. The Ni content dependency of the growth in TiC–Mo2C–Ni can be attributed to strong drag effect of contiguous boundary with low mobility.

However, various factors such as grain boundary mobility data in TiC, effect of solute, e.g. Mo on the grain boundary mobility, the estimation of contiguous boundary mobility on the overall growth rate of carbides and so on, have to be clarified for quantitatively calculating the growth rate constant and its dependence of volume fraction of binder phase. Future studies to make clear such factors are required.

V. Conclusion

The growth behavior of carbide particles in TiC–(2–60) vol%Ni and TiC–Mo2C–(2–60)vol%Ni cerments during liquid phase sintering at 1623 K was examined. The results obtained are:

(1) The linear relationship between the cube of mean particle size and heating time was obtained in both alloys, but the growth rate was remarkably retarded by Mo2C addition.
(2) The rate constant of TiC–Ni had a maximum near 10% Ni, whereas that of Mo2C-added alloys monotonously increased with increasing Ni content.
(3) The grain growth of these alloys occurred at a nearly constant contiguity of particles during sintering.
(4) The value of the rate constant in the two alloys was much lower by a factor of $10^4$ than the rate constant expected from the diffusion-controlled growth model.
(5) The grain growth behavior can qualitatively be explained by assuming that the contiguous boundaries of carbides restricts the overall grain growth in the alloys. The suppression of grain growth due to Mo2C addition may also be explained by solute dragging of grain boundary mobility in TiC.

REFERENCES

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