Sintering of Nickel-Bonded Titanium Carbides*

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An experimental investigation of the sintering process of nickel-bonded titanium carbides was carried out by means of dilatometric and metallographic methods. Linear shrinkage of compacts of mixed powders of nickel and titanium carbide of various compositions (0, 10, 20, 30, 40, 50 and 75 % nickel in the weight ratio) was measured during sintering with a silicon carbide dilatometer. The temperature was raised at the rate of 250°C/hr up to 1500°C and kept constant for 1 hr and then lowered at the same rate. In most cases, except for 0 % and 75 % nickel, linear shrinkage of the compacts was very slight up to about 1200°C, but the abrupt shrinkage corresponding to the appearance of a liquid phase was observed over the temperature range of 1200~1350°C. The total shrinkage during sintering increased, while the starting temperature of the abrupt shrinkage decreased with the increase in nickel content. The linear shrinkage at the temperature of 1500°C was proportional to logarithm of sintering time. It was shown by the metallographic examination that the shape of carbide grains changed from round to angular with the increase in nickel content. The grain size and the sphericity index of titanium carbide, however, did not change so much with the nickel content under the same sintering conditions. The change in the shape of carbide grains may be attributed to the continuity of a binder phase in compact.

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I. Introduction

Among all the variables affecting the sintering of powder compacts, sintering temperature and time are probably most important. Dimensional change, which generally occurs during sintering, is considered as a measure to describe the process of sintering and has been extensively studied on the solid phase sintering for practical or theoretical purposes. Little studies have been done, however, on the sintering in the presence of a liquid phase. The most precise method for studying the dimensional change of a compact is to measure the dimensions of compacts heat-treated at various temperatures for different lengths of time, but such a technique is highly time-consuming. In the present study, the change in length of a compact was measured with a dilatometer as heated at a constant rate. The method is simple, direct and most suitable for studying the sintering process in the presence of a liquid phase, since the additional dimensional change by the solidification of a liquid phase may cause an erroneous result in the former technique. The purpose of this paper is to study the behavior of change in length of a compact during sintering and to determine the optimum conditions for sintering of TiC-Ni cermets.

A dilatometer for studying the sintering process of TiC-Ni cermets must be usable up to about 1600°C. The principal part of a dilatometer for high temperature use has been made with graphite, sapphire or silicon carbide. Recrystallized silicon carbide was reported to be quite satisfactory for the application⁽¹⁾⁽²⁾, that is, the thermal expansion characteristic of this

material is approximately linear and is reproducible even in air atmosphere. The dilatometer used in the present study was made with recrystallized silicon carbide.

II. Experimental Procedure

A schematic drawing of the sintering dilatometer is shown in Fig. 1 and the main part of the dilatometer

① Dial indicator ② Alumina disk ③ Aluminum reflector ④ Silicon carbide rod ⑤ Silicon carbide legs ⑥ Graphite cap ⑦ Graphite mould ⑧ Powder (TiC and Ni) ⑨ Alumina tube ⑩ Alumina disk ⑪ Alumina pedestal ⑫ Alumina tube ⑬ Gas inlet ⑭ Thermocouple protection tube

Fig. 1 Vertical and horizontal sections of furnace and dilatometer.

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(1) S. D. Mark Jr., and R. C. Emanuelson : J. Amer. Ceram. Soc., 37 (1958), 193.

(2) T. Yamauchi and H. Suzuki : J. Ceram. Assoc. Japan, 64 (1956), 53.

in Photo. 1. A dial indicator set on an adaptor is supported by three recrystallized silicon carbide legs of 8 mm in diameter, and change in length of a specimen is directly transmitted to the dial indicator by a centrally located recrystallized silicon carbide

Photo. 1 Photograph of the silicon carbide dilatometer.

rod of the same diameter. The dial indicator reading is to one hundredth of a millimeter. The furnace is heated with a spiral heating element of silicon carbide, and a temperature of 1600°C is readily attainable. Temperature is measured with a platinum 13 % rhodium-platinum thermocouple and a thermometer calibrated by the melting points of pure metals. To prevent the temperature rise of the dial indicator which causes an error in dilatometric measurement, sufficient space is given between the dial indicator and the furnace and an aluminum reflector is placed under the adaptor. Moreover, a small alumina disk is attached to the top of the silicon carbide rod, so that heat transmission to the dial indicator through the rod is insulated. A preliminary test proved that the temperature rise of the dial indicator was quite small even when the furnace was heated to 1600°C.

In this apparatus, it can not be avoided that the specimen is more or less loaded by the central rod and the dial indicator during measurement of the dimensional change. The load, about 100 g, is so small that the process to be studied with this apparatus can be regarded not as the hot pressing but as the usual sintering process. At first a pressed bar was used as a specimen, and some obstacles such as spalling, bending or lateral movement of a specimen during the test were encountered. Then the powder was pressed into a cylindrical graphite mould which was correctly placed in the center of three legs as shown in Fig. 1. A graphite cap was attached to the lower end of the rod as shown in Fig. 1, because it

was considered that the silicon carbide rod might react with molten nickel during sintering. The dilatometer was calibrated by measuring thermal expansions of pure metals. It is evident that recrystallized silicon carbide can be applied quite satisfactorily to the high temperature dilatometer as already reported.*

The commercial grade powders of titanium carbide and nickel were used for this investigation. The total and free carbon contents in titanium carbide powder were 19.0% and 0.08% respectively, and the average particle size was about 6 microns. Nickel powder used was reduced one with 99% purity and -325 mesh. Six compositions, 10, 20, 30, 40, 50 and 75% Ni in the weight ratio, were ball milled with methyl alcohol for 25 hr. The average particle size of titanium carbide determined by the microscopic method after ball milling was 1 micron. The powders were pressed into graphite moulds at the pressure of 50 kg/cm². Besides those six compositions, the dilatometric measurement was carried out of the titanium carbide powder. A proper amount of the powders was used for the tests so that the height of each specimen would be about 50 mm before sintering. The temperature of the furnace was raised at the rate of 250°C/hr up to 1500°C and kept constant for 1 hr, and then cooled also at the same rate. Below 700°C, the temperature could not be lowered at the same rate because of a gradual decrease in the cooling rate. The process of heating and cooling of the specimen during the test is shown in Fig. 2. All the measurements were carried

Fig. 2 Linear shrinkage during sintering in various compositions of nickel-bonded titanium carbides and heating program.

out in an argon atmosphere. Argon was flown at the rate of 1.8 l/min, but the surface of the graphite mould was little oxidized even after heating at 1500°C.

* It should be noted, however, that vaporized nickel condenses on the silicon carbide rod and legs when the specimen of a high nickel content is tested (at higher temperatures than the melting point of nickel) and, in such case, a little change in the coefficient of thermal expansion of silicon carbide will occur after a long period of use.

III. Experimental Results

The temperature change and the linear shrinkage of powder compacts of various compositions against time are plotted in Fig. 2, while Fig. 3 shows the linear shrinkage of the compacts against temperature.

Fig. 3 Linear shrinkage during sintering vs. temperature curves for various compositions of nickel-bonded titanium carbides.

The shrinkage was very small up to 1200°C, but an abrupt shrinkage occurred over the temperature range from 1200 to 1350°C depending on compositions. The total shrinkage increased, but the starting temperature of the abrupt shrinkage lowered with the increase in nickel content. The temperature was kept constant for 1 hr after reaching 1500°C, but the shrinkage occurring in this period was much smaller than the abrupt shrinkage during heating up to 1500°C. After 1 hr at 1500°C, the shrinkage became almost zero and

in the same order as that of recrystallized silicon carbide⁽¹⁾⁽³⁾. Gurland and Norton⁽⁴⁾ reported a discontinuous change in the length of a compact of sintered WC-Co alloy on cooling. The difference in the behaviors on cooling may be due to the difference in solubility changes of carbide in the binder phase at the solidification temperature.

The total shrinkage during sintering and the shrinkage of the specimens kept at 1500°C during sintering are separately plotted in Fig. 4. Both of them change

Fig. 4 Total shrinkage during sintering and shrinkage at 1500°C for various compositions of nickel-bonded titanium carbides.

gradually with the nickel content up to 40%. For 50% Ni, however, both shrinkages become much larger. The reason is that a bend of the specimen (Photo. 2) which was caused during sintering by the load from the dilatometer is included in the observed values of shrinkage. For 75% Ni, the shrinkage at 1500°C is practically zero, because the specimen melted down completely below 1500°C as shown also in Photo. 2. Therefore, the two cases should be excepted in comparison of the total shrinkage and of the shrinkage at 1500°C. The shrinkage at 1500°C against logarithm of sintering time is

Photo. 2 Specimens of various compositions of nickel-bonded titanium carbides after dilatometric measurement.

any discontinuous shrinkage was not observed during cooling to room temperature. The shrinkage curves in Fig. 3 are leveled off during cooling, where the coefficient of thermal expansion of TiC-Ni cermets is

plotted in Fig. 5. The shrinkage changes linearly

(3) F. P. Knudsen, R. E. Moreland and R. F. Geller : J. Amer. Ceram. Soc., 38 (1955), 312.

(4) J. Gurland and J. T. Norton : Trans. AIME, 194 (1952), 1051,

with logarithm of sintering time as reported by Lenel⁽⁵⁾ and the gradient of curves becomes steeper with the lower nickel content. In Fig. 5, the shrinkage deviates a little from linearity for the first 5~10 min, which may be due to the effect of stopping the

Fig. 5 Linear shrinkage vs. log sintering time for various compositions of nickel-bonded titanium carbides at 1500°C.

temperature rise at 1500°C.

The starting temperature of the abrupt shrinkage against the nickel content is plotted in Fig. 6. The temperature presumably corresponding to the appearance of a liquid phase, becomes lower with the

Fig. 6 Temperature of the beginning of abrupt shrinkage during sintering.

increase in nickel content. There are some differences between the observed values and those determined by the phase diagram of the Ni-TiC system⁽⁶⁾⁽⁷⁾. The reason is probably that the binary diagram reported was determined with melted alloys instead of the powder mixtures used in this study. In a mixture of two kinds of powders, a liquid phase will appear by diffusion at the temperature lower than melting points of the two components provided that an eutectic exists between

those components⁽⁸⁾. In the Ni-TiC binary system, there is an eutectic close to the nickel side at the temperature lower than the melting point of nickel⁽⁶⁾⁽⁷⁾. Compacts with a low nickel content are hardly deformed on pressing, and Ni and TiC particles are not brought into enough contact. As a result, the formation of a liquid phase during heating will be delayed. This is the reason why the smaller nickel content results in the higher temperature of the abrupt shrinkage.

Since the sintering in the presence of a liquid phase may be carried out even at the temperature at which a liquid phase begins to appear, the sintering behavior at the starting temperature of a liquid phase formation was compared with that of 1500°C. A specimen of 20% Ni was heated and the temperature was kept constant as soon as the abrupt shrinkage had occurred. In practice, the temperature was kept at 1350°C after raising at the rate of 250°C/hr. The heating process and the linear shrinkage during the sintering at 1350°C and at 1500°C are compared in Fig. 7. In the

Fig. 7 Linear shrinkage during sintering of 20% Ni-80% TiC for two different sintering program.

sintering at 1500°C the shrinkage was almost leveled off in 1 hr, but in the sintering at 1350°C the shrinkage was still proceeding even after 7 hr sintering. The total shrinkage in the sintering at 1350°C is less than that in the sintering at 1500°C, the density of sintered bodies being 5.23 g/cm³ for 1500°C and 4.13 g/cm³ for 1350°C, respectively. The linear shrinkage of the specimens at a constant temperature against logarithm of sintering time is plotted in Fig. 8. The curve is not linear for the sintering at 1350°C, which includes the change occurred immediately after the appearance of a liquid phase. On the other hand, the curve for the sintering at 1500°C indicates only the change occurring far later than the appearance of a liquid phase. The former corresponds to the rearrangement process and the solution-precipitation process, and the latter corresponds only to the solution-precipitation process, which will be discussed later. For this reason, these two curves are different. The gradient of the curve of the sintering at 1350°C is steeper than that at 1500°C, which probably shows that the shrinkage at 1350°C includes the rearrangement process even

(5) F. V. Lenel: *The Physics of Powder Metallurgy*, 238, McGraw-Hill New York, (1951).

(6) E. R. Stover and J. Wulff: PB Report, PB-1128268, (1954).

(7) E. R. Stover and J. Wulff: *Trans. AIME*, 215 (1959), 127.

(8) R. Steinitz: *J. Metals*, 5 (1953), 891.

after a long period. The curve becomes linear in the later stage and the gradient is almost the same as that of the sintering at 1500°C, which means ending of the rearrangement process. At any rate, it is likely that the shrinkage in the solution-precipitation process is

Fig. 8 Linear shrinkage vs. log sintering time for 20 % Ni-80 % TiC at different sintering temperatures.

proportional to logarithm of sintering time.

From the above mentioned results, the following are to be proposed for the sintering of TiC-Ni cermets. (1) The heating rate should be slowed down within the temperature range of 1200~1350°C because the liquid

to that temperature, sintering will be incomplete even after a long period of heating. (3) The binder content is limited to less than 50 %, for the higher binder content results in the deformed sintered body.

The microstructures of specimens sintered at 1500°C for 1 hr are shown in Photo. 3. The micrographs were obtained from the cross-sections of the specimens used for measuring the shrinkage. In the composition of 10 % Ni, TiC grains are small and round but the grain growth is remarkable in the compositions higher than 20 % Ni. It should be noted in Photo. 3 that the shape of TiC grains changes from round to angular with the increase in nickel content, and all grains are angular in 75 % Ni. The transition in the grain shape from round to angular in most of the carbide grains is shown to occur in 40 % Ni. Besides TiC grains, some of a different kind of grains are seen in 75 % Ni; the black one is graphite and the other may be an intermediate compound between nickel and titanium. Pores are also seen in the micrographs as small black dots, but are distinguishable from the precipitated graphite by the shape. The microstructure of the specimen of 20 % Ni sintered at 1350°C for 7 hr, corresponding to the sintering procedure (B) in Fig. 7, is shown in Photo. 4. TiC grains are smaller but more angular, compared with the same composition sintered at 1500°C for 1 hr (Photo. 3 (b)).

In order to show the change in grain shape and size more clearly, the average diameter and the size

Photo. 3 Micrographs of nickel-bonded titanium carbides sintered at 1500°C for 1 hr, unetched. $\times 640$

phase appears over this temperature range whereby causing a large dimensional change. However, a rather rapid heating rate can be used up to 1200°C. (2) The sintering temperature is preferable to be 50~100°C higher than the temperature at which a liquid phase appears. When the sintering temperature is too close

distribution range of carbide grains are plotted in Fig. 9. In this plotting, the average diameter and the size distribution range are shown with a median and 10-90 percentile range. The grain diameter and the size distribution range were determined from the micrographs of cross-section of the specimens and

more than 500 grains are measured for one specimen. As shown in Fig. 9, the average diameter and the size distribution range are almost identical for the compositions higher than 20 % Ni. A little lower values for both grain diameter and size distribution range in

Photo. 4 Micrograph of 20% Ni-80% TiC sintered at 1350°C for 7 hr, unetched. $\times 640$

Fig. 9 The average diameter and the size distribution range of carbide grains in nickel-bonded titanium carbides sintered at 1500°C for 1 hr.

75 % Ni than the other compositions are due to the fact that all grains are angular in this composition. The sphericity index, the average ratio of minimum particle diameter to maximum particle diameter, proposed by Kingery and Narasimhan⁽⁹⁾, is plotted against the nickel content as shown in Fig. 10. The

Fig. 10 Sphericity index for carbide grains in nickel-bonded titanium carbides sintered at 1500°C for 1 hr.

values of sphericity index are almost identical for all compositions except a little higher value of 40 % Ni, which corresponds to the transition of grain shape from round to angular. In Fig. 11, the percentage of angular grains to all carbide grains are plotted

against the nickel content to show the change in grain shape more clearly. The percentages of completely polygonal grains and of partially polygonal grains and of the sum of both grains are plotted in the figure. From 10 % Ni in which most of the grains are

Fig. 11 The percentage of angular grains to total number of carbide grains in nickel-bonded titanium carbides sintered at 1500°C for 1 hr. Open circle indicates the percentage of completely polygonal grains; solid circle, the percentage of partially polygonal grains with rounded edges; triangle, sum of those percentages.

round to 75 % Ni in which most of the grains are angular, the ratios of angular grains increase gradually with the increase in nickel content. As sintering condition is identical for all the compositions in this study, it may be concluded that the shape of TiC grains in sintered TiC-Ni cermet changes with the amount of binder phase.

IV. Discussion

It is generally recognized that the densification during sintering in the presence of a liquid phase proceeds through three stages, viz., rearrangement process, solution-precipitation process and coalescence process⁽¹⁰⁾, and this has experimentally been proved by several investigators⁽⁹⁾⁽¹¹⁾. In the rearrangement process, the wettability between solid and liquid phase is an important factor. Assuming that all the solid particles are spheres of the same diameter, the volume ratio of solid body to space between spheres becomes 74:26 for the closed-packed assembly⁽¹²⁾. If the volume ratio of solid phase to liquid phase in a compact is close to this ratio and the solid phase is wetted by the liquid phase, then complete densification can take place by the rearrangement process. For the combination of titanium carbide and nickel, the volume ratio becomes 61:39 in the weight ratio; therefore the composition of 40 % Ni is most close to this ratio. It should be noted, however, that the components are soluble each other at the sintering temperature. According to the work by Stover and Wulff⁽⁶⁾⁽⁷⁾ the solubility of titanium carbide in nickel is more than 15 % and that of nickel in titanium carbide is almost

(10) W. D. Kingery: J. Appl. Phys., **30** (1959), 301.

(11) J. Gurland: Trans. AIME, **215** (1959), 601.

(12) J. M. Dallavalle: *Micromeritics*, 123, Pitman, New York, (1948).

(9) W. D. Kingery and M. D. Narasimhan: J. Appl. Phys., **30** (1959), 307.

zero at 1500°C. At this temperature the above mentioned ratio must shift to the nickel side, and moreover, TiC grains in the powder used are neither of complete spheres nor of the same size. From these consideration, the compositions from 30 to 40 % Ni are expected to be optimum ones to get a good result in the sintering of TiC-Ni cermets. Though the densification may proceed even after completion of the rearrangement process, the densification by the solution-precipitation process is much smaller than that of the rearrangement process. Therefore the composition, in which the complete densification by the rearrangement process will take place, is desirable for a good sintered body.

Kingery proposed a theory on the solution-precipitation process⁽¹⁰⁾ and revealed by the experiment of the sintering of Fe-Cu system that a substantial part of this process is diffusion rate controlling⁽⁹⁾. The data in the present study can not be directly compared with the results by Kingery and Narasimhan⁽⁹⁾, because the heating procedures are quite different. However, it seems that the linear shrinkage at 1500°C, presumably corresponding to the solution-precipitation process, changes almost linearly with the logarithm of sintering time as demonstrated by Lenel⁽⁶⁾. As shown in Fig. 10, the sphericity index does not change so much with the nickel content. Even after the completion of the rearrangement process, the solution-precipitation process will proceed unless the temperature is lowered below the eutectic temperature. The shape of TiC grains will change towards an equilibrium state; therefore, if large quantity of liquid content is present, most of TiC grains will change to the three dimensional equiaxial type, diminishing the sharp edges. It means that the sphericity indice determined by the cross-section of the grains become almost identical values for a higher Ni content after sufficiently long sintering as shown in Fig. 10. The rate of reaction in the solution-precipitation process can be considered as a function of temperature. Since the TiC powder of the same grain size distribution was used and the compacts were sintered under the same conditions, the grain size distributions in each compact are expected to be almost identical if large liquid content is present during sintering as shown in Fig. 9.

In the solution-precipitation process, the transfer range of TiC through the liquid phase will differ with the amount of a liquid phase. In the case of a small liquid content, the contact among TiC grains occurs and the transfer range of TiC will be limited to a small domain. In the case of a large liquid content, titanium carbide transfers widely through the liquid phase and precipitates on the low energy surface of large TiC grains; therefore the shape of TiC grains will change with the binder content. If a sufficient liquid phase is present and the solid phase is completely wetted by the liquid phase, the TiC grains distribute apart each other and the precipitation occurs along the definite crystallographic planes of large TiC grains, lowering the interfacial energy. The titanium carbide crystal has a cubic NaCl-type

structure; if the precipitation of TiC through the liquid phase occurs along (100) planes of the crystal, the grain will grow to a cubic shape. The random cross-sections of a cube by a plane become three to six sided polygons and most of them are rectangular or square as shown in Photo. 3 (f).

Gurland⁽¹³⁾ reported that the grain size of WC in the sintered body increased with the amount of binder. In the present investigation, the grain sizes of TiC in the sintered bodies are almost identical except the composition of 10 % Ni. Since the grain growth is inhibited in the composition of low nickel contents because of the limited transfer of TiC by the discontinuity of a liquid phase, it may be valid only for a low binder content that the grain growth of TiC increases with the amount of binder. Whalen and Humenik⁽¹⁴⁾ reported that the spheroidization of TiC grains was brought about by oxygen. The identical conditions of sintering were maintained in this experiment, but the grain shape in the sintered bodies varied with the amount of the binder phase. The influence of oxygen is probably greater in the case of the sintering at 1350°C for 7 hr than the sintering at 1500°C for 1 hr, but more angular grains were observed in the sintering for 7 hr at 1350°C as seen in Photo. 3 (b) and Photo. 4. This fact shows that the grain shape of TiC was rather influenced by the transfer of TiC through the liquid phase. It was proposed that the coalescence process occurs following the solution-precipitation process⁽⁹⁾, but the occurrence of this process depends on the amount of the binder phase. The coalescence process tends to occur in the composition of a low binder content, because the TiC particles contact with each other in the compact. The rectangular or square grains observed in the compositions of 50 % and 75 % Ni are hardly formed by the coalescence process; therefore it may be said that those grains were formed by solution-precipitation process. The coalescence is an important process only for a composition low in the binder content.

V. Conclusions

(1) For the sintering of TiC-Ni cermets, the heating rate must be slowed down over the temperature range 1200~1350°C, in which the appearance of a liquid phase results in an abrupt shrinkage of a compact, while a relatively higher heating rate can be used up to about 1200°C.

(2) The sintered bodies of TiC-Ni cermets with reduced faults can be obtained for the compositions ranging 30~40 % Ni. The compacts of the compositions higher than 50 % Ni show large shrinkage and tend to deform during sintering.

(3) The behavior of grain growth during the solution-precipitation process varies with the composition; the shape of TiC grains changes from round to angular with the increase in the amount of a binder phase. The change in grain shape from round to angular in most of the carbide grains of TiC-Ni cermets

(13) J. Gurland: Trans. AIME, 200 (1954), 285.

(14) T. J. Whalen and M. Humenik, Jr.: Trans. AIME, 218 (1960), 401.

occurs in the composition higher than about 30 % Ni, corresponding to the formation of the continuous binder phase in the cermet.

(4) The coalescence process plays an important role

only in the compositions of low binder contents. In the case of a high binder content, the TiC grains grow by the solution-precipitation process.