Structure and Property of Binder-Phase of Sintered TiC-Ni Compact*

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In order to obtain a better understanding of the condition of the sintering of TiC-base cermets, the structure and property of the metal binder phase of 70 % TiC-30 % Ni compacts sintered at various temperatures were investigated by means of X-ray diffraction, thermomagnetic analysis and carbon analysis. In the sintering process, TiC begins to diffuse into the Ni-binder at about 800°C, its amount increased up to 1.5 wt % with the increase of the sintering temperature below the eutectic temperature and about 1 wt % of TiC remained in the binder phase of the compacts sintered above the eutectic temperature. As a result of the diffusion of TiC into Ni, free carbon was formed, and its amount increased up to 0.9 wt % in relation to the amount of TiC dissolved. Such free carbon was observed as graphite in the binder phase. This graphite phase is detrimental to the strength of the sintered compact, therefore it is necessary to avoid its formation. For the purpose of suppressing the graphite formation, the effect of Mo added was examined, and it was found that Mo is very suitable for this purpose.

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I. Introduction

TiC-base cermet is well known as a superior heat- and abrasive-resistant material. Also, a TiC-Ni-Mo sintered alloy has been developed recently as an excellent cutting tool⁽¹⁾. Many investigations on the fabrication of these cermets have revealed that the TiC-base cermet is more sensitive to various processing conditions than WC-base sintered compacts⁽²⁾. On the other hand, some fundamental properties have been studied on the wetting of TiC by Ni-base alloys⁽³⁾ and on the phase-diagram of the ternary system of Ti-Ni-C⁽⁴⁾. There remains, however, some problems to be clarified. One of these is the mechanism of the reaction between TiC and Ni powders during sintering. This is very important for the control of the heating or cooling rate. In the present study, changes in the structure and property of binder phase during sintering are investigated for TiC-Ni sintered alloy by means of X-ray diffraction, thermomagnetic analysis and chemical analysis of carbon.

II. Experimental Procedures

Commercial powders of TiC and Ni were used for this experiment, chemical analyses of which are shown in Table 1. The powders were used without any pretreatment. Sintered TiC-Ni compacts were prepared by the following procedures; A mixture of 70 % TiC-30 % Ni (in weight) was ball-milled in acetone for 72 hr. After milling, the mixture was heated to evaporate the

acetone, and the powders were compacted into a rectangular test block, 10 × 30 × 5 mm, at 1 t/cm². The green compact was sintered in a hydrogen tube furnace for 1 hr over the temperature range of 600~1400°C at which the compact was mounted on a

Table 1 Chemical analysis and particle size of TiC and Ni powder used in the present experiments.

TiC powder	
Total carbon	19.3 %
Free carbon	< 0.2 %
Combined carbon	19.1 %
Fe	0.3 %
Co	0.3 %
av. particle size	5.1 μ
Ni powder	
Ni	99.1 %
Co	0.8 %
Fe	0.035 %
Cu	0.013 %
Pb	0.008 %
Si	0.003 %
av. particle size	- 325 mesh

sintered plate of MgO in a graphite boat. The sintered compact was cooled in the furnace at a rate of about 10°C/min from the sintering temperature to 1000°C, and the compact was brought into a cooler attached to the one end of the furnace (at 1000°C) together with the graphite boat. In the case of sintering at temperatures below 1000°C, the compact was brought into the cooler immediately after sintering.

After determining the chemical composition of the compacts by the X-ray diffraction method, the lattice constant and Curie temperature of the binder phase in each specimen were measured to examine the effect of the sintering temperature on the structure and properties of the binder phase. In the description of these data, it is necessary to refer to the relationships

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- (1) M. Humenik : Amer. Machinist, March, 23 (1959), 125 ; The Iron Age, March 19 (1959), 101.
- (2) P. Schwarzkopf and R. Kieffer: Refractory Hard Metals, Mac Millan Co., New York, (1953), 369 ; M. Sugiyama and H. Suzuki : J. Japan Inst. Metals, 24 (1960), 618, 622, 689, 740 ; 25 (1961), 1, 4, 8, 167, 321.
- (3) W. D. Kingery : J. Amer. Ceram. Soc., 36 (1953), 362 ; G. Economos and W. D. Kingery : J. Amer. Ceram. Soc., 36 (1953), 403 ; M. Humenik and W. D. Kingery : J. Amer. Ceram. Soc., 37 (1954), 18.
- (4) E. R. Stover and J. Wulff : Trans. AIME, 215 (1959), 127.

between the lattice constant or Curie temperature and the TiC content of Ni-solid solution. In this regard, Stover and Wulff⁽⁴⁾ reported that the lattice constant of the Ni-solid solution increased at a rate of about 0.011 Å/wt % TiC and the Curie temperature decreased with the increasing amount of TiC by about 70°C/wt % TiC. In the present experiment these relationships were also examined with Ni-solid solution prepared from the same powders of TiC and Ni as that of the sintered compact. The solid solution was prepared as follows; Ni and TiC powders were mixed in an agate-mortar. The mixture was pressed into a compact and melted in hydrogen in an alumina crucible. The ingot was slowly cooled down to 1280°C and then quenched rapidly in water. Test pieces were slit from the ingots, annealed in argon atmosphere at 1200°C for 8 hr, and then quenched in water. Since complete homogenization was confirmed in the specimens containing less than 3 wt % TiC, the lattice constant and Curie temperature were determined as a function of the composition by means of metallographic observation and X-ray diffraction analysis.

As an additional test for analyzing the mechanism of reaction between TiC and Ni powders during the sintering process, the free carbon content in the sintered compacts was determined by a combustion analysis.

The Curie temperature was measured in argon atmosphere at the field strength of 4500 Oe by a quartz-spring type thermomagnetic balance. For the X-ray technique, a conventional X-ray diffractometer with CuK α radiation was used. Moreover, metallographic observation was made on a specimen polished by diamond powder and etched by 10 % alkaline potassium ferricyanide solution.

III. Experimental Results and Discussion

1. Properties of Nickel solid solution containing TiC

In order to obtain a better understanding of the structure and properties of the metal binder phase of sintered TiC-Ni compact, the lattice constant and Curie temperature of the Ni-solid solution were measured. As shown in Fig. 1, the results indicated a linear increase in lattice constant with the increasing amount of TiC at a rate of 0.007 Å/wt % TiC and a linear decrease in Curie temperature at a rate of 50°C/wt % TiC. In Fig. 1 comparative data are also plotted for Ni-solid solution containing Ti.⁽⁵⁾⁽⁶⁾ In comparing the Ni-TiC and Ni-Ti systems, the changes in lattice constant are almost identical, but in detail the slope of the curve for the Ni-TiC system is slightly steeper than that for the Ni-Ti system⁽⁵⁾ and the Curie temperature curve for the Ni-TiC system shows a slight deviation towards the upper side than that for the Ni-Ti system⁽⁶⁾.

With regard to such properties of the Ni-TiC system, Stover et al.⁽⁴⁾ have reported, a larger rate of

increase in lattice constant and a lower rate of decrease in Curie temperature than those in the present experiment. In the present investigation, the Curie temperature was determined by extrapolating the thermomagnetic curve to the temperature-axis where

Fig. 1 Curie temperature and lattice constant of Ni-solid solution containing TiC.

the saturation-intensity of magnetization becomes zero. However, since Stover et al. did not describe it in detail, the difference between the two methods could not be discussed. For this investigation the relationships shown in Fig. 1 were used as the fundamental data for the Ni-TiC solid solution.

2. Changes in the structure and properties of the metal binder phase during sintering

(1) Lattice constant

The 70 % TiC-30 % Ni compacts sintered at various temperatures were examined by X-ray diffraction, and all the compacts before sintering were confirmed to consist of only the two phases, TiC and Ni, with no intermetallic compounds of the Ni-Ti system. Then the lattice constant and the Curie temperature of these specimens were measured. The results obtained are plotted against the sintering temperature. As shown

Fig. 2 Changes in lattice constant and Curie temperature of 70 % TiC - 30 % Ni compacts sintered at various temperatures for 1 hr in H₂.

(5) W. B. Pearson: A Handbook of Lattice Spacings and Structures of Metals and Alloys, Pergamon Press, London, (1958), 791.

(6) R. M. Bozorth: Ferromagnetism, D. Van Nostrand Co., New York, (1951), 305, 325, 440.

in Fig. 2, little changes are observed in the lattice constant of the TiC-phase, but in the Ni-phase a slight increase of the lattice constant begins to appear in the specimens sintered at 700°C, a gradual increase of the Ni lattice is seen with the increasing sintering temperature up to 1270°C, followed by a marked increase above 1270°C as shown in Fig. 2.

(2) Curie temperature

Thermomagnetic curves of the specimens are illustrated in Fig. 3. As the curve of the specimen sintered at 600°C for 1 hr is similar to that of the "as pressed", the Ni-binder phase is considered to be in a state of

Fig. 3 Thermomagnetic curves of 70 % TiC-30 % Ni compacts sintered at various temperatures for 1 hr in H_2 .

pure nickel. But for the specimen sintered at 700°C the Curie temperature is nearly the same as pure nickel, while the curve assumes a slight inward deviation. With further increase in the sintering temperature, there appears a decrease in the Curie temperature as well. However, it is observed that the deviation of the curve is reverted by sintering above 1270°C. Curie temperatures obtained from these curves are plotted as a function of the sintering temperatures in Fig. 2 in which a discontinuous change as in the lattice constant is also observed at 1270°C. A similar result has been observed in the WC-Co system.⁽⁷⁾ This is probably due to the fact that a liquid phase is formed by a eutectic reaction between TiC- and Ni-phases at this temperature, as evidenced by a complete microstructural densification of the compacts by sintering at a temperature above 1270°C. The eutectic temperature of the TiC-Ni system has been hitherto reported to be at 1270°C⁽⁴⁾ or 1280°C⁽⁸⁾. Therefore, it can be said that the densification of TiC-Ni compact is caused by the diffusion between the solid particles in the sintering process below 1270°C and by the wetting of TiC particles with the liquid phase formed by the eutectic reaction above 1270°C.

During the process of diffusion-sintering, the increase in lattice constant and the reduction in Curie temperature of the binder-phase were found to appear in the specimen sintered at 800°C. This indicates the

diffusion of TiC into the Ni binder phase at this temperature and the increases in solubility with the increasing temperature. On the other hand, in the sintering process with the liquid phase, the solubility of TiC in the Ni phase may be considered to attain a saturated value at the sintering temperature, whereas the Curie temperature of the specimen was higher than that of the specimen sintered at 1200°C at which diffusion-sintering took place. This can be explained as follows: TiC is precipitated from the Ni phase during cooling from the sintering temperature, but the precipitation can not occur easily in the compact sintered during the diffusion-sintering because of the poor condition in contact between particles.

Due to the changes in the lattice constant or Curie temperature as shown in Fig. 2, the solid solubility of TiC in the Ni phase increases with increase in the sintering temperature of the compacts sintered below 1270°C and the results of both curves coincide with each other. In the compacts sintered above 1270°C, however, the solubility decreases discontinuously in the light of the Curie temperature, but it increases in the light of the lattice constant. This disagreement may be caused by an abnormal expansion of the Ni-lattice due to the difference in the thermal expansion coefficient between TiC and Ni.⁽⁹⁾ Therefore, the result deduced from the Curie temperature is more likely to hold the true situation. This experimental confirmation will be made later.

(3) Analysis of free carbon

Free carbon contents of the TiC-Ni compacts are shown in Fig. 4 as a function of the sintering temperature. It seems to increase at elevated temperatures.

Fig. 4 Changes in the free carbon content during the sintering of 70 % TiC - 30 % Ni compact for 1 hr in H_2 .

For example, the free carbon content in the compact sintered at 1200°C is about 0.9 wt % which has the lowest Curie temperature of all compacts and the maximum amount of TiC dissolved in the Ni phase. In the compact sintered at 1300°C, 0.7 wt % free carbon is observed. Since the amount of free carbon contained in the compact before sintering was about 0.2 wt %, the increase in free carbon could be estimated 0.7 wt % by heating up to 1200°C or 0.5 wt % up to 1300°C. As a result of the formation of free carbon, the graphite

(7) T. Fukatsu: J. Japan Soc. Powder Met., 8 (1961), 183.

(8) V. N. Eremenko: Z. Neorgan. Khim., 1 (1956), 2131; Ceram. Abst., (1957), 148.

(9) H. W. Newkirk and H. H. Sisler: J. Amer. Ceram. Soc., 41 (1958), 93.

phase was precipitated in the binder phase. As an example of such a sintered compact, a microstructure of the 70 % TiC-30 % Ni sintered at 1400°C for 1 hr is presented in Photo. 1. The precipitation of the graphite-phase may be caused by dissociation of TiC during the sintering. However, free Ti was not found

($\times 1500$)

Photo. 1 Microstructure of 70 % TiC-30 % Ni compact sintered at 1400°C for 1 hr, angular gray grains are titanium carbide phase, narrow white zones are binder nickel layer and dark patches are graphite.

by the X-ray diffraction analysis. It may be said that part of the carbon content in TiC remains when TiC diffuses into the Ni phase, and as a consequence, the Ni-binder phase can be inferred to become a solid solution state dissolving more Ti than carbon. The free carbon did not disappear even if the compact was sintered above the eutectic temperature. However, the free carbon is detrimental to the strength of sintered compact, so that it must be eliminated.

3. Effect of addition of molybdenum

Methods for the elimination of the free carbon in the stage of diffusion-sintering and protection of TiC against the liquid in the stage of liquid phase-sintering were examined. In this regard, the effect of addition of Mo was investigated. A 70 % TiC-20 % Ni-10 % Mo compact was prepared and sintered under the same condition as that of the 70 % TiC-30 % Ni compact. As shown in Photo. 2, there appears a graphite-phase hardly observable microstructurally. This effect of addition of Mo may also be explained in the following way: Mo₂C formed in the stage of diffusion-sintering is combined with TiC as a solid solution on the surface of the TiC particle at a higher temperature, whereby TiC particle would be protected against the liquid phase.⁽¹⁰⁾

Humenik et al.⁽¹¹⁾ has made a study of the effect of addition of Mo. According to them, the contact angle between binder-metal and TiC did not become zero when only Ni was used as a binder, but with the addition of 10 wt % Mo to the Ni-binder, the contact angle became zero. The addition of molybdenum would

not only improve the wettability which is indispensable for the sintering process, but also play an important role in suppressing the formation of free carbon.

4. Structure of the binder phase

The amount of TiC dissolved in the Ni-binder phase

($\times 1500$)

Photo. 2 Microstructures of 70 % TiC-20 % Ni-10 % Mo compact sintered under the same condition as the specimen of Photo. 1.

of the sintered compact can be estimated from the Curie temperature or the lattice-constant of Ni-TiC solid solution in the compact. The result obtained are plotted in Fig. 5 in which the notation of $\odot$ and $\times$ represents the data of the Curie temperature and X-ray

Fig. 5 Amounts of TiC dissolved in Ni-binder phase.

analysis, respectively. In these curves, it is found that the amount of TiC in the Ni phase determined from the Curie temperature is smaller by about 0.5 % than that from the lattice constant. This difference is probably due to the following two reasons: First, since the amount of free carbon in the compact increased during sintering as already noted, Ni did not dissolve Ti and C in equal amounts corresponding to the stoichiometric composition of TiC but a larger amount of Ti than C. For this reason, strictly speaking, it is not accurate to estimate the amount of TiC from the relationship shown in Fig. 1, and therefore the results shown in Fig. 5 are regarded as approximate values. Secondly, since the thermomagnetic curves in Fig. 3 deviate towards the lower side of the normal curve for a homogeneous ferromagnetic substance except the curve as pressed, the concentration of TiC in the Ni-binder is not homogeneous. For the two reasons

(10) T. Fukatsu: To be published.

(11) M. Humenik and N. Parikh: J. Amer. Ceram. Soc., 39 (1956), 60.

mentioned above, a lower estimation was made for the amount of TiC from the Curie temperature. On the other hand, according to a study of the phase diagram of Ti-Ni-C by Stover et al. the solubility of Ti and C in the solid Ni phase is reported to be 3.2 at % Ti and 1.2 at % C at 1000°C, 3.4 at % Ti and 2.2 at % C at 1200°C and 3.3 at % Ti and 2.7 at % C at 1260°C. In view of the above values much larger than those in the present experiment, the diffusion of TiC into the Ni phase does not probably reach an equilibrium state.

The exact estimation of solubility of TiC in Ni remains a debatable question. However, from these results it seems that TiC diffuses into the Ni-binder phase during sintering below the eutectic temperature of TiC-Ni, and free carbon is formed in relation to this diffusion. In practice the rate of heating up to the eutectic temperature must be controlled strictly.

IV. Summary

In order to study the structure and properties of the metal binder phase of sintered TiC-Ni compact, Ni-solid solution containing 0~3.0 wt % TiC were made, the lattice-constant and Curie temperature of which were measured as a function of the amount of TiC dissolved in the solid Ni phase. Based on these data, the binder phase of TiC-Ni compacts sintered at various temperatures were investigated by means of X-ray diffraction and thermomagnetic analyses as well as chemical analysis of free carbon. The results

obtained may be summarized as follows:

(1) The lattice constant of Ni-TiC solid solution increases linearly at a rate of about 0.007 Å/wt % TiC and the Curie temperature decreases at a rate of about 55°C/wt % TiC with the increasing amount of TiC in the solid Ni phase, respectively.

(2) In the sintering process, TiC begins to diffuse into Ni-binder at about 800°C its amount increases with increase of the sintering temperature up to the eutectic temperature. For example, the amount of TiC in the Ni phase of the compact sintered at 1200°C for 1 hr was 1.5 wt %. But it did not increase more than 1 wt % when the compacts were sintered above the eutectic temperature, 1270°C.

(3) As a result of the diffusion of TiC into the Ni phase, free carbon was formed. The amount seems to increase as the amount of TiC dissolved increases. For example, the maximum amount of free carbon was evaluated to be about 0.7 wt % in the specimen sintered at 1200°C for 1 hr where the lowest Curie temperature was observed. But the amount of free carbon was evaluated 0.5 wt % in the specimens sintered above the eutectic temperature.

(4) Such free carbon formed appears in the binder phase of the TiC-Ni compact as a graphite phase, but it can be eliminated by the addition of molybdenum.

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