研究

A Consideration on TiC-Core/(Ti,Mo)C-Rim Structure of TiC-Mo₂C-Ni Cermet in Relation to Hypothesis "Exhaustion of Diffusion-Contributable Atomic Vacancies in Core/Rim Structure"Yutaka Yanaba^{★1}, Toshiyuki Takahashi^{★2} and Koji Hayashi^{★1}^{★1}Institute of Industrial Science, The University of Tokyo, 4-6-1 Komaba, Meguro-ku, Tokyo-to 153-8505, Japan.^{★2}Tungaloy Corp., 114 Kamijo-Higashiwari, Ohkusa-cho, Nirasaki 407-0036, Japan.

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SYNOPSIS

TiC-core/(Ti,Mo)C-rim structure in TiC-Mo₂C-Ni cermet where the equilibrium phase of carbide is only (Ti,Mo)C is known to be not generated by solid-diffusion process, but by solution-reprecipitation process in the case of usual sintering temperatures (1528~1723 K). On the other hand, in our recent study on the microstructure of Fe-66.7at%Si peritectoid alloy where the equilibrium phase is FeSi₂, it was found that FeSi-core in FeSi-core/FeSi₂-rim structure hardly disappeared by solid-diffusion process in the compact inside, but relatively easily disappeared and/or shrunk near the compact surface to the depth of FeSi-core size (about 15 μm) by heating at high temperature. The phenomenon in the compact inside could be explained by our newly proposed hypothesis "Exhaustion of diffusion-contributable atomic vacancies in core/rim structure".

In this study, it was investigated in relation to the above hypothesis whether TiC-core in the compact inside disappears or not due to solid-diffusion process by heating at 2073~2473 K which are extremely higher than the usual sintering temperature. As the result, it was judged that TiC-core in the compact inside really disappeared by solid-diffusion process at 2273~2473 K, differing from FeSi-core in the compact inside. Based on these results on Fe-66.7at%Si alloy and the cermet, it was generally concluded that our new hypothesis can be applied to the alloy where the rim phase is a stoichiometric compound unable to dissolve the core elements and also the diffusion from the core to the rim is not thermodynamically allowed like in Fe-66.7at%Si alloy, but not to the alloy where the rim is a solid solution able to dissolve the core elements and thus the diffusion from the core to the rim is thermodynamically allowed like in the cermet.

KEY WORDS

diffusion, core/rim structure, exhaustion, vacancy, cermet

1 Introduction

1.1 Background

TiC-Mo₂C-Ni cermet is the base for various kinds of the present commercial cermets which generally contain also N, Co, WC, TaC, etc., and are used as cutting tool materials particularly in Japan. The carbide grains in TiC-Mo₂C-Ni cermet has a specific microstructure due to Mo₂C addition which is for both sintering densification of compact and carbide grain growth inhibition. Namely, the carbide grains which are dispersed in Ni binder phase have a duplex structure, i.e., core/rim structure: TiC grain (core) is surrounded by (Ti,Mo)C solid solution phase (rim or surrounding structure¹⁾), although the equilibrium phase of the carbide is only (Ti,Mo)C solid solution¹⁾.

TiC-core which has a high hardness of Hv 3200 compared with Hv 1500 of Mo₂C²⁾ is generally believed to strongly contribute to the performance of high precision surface finishing in the cutting of steels. Thus, the existence of

TiC-core as well as the mean carbide grain size, etc., are thought to be very essential for the mechanical performance of the cermet tools.

In our previous study¹⁾ on the generation of TiC-core/(Ti,Mo)C-rim structure in TiC-Mo₂C-Ni cermet sintered at 1528~1723 K {the ratios to the melting point of TiC (3523 K²⁾), $T_m(\text{TiC})$, are 0.43~0.49}, we clarified by taking into consideration both the microstructure and Mo concentration profile in both TiC-core and (Ti,Mo)C-rim that the structure is generated not by the previously proposed "solid-diffusion" process^{3,4)}, but by our newly proposed "solution-reprecipitation" process: (1) mainly smaller TiC particles and Mo₂C particles firstly dissolve into Ni liquid phase, (2) these Ti, Mo and C solutes diffuse in Ni liquid phase to larger TiC particles, (3) these solutes react with each other and then precipitate in the form of (Ti,Mo)C solid solution onto the larger TiC particles and thus TiC-core/(Ti,Mo)C-rim structure is generated on each TiC grain,

(4) after the disappearance of Mo₂C particles, the width of (Ti,Mo)C-rim further increases due to Ostwald ripening, i.e., grain growth by solution-reprecipitation process, and (5) the width of the rim increases by a slight amount due to the precipitation of the solutes during the cooling stage of the sintering process.

Furthermore, it was noted that the shrinkage of TiC-core due to solid-diffusion process hardly occurred by heating for 7.2 ks even at 2173 K³⁾ {the ratio to $T_{m(TiC)}$ is 0.62} which is extremely higher than usual sintering temperature, although the equilibrium carbide phase is only (Ti,Mo)C solid solution¹⁾ and also TiC-core sizes are small, i.e., the width was generally 1~2 μm , and the length was generally 2~4 μm and rarely 10 μm .

1.2 Our new hypothesis for non-disappearance of core in FeSi-core/FeSi₂-rim structure

On the other hand, in our recent studies^{6,7)} on Mn-doped FeSi₂ stoichiometric compound which is said to be a promising thermoelectric material (p-type semiconductor) useful at high temperatures below 1130 K in air⁸⁾, we noticed that a core/rim structure is also generated similarly to the above TiC-core/(Ti,Mo)C-rim structure in the cermet. Fe-Si binary equilibrium phase diagram⁹⁾ indicates that FeSi₂ is generated by the following three reactions: (1) the peritectoid reaction of FeSi (core: cubic structure) + Fe₂Si₅ (matrix: tetragonal structure) $\rightarrow$ 3FeSi₂ (rim: orthorhombic structure) below 1259 K, (2) the eutectoid reaction of Fe₂Si₅ (matrix) $\rightarrow$ 2FeSi₂ (rim and matrix) + Si (matrix) below 1228 K, or (3) the peritectoid reaction of FeSi (core) + Si (matrix) $\rightarrow$ FeSi₂ (rim) below 1228 K, where Si is one of the product of the eutectoid reaction.

However, even at the composition of FeSi₂ (Fe-66.7 at% Si), the shrinkage as well as disappearance of FeSi-core whose average size was about 15 μm hardly occurred in the compact inside by heating for a long time of 720 ks at 1123 K. Here, the ratio of 1123 K to the decomposition temperature (1255 K) of FeSi₂ compound and to the melting temperature (1485 K) of Fe-66.7 at% Si alloy are 0.89 and 0.76, respectively, and the above eutectoid reaction of Fe₂Si₅ $\rightarrow$ 2FeSi₂ + Si takes place most rapidly at about this 1123 K⁹⁾. Additionally, FeSi₂-rim with the average thickness of about 5 μm is generally observed in a partial or whole periphery of FeSi grain in the microstructure of Fe-66.7 at% Si alloy. However, such FeSi₂-rim is not one generated by the above peritectoid reaction, but by the preferential precipitation of FeSi₂ product of the above eutectoid reaction^{6,7)}.

Generally speaking, peritectoid reactions are known to be extremely slow. The opinions which had been previously proposed on the cause or mechanism are the following^{10,11)}.

- (1) The thickness of the rim, i.e., the diffusion distance of reaction atoms, increases with proceeding reaction and thus the heating time (t) needed for the diffusion or reaction of a definite amount increases proportionally to the square of the thickness (x), because x is proportional to the square root of Dt (D : diffusion coefficient)¹⁰⁾.
- (2) The rate of diffusion in solid is extremely slow, compared with the rate of diffusion in liquid¹¹⁾.

However, these two opinions, particularly the latter, are thought not to be logical.

In contrast to the above conventional opinions, we have proposed the following new hypothesis "Exhaustion of diffusion-contributable atomic vacancies in core/rim structure" in the study^{6,7)} on Fe-66.7 at% Si alloy. In the proposal, the diffusion of atoms in the reaction process is supposed to be of course vacancy-assisted: the diffusion of atom takes place by exchanging the lattice site of V_c . The essence of the hypothesis which is necessary for understanding the objective of this study is as follows.

- (1) When Si atoms in the matrix, i.e., Fe₂Si₅ or FeSi₂ + Si, diffuse by solid-diffusion process via FeSi₂-rim to FeSi-core/FeSi₂-rim closed interface, i.e., the site of the reaction of FeSi + Si $\rightarrow$ FeSi₂, so that the system approaches to the equilibrium state (the phase of the alloy becomes only FeSi₂), diffusion-contributable atomic vacancies (V_c) in FeSi-core as well as FeSi₂-rim have to diffuse out in the counter-wise direction to the matrix {refer to later Fig. 11 (a)}.
- (2) After a some amount of Si diffused to the core, vacancy sources such as dislocation and grain boundary¹⁰⁾ in the core/rim structure disappear due to the dislocation climbing and grain boundary migration. Then, V_c are exhausted in FeSi-core and also in FeSi₂-rim, keeping the equilibrium concentration of vacancies.

Additionally, the following two items would be mentioned so that the concept of "the exhaustion of V_c " can be comprehended.

- (i) The equilibrium atomic vacancies are of course generated by thermal activation process. The generation, however, is believed to be extremely hard in a perfect crystal, but occurs from lattice imperfections such as dislocations, grain boundaries, etc.¹⁰⁾
- (ii) Furthermore, V_c thermodynamically hardly be supplied from the matrix of Fe₂Si₅ or FeSi₂ + Si to the FeSi-core. Because, the free energy of the alloy system increases by the following process, if V_c are supplied in such direction. Namely, such supply of V_c needs the diffusing out of Fe or Si atoms in FeSi-core to the matrix via FeSi₂-rim, i.e., the reaction of 2FeSi $\rightarrow$ FeSi₂ + Fe or FeSi $\rightarrow$ Fe + Si need to occur

under the co-existence of FeSi_2 (rim and matrix) and Si (matrix). Such reactions, however, are considered to be thermodynamically impossible at the chemical composition of Fe-66.7 at% Si alloy, based on Fe-Si binary equilibrium diagram showing that the phases changes as follows with increasing Si content near the composition of Fe-66.7 at% Si: $\text{Fe} + \text{FeSi} \rightarrow \text{FeSi} \rightarrow \text{FeSi} + \text{FeSi}_2 \rightarrow \text{FeSi}_2 \rightarrow \text{FeSi}_2 + \text{Si}$ at 1123 K.

- (3) Therefore, the peritectoid reaction of $\text{FeSi}(\text{core}) + \text{Fe}_2\text{Si}_5$ or Si (matrix) $\rightarrow 3\text{FeSi}_2$ or $\text{FeSi}_2(\text{rim})$ nearly stop after the disappearance of such lattice imperfections, i.e., the exhaustion of V_c , resulting in almost non-shrinkage or non-disappearance of FeSi-core.

Furthermore, we have already verified the hypothesis by experimentally clarifying that the reaction occurred, i.e., FeSi-core phase and Fe_2Si_5 matrix phase or Si in $\text{FeSi}_2 + \text{Si}$ matrix phases completely disappeared and thus the phase became all FeSi_2 in the compact surface layer⁷⁾. This was considered to be because V_c are continuously supplied from the compact surface to FeSi-core and thus the diffusion of Si in the matrix toward FeSi-core can occur, differing from in the compact inside⁷⁾. The depths of such compact surface layers where complete and partial disappearance of FeSi-core occurred were about $8\text{ }\mu\text{m}$ and $15\text{ }\mu\text{m}$, respectively in the case of the above heating of 1123 K - 720 ks⁷⁾. The latter $15\text{ }\mu\text{m}$ is nearly equal to FeSi-core average size, indicating that V_c are supplied from the compact surface to FeSi-core initially contacting the compact surface. Such large thickness also indicates that the diffusion mechanism contributing to the shrinkage and/or disappearance of FeSi-core is not surface-diffusion, but surely bulk-diffusion.

1.3 Objectives

Taking into consideration the above study on Fe-66.7 at% Si alloy, the above described phenomenon that TiC-core in TiC-core/(Ti,Mo)C-rim structure (the crystal structures are both NaCl-type) of the cermet did not shrink and/or disappear by heating at a high temperature such as 2173 K³⁾ was anticipated in the first stage to be also explained by the above our new hypothesis, although there is the following difference in the process of approaching to the equilibrium state between these two kinds of structures. Namely, the elements taking a part in the process besides the core elements are those in the matrix for FeSi-core/ FeSi_2 -rim structure, and those in the rim for TiC-core/(Ti,Mo)C-rim structure.

In this study, we investigated whether TiC-core disappears or not due to solid-diffusion process by heating for longer time of 14.4 ks at lower and higher temperatures of 2073~2473 K (the ratios of these temperatures to $T_{\text{m(TiC)}}$

are 0.59~0.70) than those in the previous study⁵⁾. As the result, it was judged by surmounting two complicated problems caused by Ostwald ripening that almost all TiC-core really disappeared by solid-diffusion process, differing from below 2073 or 2173 K and also differing from FeSi-core in FeSi-core/ FeSi_2 -rim structure.

This paper reports the details of the above judgement process and also the generalization of our new hypothesis "Exhaustion of diffusion-contributable atomic vacancies in core/rim structure". Additionally, no diffusion data on the diffusion couples of TiC/(Ti,Mo)C, FeSi/ Fe_2Si_5 and FeSi/Si, etc., have been reported.

2 Consideration process, specimen preparation and experimental procedures

2.1 Consideration process

The solving of the above problem whether a TiC-core in each carbide grain shrinks or disappears by bulk solid-diffusion process was made difficult by the following two phenomena which are supposed to arise when a considerable amount of Ostwald ripening occurs by heating at high temperatures.

- (1) Decrease in appearance probability of TiC-core in each carbide grain

Even if the initial size of TiC-cores is kept at the original value, the appearance probability of TiC-core in each carbide grain on an observation plane considerably decreases, accompanying Ostwald ripening, i.e., rim growth. Because the appearance probability of TiC-core is numerically expressed by the ratio of TiC-core size to the carbide grain size, i.e., the outer diameter of (Ti,Mo)C-rim, which increases by Ostwald ripening, as schematically illustrated in Fig. 1 (a). In the figure, the probability decreases from 100% (2/2) to 0% (0/1).

- (2) Decrease in the number density of TiC-core on an observation plane

Almost all TiC-core disappears by the occurrence of a considerable amount of Ostwald ripening, even when solid-diffusion between TiC-core and (Ti,Mo)C-rim does not occur. Namely, when a considerable amount of Ostwald ripening occurs, smaller grains continuously dissolve into Ni liquid phase and finally disappear together with TiC-core in them. This results in the decreasing of the number density of TiC-core together with the above decrease in the appearance probability of TiC-core in each carbide grain, as schematically illustrated in Fig. 1 (b). In the figure, the number of TiC-core observed in an observation plane of the same area decreases from 59 to 2.

Fig.1 (a) (b) Schematic drawings for explaining two phenomena which complicate the solving of the problem whether TiC-core in TiC-core/(Ti,Mo)C-rim structure in TiC-Mo₂C-Ni cermet disappear or not due to solid-diffusion process. (a) The appearance probability of TiC-core in a carbide grain on observation plane considerably decreases, and (b) the number density of TiC-core on an observation plane decreases, both due to Ostwald ripening, even if TiC-cores do not disappear due to solid-diffusion process between core and rim. In the figure (a), the orientation of TiC-core axes are equalized and the places of all TiC-cores and carbide grains are set on the same plane so that the concept can be easily understood.

Thus, the two phenomena that TiC-core became not to be observed in carbide grain and the number density of TiC-core in an observation plane decreased do not necessarily mean that TiC-core really shrunk or disappeared due to solid-diffusion process. Taking into consideration these two difficulties, we solved the problem by the following procedure based on the probability.

- (1) The heating temperature (T_{active}) at which the solid-diffusions of Ti and Mo become active in the diffusion-couple of TiC-sintered compact and (Ti,Mo)C-sintered compact, i.e., TiC/(Ti,Mo)C diffusion-couple, was firstly investigated. This is because a lot of vacancy source such as dislocation, grain boundary and also pores exist in these two compacts and thus V_c are easily supplied to the bonded-interface of the diffusion-couple, i.e., the reaction site. Namely, the mechanism indicated by our new hypothesis does not operate in this diffusion-couple.
- (2) In TiC-Mo₂C-Ni cermet specimens heated at the above

T_{active} , the experimental appearance probability (P_{exp}) of TiC-core in carbide grains on an observation plane was secondly measured. Namely, the ratio of the number of carbide grains where a TiC-core was observed to the total number of carbide grains was calculated.

- (3) The hypothetical appearance probability (P_{hyp}) of TiC-core in carbide grains on an observation plane, i.e., the probability obtained under an assumption that the solid-diffusion does not occur between TiC-core and (Ti,Mo)C-rim regardless of the real phenomenon and thus the initial maximum TiC-core size is kept at the original value was thirdly calculated. The P_{hyp} for the specimen heated above T_{active} was obtained by dividing the following largest TiC-core size with the average carbide grain size in the specimens heated at T_{active} . As the largest TiC-core size, the largest one among all TiC-core sizes in the cermet which was heated at the highest temperature (T_{highest}) where the diffusion was hardly observed in the diffusion-couple was selected. T_{highest} is of course lower than the above T_{active} . This selection was done, because the largest TiC-core does not shrink at T_{highest} , while smaller TiC-cores disappear by Ostwald ripening. On the other hand, P_{hyp} for the specimen below T_{active} can logically be said to be the same as P_{exp} , because TiC-core does not shrink and/or disappear by solid-diffusion process.

- (4) The judgement on the problem whether TiC-core shrunk or disappeared not by Ostwald ripening, but by solid-diffusion process at temperatures above T_{active} was done by comparing P_{exp} with P_{hyp} . Namely,
 - (i) If P_{exp} is smaller than P_{hyp} → TiC-core shrunk or disappeared by solid-diffusion process.
 - (ii) If P_{exp} is equal to P_{hyp} → TiC-core did not shrink or disappear by solid-diffusion process.

2.2 Specimen preparation

TiC/(Ti,Mo)C diffusion-couple and TiC-Mo₂C-Ni cermet were prepared as follows by using commercial powders of TiC (average particle size: about 1.5 μm , carbon content: 19.43 mass%), Mo₂C (2.6 μm , 5.7 mass%) and Ni (4.5 μm). The SEM microstructures of these powders are shown in Fig. 2 for the reference.

2.2.1 Preparation of TiC/(Ti,Mo)C diffusion-couple

TiC and (Ti,Mo)C sintered compacts were firstly prepared, and then they were sinter-bonded to get their diffusion-couple as follows.

TiC powder compact was hot-pressed under 20 MPa at 2073 K for 3.6 ks in vacuum of 7 Pa by using graphite die and punch. TiC hot-pressed compacts were further heated at 2273 K for 14.4 ks in vacuum in order to reduce the

Fig.2 SEM microstructures of TiC, Mo₂C and Ni starting powders ($\times 5000 \times 0.8$).

porosity and to progress the grain growth.

For the preparation of (Ti,Mo)C sintered compact, TiC and Mo₂C powders were compounded at the weight ratio of TiC : Mo₂C = 3 : 1, i.e., TiC-25 mass% Mo₂C (TiC-6.4 mol% Mo₂C) which was the same as that in the used cermet, i.e., TiC-20 mass% Mo₂C-20 mass% Ni cermet. At this composition, the equilibrium phase of carbide is (Ti,Mo)C solid solution²⁾. The atomic ratio of Ti+Mo to C was 1:0.91. The compounded powder was mixed by wet ball-milling for 230.4 ks in hexane dispersant. For the ball milling, a pot which is internally coated with polyurethane and balls which are made from TiC-Mo₂C-Ni cermet were used in order to prevent the contamination during ball milling as little as possible. The mixed powder was hot-pressed under 20 MPa for 14.4 ks at 2073 K in vacuum. (Ti,Mo)C sintered compacts were further heated for 14.4 ks at 2273 K in vacuum in the same way as TiC sintered compacts.

The sizes of TiC and (Ti,Mo)C hot-pressed compacts were both about $32 \times 32 \times 5 \text{ mm}^3$. Pieces with the size of $10 \times 10 \times 3 \text{ mm}^3$ were cut and ground off from those two kinds of compacts. The piece surfaces of $10 \times 10 \text{ mm}^2$ for the sinter-bonding were mirror-finished by polishing with diamond paste after grinding with diamond wheel. Their diffusion-couples were prepared by sinter-bonding with each other under 20 MPa in vacuum for 3.6 ks at a low temperature of 1573 K in order to suppress the diffusion as little as possible during the bonding.

Additionally, in our study of FeSi-core/FeSi₂-rim structure⁷⁾, FeSi/Fe₂Si₅ diffusion-couple could not be prepared, differing from TiC/(Ti,Mo) diffusion-couple. Because, FeSi/Fe₂Si₅ and FeSi/Si couples were both fractured mainly along the bonded-interface of diffusion-couple during the cooling stage of the diffusion bonding process, due to the thermal stress caused by the difference in their thermal expansion coefficients.

2.2.2 Preparation of TiC-20 mass% Mo₂C-20 mass% Ni cermet

The above three kinds of powders were compounded at the weight ratio of TiC : Mo₂C : Ni = 3 : 1 : 1, i.e., TiC-20 mass% Mo₂C-20 mass% Ni. The compounded powder was mixed by wet ball-milling for 144 ks with the same dispersant, pot and balls as in the mixing process of TiC and Mo₂C powder. The dried mixed powder was compacted by uni-axial die-pressing under 118 MPa, and pressureless-sintered at 1723 K for 3.0 ks in vacuum of about 1 Pa. The size of sintered compacts were about $5 \times 12 \times 30 \text{ mm}^3$.

2.3 Experimental procedures

The above two kinds of specimens, i.e., TiC/(Ti,Mo)C diffusion-couple and TiC-20 mass% Mo₂C-20 mass% Ni cermet were heated at 2073, 2273 and 2473 K {the ratios to $T_{m(\text{TiC})}$: 0.59, 0.65 and 0.70, respectively} for 14.4 ks. The heating atmospheres of both specimens were vacuum for the temperature of 2073 K in the same way as that in the sinter-bonding and the sintering. However, Ar of about 0.1 MPa was selected for the temperatures of 2273 and 2473 K, because of the following. In vacuum, Ni rapidly evaporated above 2273 K and the graphite as the heater and insulator materials in the heating furnace rapidly sublimated at 2473 K. Thus, Ar was commonly selected as the atmosphere in the heating at 2273 and 2473 K for the unification of the heating atmosphere.

The cross-section of these heated specimens were prepared by cutting, grinding and polishing, and then slightly etched with Murakami's reagent. On the diffusion-couple, SEM observation and XMA analysis were carried out near the bonded-interface of TiC/(Ti,Mo)C. On the cermet, 600 carbide grains on the cross-section for each specimen were observed with optical and/or SEM microscope in order to investigate the two-dimensional diameters of carbide grains. From the two-dimensional diameter, three-dimensional diameter was calculated by multiplying $3/2^{12)}$ with it. The fluctuation of averages of the three-dimensional diameter was investigated as a function of measuring numbers, and the average was

confirmed to become a constant above about 200 measuring numbers. Auger electron spectroscopy (AES) analysis were carried out to investigate the diffusion of Ti and Mo in TiC-core/(Ti,Mo)C-rim structure. According to the procedure described in the above "2.1 Consideration process", the calculations of P_{exp} and P_{hyp} of TiC-core in carbide grains were carried out and then the judgement on the problem whether TiC-core really disappears or not by solid-diffusion process was done.

The observation place on the core in this study on TiC-core/(Ti,Mo)C-rim structure was the compact inside, differing from FeSi-core in the study on FeSi-core/FeSi₂-rim structure where the place was near the compact surface. This is because TiC-core size (generally 1~4 μm) was considerably small, compared with FeSi-core size of about 15 μm , and thus the observation was difficult near the compact surface, where some amount of evaporation occurred and thus the microstructure changed to the depth of about 2 μm in the case of heating temperature of 2173 K⁵⁾.

3 Experimental results and discussions

3.1 Temperatures for non-active and active solid-diffusion in diffusion-couple

Fig. 3 (a) and (b) show the SEM microstructures of both as-sinter-bonded TiC/(Ti,Mo)C diffusion-couple and also as-sintered TiC-20mass%Mo₂C-20mass%Ni cermet, and those of two specimens heated for 14.4 ks at 2073 K {0.59 $T_{\text{m(TiC)}}$ } after the bonding or sintering, respectively.

Here, 2073 K is lower than the maximum temperature (2173 K) used in the previous study, while the heating time is longer⁵⁾. TiC and (Ti,Mo)C region in the diffusion-couple can clearly be distinguished from the difference in the contrast between them for two kinds of temperatures: TiC is darker than (Ti,Mo)C. These microstructural observation and also XMA or AES analysis clarified that the solid-diffusion of Ti and Mo in the diffusion-couple hardly occurred and also reconfirmed that TiC-core in the cermet remained after heating at such relatively low temperature. Therefore, the remaining or non-disappearance of TiC-core in TiC-core/(Ti,Mo)C-rim structure at the temperatures below 2073 K (time: 14.4 ks) was judged to be due to the extremely slow diffusivities of Ti and Mo atoms, i.e., not due to "the exhaustion of diffusion-contributable atomic vacancies in the core" which is suggested by the above hypothesis.

Additionally, the adjusting of the contrast between TiC and (Ti,Mo)C in the cermet to that in the diffusion-couple was difficult in Fig. 3, probably due to the existence of Ni phase. A slight amount of TiC particles remained in (Ti,Mo)C compact, which was probably due to the existence of large TiC agglomerate particles in TiC+Mo₂C mixed powder.

Fig. 4 shows the SEM microstructures near the interface of TiC/(Ti,Mo)C diffusion-couples heated for 14.4 ks at 2273 and 2473 K {0.65 and 0.70 $T_{\text{m(TiC)}}$ }. It was made clear from XMA analysis as well as SEM microstructure that Mo and Ti diffusions took place at 2273 and 2473 K in

Fig.3(a)(b) SEM microstructures of TiC/(Ti,Mo)C diffusion-couple (a) and TiC-20mass%Mo₂C-20mass%Ni cermet (b). Left: as-joined (1573 K) and as-sintered (1723 K), respectively. Right: both are after heating of 2073 K {0.59 $T_{\text{m(TiC)}}$ } for 14.4 ks in vacuum of about 1 Pa. These show that solid-diffusion in diffusion-couple hardly occurred below 2073 K, and thus the phenomenon that TiC-cores were not observed in a part of carbide grains is not due to solid-diffusion, but due to Ostwald ripening ($\times 5000 \times 0.8$ or $\times 1000 \times 0.8$).

Fig.4 SEM microstructures of TiC/(Ti,Mo)C diffusion-couples after heating at 2273 and 2473 K $\{0.65 \text{ and } 0.70T_{m(TiC)}\}$ for 14.4 ks in Ar of about 0.1 MPa, showing that solid-diffusion (grain boundary- or interface-diffusion) considerably occurred in both compacts ($\times 5000 \times 0.8$).

Fig.5 Schematic drawing of grain boundary- or interface-diffusion in TiC/(Ti,Mo) diffusion-couple at 2273 K, which was illustrated based on Fig. 4

both TiC and (Ti,Mo)C regions respectively, differing below 2073 K, and that the diffusion path are mainly their crystal grain boundaries, i.e., TiC/TiC and (Ti,Mo)C/(Ti,Mo)C in the initial stage. After some amount of diffusion took place, the diffusion path was assumed to change to the interface of TiC/(Ti,Mo)C, because the diffusing TiC reacts with (Ti,Mo)C crystal grain to form (Ti,Mo)C with higher Ti content and the diffusing (Ti,Mo)C reacts with TiC crystal grain to form (Ti,Mo)C with lower Mo content. The change in the microstructure near the

bonded-interface was confirmed to be almost uniform in the whole bonded-interface from the one end to another of the cross-section. It was also clarified that Mo diffused by about 32 and 38 μm along grain boundary or interface into TiC region at 2273 and 2473 K respectively, and Ti diffused by about 100 and 120 μm along grain boundary or interface into (Ti,Mo)C region respectively.

The above results indicate that solid-diffusion of Ti and Mo in the diffusion-couple actively occurred along grain boundary or interface as schematically illustrated in Fig. 5,

and that the diffusion distances were larger than the width of TiC-core size (generally 1–2 μm). In TiC compact, the interface of TiC crystal grain and the diffused-in (Ti,Mo)C phase is generally clear. On the other hand, in (Ti,Mo)C compact, the interface of (Ti,Mo) crystal grain and the diffused-in TiC which form (Ti,Mo)C solid solution phase by reacting with (Ti,Mo)C crystal grain is not clear in the specimen heated at 2473 K, compared with that as 2273 K. XMA results corresponded to these observation results. These suggest the following two, respectively. (1) The shrinkage of TiC crystal grain in TiC compact occurred not by the lattice diffusion of Mo and C of (Ti,Mo)C compact into TiC crystal grain, but mainly by the dissolution of Ti and C of TiC crystal grain into the diffused-in (Ti,Mo)C solid solution phase, and (2) TiC which diffused into (Ti,Mo)C compacts along the grain boundary dissolved into (Ti,Mo)C crystal grains, particularly in the specimen of 2473 K. Namely, the diffusion direction is mainly from TiC phase to (Ti,Mo)C phase.

Therefore, there are the following two candidates for the cause for the shrinkage and/or disappearance of TiC-core in the cermet above 2273 K: (1) the solid-diffusion between TiC-core and (Ti,Mo)C-rim, as well as (2) Ostwald ripening. Then, the above two appearance probabilities of TiC-core were investigated as below to solve the problem from the viewpoint of probability.

3.2 Experimental appearance probability (P_{exp}) of TiC-core

Fig. 6 shows SEM microstructures of the cermets heated at 2273 and 2473 K for 14.4 ks. These microstructures with relatively low magnification ($\times 750 \times 0.9$) are not for the observation of TiC-core, but for the observation of carbide grain size. The three-dimensional average diameters were about 1.4, 18, 64 and 110 μm for 1723, 2027, 2273 and 2473 K, respectively, as shown in Fig. 7. The carbide grain size increased considerably with increasing heating temperature, which is of course due to Ostwald ripening.

The observation at high magnification ($\times 5000 \times 0.8$)

revealed that TiC-core could not generally be detected in carbide grains on the observation plane for the specimens heated at 2273 K and 2473 K. This was of course mainly caused by Ostwald ripening as described above. However, there were an extremely small amount of carbide grains where a core was observed. An example observed in the specimen heated at 2473 K is shown in Fig. 8. The core was $1.5 \times 9 \mu\text{m}^2$ in size and was confirmed to be surely TiC as indicated by Fig. 9 which was AES analysis on the core

Fig. 7 Three dimensional carbide grain size in TiC-20mass%Mo₂C-20mass%Ni cermet as a function of heating temperature.

Fig. 8 An example of TiC-core barely observed in a large carbide grain in TiC-20mass%Mo₂C-20mass%Ni cermet heated at 2473 K $\{0.70T_{\text{m(TiC)}}\}$ for 14.4 ks ($\times 500 \times 0.9$).

Fig. 6 SEM microstructures of TiC-20mass%Mo₂C-20mass%Ni cermet heated at 2273 and 2473 K for 14.4 ks, showing that a considerable amount of Ostwald ripening occurred at these temperatures ($\times 200 \times 0.8$).

and the rim. Then, the number of carbide grains where a TiC-core was observed on an observation plane was investigated for 600 carbide grains for each specimen heated at 2073, 2273 or 2473 K. The number were 120, 1 and 2, respectively. Thus, P_{exp} of TiC-core which was calculated by dividing these numbers with 600 were about 0.20, 0.0017 and 0.0033, respectively, where the last two values seemed to be nearly the same with each other. These values are shown with solid marks and a solid line in Fig. 10.

3.3 Hypothetical appearance probability (P_{hyp}) of TiC-core

The P_{hyp} of TiC-core was calculated for the specimens of 2273 and 2473 K by the method shown in the section “2.1 Consideration process”. The largest TiC-core size used in the calculation was $10\text{ }\mu\text{m}$ (the average of 9.0 and $11\text{ }\mu\text{m}$) of the core detected in the specimen heated at 2073 K which was the highest temperature where the solid-diffusions of Ti and Mo were not observed in the diffusion-couple. The P_{hyp} were 0.16 (10/64) and 0.09 (10/110), respectively, and drawn with open marks and a broken line also in the above Fig. 10. The P_{hyp} for the specimens of 2073 K as well as 1723 K can theoretically be said to be the same as P_{exp} as already described in “2.1 Consideration process”. Thus, P_{hyp} at 2073 K was not investigated and P_{exp} at 2073 K was drawn as P_{hyp} at 2073 K for the reference in the figure.

As for the TiC-core size of the above $10\text{ }\mu\text{m}$, it is considerably large, compared with general size of $1\sim 4\text{ }\mu\text{m}$. However, such large TiC-core could be observed in the fracture origin of the broken test piece of TiC-Mo₂C-Ni cermet¹³⁾.

3.4 Judgement on the problem by comparing two appearance probabilities

Fig.9 AES analysis of a core and rim in TiC-20mass%Mo₂C-20mass%Ni cermet shown in Fig. 8, indicating that the core is pure TiC grain. This suggests that the shrinkage and/or disappearance of TiC-core occurred by the dissolution of TiC into (Ti,Mo)C-rim.

From Fig. 10, it is clear that P_{exp} are extremely small at 2273 and 2473 K, compared with P_{hyp} : the ratio of P_{exp} to P_{hyp} was calculated to be about 0.01 (0.0017/0.16) and 0.04 (0.0033/0.091), respectively. Even if the general size of TiC-core, i.e., $3\text{ }\mu\text{m}$ ($2 \times 4\text{ }\mu\text{m}^2$) is used instead of above $10\text{ }\mu\text{m}$, P_{hyp} was calculated to be 0.047 (3/64) and 0.027 (3/110) at 2273 and 2473 K, respectively. Therefore, the ratio of P_{exp} to P_{hyp} at two kinds of heating temperatures are 0.04 (0.0017/0.047) and 0.12 (0.0033/0.027), respectively. From this result as well as the above result that the solid-diffusion in the diffusion-couple became active above 2273 K, it can be concluded that almost all TiC-core except for a considerably large core really disappeared by solid-diffusion process above 2273 K, differing from below 2073 K.

3.5 Generalization of our hypothesis

As described above, it was made clear that the hypothesis “Exhaustion of diffusion-contributable atomic vacancies in core/rim structure” can not be applied to TiC-core/(Ti,Mo)C-rim structure, differing from FeSi-core/FeSi₂-rim structure. This difference was considered to arise from the following two items: (1) (Ti,Mo)C is a solid solution which can vary its composition and thus is able to dissolve Ti and C atoms of TiC-core, differing from FeSi₂ which is a stoichiometric compound and thus is unable to dissolve Fe or Si of FeSi-core and Si from FeSi₂+Si matrix, and therefore (2) Ti and C atoms in TiC-core can diffuse toward the rim, i.e., (Ti,Mo)C, differing from Fe or Si atoms of FeSi-core. Such diffusion direction of Ti and C atoms, i.e., from the core to the rim which is reverse in FeSi-core/FeSi₂-rim structure, can not cause the exhaustion of diffusion-contributable atomic vacancies in the core or the

Fig.10 Comparison of experimental (P_{exp}) and hypothetical appearance probabilities (P_{hyp}) of TiC-core. The former became considerably smaller than the latter at 2273 and 2473 K where the diffusion in the diffusion-couple became active. This indicates that almost all TiC-core except for a considerable large one really disappeared due to solid-diffusion between the core and (Ti,Mo)C-rim, differing from below 2023 K.

Fig.11(a)(b) Schematic illustrations of two types of core/rim-structure, to which our hypothesis "Exhaustion of diffusion-contributable atomic vacancies in core/rim structure" can be applied (a) and not applied (b). "V_c" denotes the diffusion-contributable atomic vacancy. The diffusion directions of both atoms and V_c causing the reaction are reverse between (a) and (b).

core/rim structure. Because, V_c are supplied from (Ti,Mo)C/Ni interface to TiC-core/(Ti,Mo)C-rim interface and TiC-core, accompanying the dissolution of TiC-core into (Ti,Mo)C-rim.

It can be concluded that our hypothesis "Exhaustion of diffusion-contributable atomic vacancies in core/rim structure" can be applied to a core/rim structure where the rim is a stoichiometric compound unable to dissolve the elements of the core and also the diffusion from the core to the rim is not thermodynamically allowed like in FeSi-core/FeSi₂-rim structure, as schematically shown in Fig. 11 (a), and not applied to a core/rim structure where the rim is a solid solution able to dissolve the elements of the core and thus the diffusion from the core to the rim is thermodynamically allowed like in TiC-core/(Ti,Mo)C-rim structure, as schematically shown in Fig. 11 (b).

4 Conclusion

In relation to our hypothesis "Exhaustion of diffusion-contributable atomic vacancies in core/rim structure" which was proposed to FeSi-core/FeSi₂-rim structure, it was investigated whether TiC-core in TiC-core/(Ti,Mo)C-rim structure of TiC-Mo₂C-Ni cermet disappear or not due to solid-diffusion process by heating for 14.4 ks at 2073, 2273 and 2473 K considerably higher than the usual sintering temperature (1528~1723 K). In solving the problem, the following two phenomena caused by Ostwald ripening were taken into consideration: the appearance probability of TiC-core on a carbide grain and the number density of TiC-core on an observation plane considerably decreased, even if TiC-cores do not disappear due to the solid-diffusion between the core and the rim.

(1) By comparing the experimental appearance probability

of TiC-core in carbide grain with the hypothetical one, i.e., the value calculated under the assumption that TiC-core with the original size remains, it was concluded that almost all TiC-core really disappeared by solid-diffusion process above 2273 K where the solid-diffusion in TiC/(Ti,Mo)C diffusion-couple became active, differing from below 2073 K.

(2) Generally speaking, our new hypothesis can be applied to a core/rim structure where the rim is a stoichiometric compound unable to dissolve the elements of the core and also the diffusion from the core to the rim is not thermodynamically allowed like in FeSi-core/FeSi₂-rim structure, but not applied to a core/rim structure where the rim is a solid solution able to dissolve the elements of the core and thus the diffusion from the core to the rim is thermodynamically allowed like in TiC-core/(Ti,Mo)C-rim structure.

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