Wetting Behavior for Ni on (Ti$_{0.95}$Mo$_{0.05}$)(C$_{0.5}$N$_{0.5}$), (Ti$_{0.9}$Nb$_{0.1}$)(C$_{0.5}$N$_{0.5}$) and (Ti$_{0.85}$Nb$_{0.1}$Mo$_{0.05}$)(C$_{0.5}$N$_{0.5}$) Substrates

Hiroyuki Hosokawa$^{1,*}$, Koji Shimojima$^1$, Akihiro Matsumoto$^1$, Kiyotaka Kato$^1$, Tetsushi Matsuda$^2$ and Hideaki Matsubara$^2$

$^1$Materials Research Institute for Sustainable Development, National Institute of Advanced Industrial Science and Technology, Nagoya 463-8560, Japan
$^2$Materials Research and Development Laboratory, Japan Fine Ceramics Center, Nagoya 456-8587, Japan

Wetting tests for Ni on (Ti$_{0.95}$Mo$_{0.05}$)(C$_{0.5}$N$_{0.5}$), (Ti$_{0.9}$Nb$_{0.1}$)(C$_{0.5}$N$_{0.5}$), and (Ti$_{0.85}$Nb$_{0.1}$Mo$_{0.05}$)(C$_{0.5}$N$_{0.5}$) ceramics were carried out at 1823 K and compared with those for the previous data. The larger the Mo content was, the smaller the contact angles were. The contact angle for region samples and microstructures could be divided into three regions: a Ni-rich region, reactive region, and substrate region. The depth of reactive region/hard phase ratios for titanium carbonitrides containing Nb were larger than those for them containing Mo, and (Ti$_{0.85}$Nb$_{0.1}$Mo$_{0.05}$)(C$_{0.5}$N$_{0.5}$) had the largest ratio in all the samples.

1. Introduction

TiC- and Ti(C,N)-based cermets are candidates for an alternative to WC–Co cemented carbide, and they are known to have higher wear resistance than WC–Co cemented carbide, which is used for fabricating tools used in the steel industry. However, it is difficult to replace WC–Co cemented carbides with the cermets because of the low fracture toughness.

It is well-known that one of the important matters to improve fracture toughness is to improve wettability, which is effective to shrinkage and vanish of the voids and to be better homogeneous microstructures. It is well known that the main disadvantage of TiC- and Ti(C,N)-based cermets is poor wettability between TiC and Ti(C,N) and binder materials. Humenik and Parikh reported$^{11}$ that molybdenum enhances the wettability of hard phase with binder phase and the cermets including molybdenum were improved mechanical properties. After that, there have been many reports about TiC or TiCN-based cermet containing Mo and Mo$_2$C.$^{1-8}$

Focusing on microstructures in TiC or TiCN based cermet containing Mo and Mo$_2$C, they have a core-rim structure, that is, a (Ti,Mo)C or (Ti,Mo)CN rim surrounding a TiC or TiCN core. Those rim structures maintain wettability to Ni. However, the rim structure is not always located on the interface and one of reasons for microstructural inhomogeneity. The solid solution cermets, which are constructed of (Ti,Mo)C and/or (Ti,Mo)(C,N) hard phase and binder phase, have attracted attentions.$^{9,12}$ Because all interface is Ni/ (Ti,Mo)C and/or Ni/(Ti,Mo)(C,N). Additionally, Chen and Bieławski$^{17}$ derived that the fracture toughness for Ti$_{0.75}$X$_{0.25}$C ceramics (X = Ta, W, Mo, Nb and V) are higher than that for TiC. In addition, Park and Kang indicated that the fracture toughness of the solid solution (Ti,W)/C-Ni cermets have higher than those of the ordinary TiC-WC-Ni cermets with almost same hardness.$^9$ Therefore, solid solution cermets are better method to improve mechanical properties.

Promoting solid solution cermets as high performance cermets, it is important to accumulate the data about wettability between binder phase materials/hard phase materials. There are some papers about the wetting behaviour of binder/titanium based ceramics,$^{14-18}$ describing metallographic and thermal analysis in detail. The authors reported the effect of the Mo and W content and C/N ratio on the wettability of the Ni/solid solute TiCN ceramic system.$^{18}$ It is noted that the molybdenum and tungsten are effective in improving the wettability and that molybdenum is more effective than tungsten and carbide is more effective than nitride in improving the wettability of this system.

In this study, the effect of the molybdenum and niobium content on the wettability of the Ni/solid solute TiCN ceramic system was studied by performing a wetting test at 1823 K.

2. Experimental Procedure

(Ti$_{0.85}$Mo$_{0.05}$)(C$_{0.5}$N$_{0.5}$), (Ti$_{0.9}$Nb$_{0.1}$)(C$_{0.5}$N$_{0.5}$) and (Ti$_{0.85}$Nb$_{0.1}$Mo$_{0.05}$)(C$_{0.5}$N$_{0.5}$) powders were prepared for substrates. These materials were pulsed-current sintered at 2123 K in vacuum. The densities of substrates were measured by Archimedian method to confirm the sound substrates with less-voids. The substrates were ground to obtain a plane surface, and they were subsequently polished on one side with 0.25 µm diamond pastes. Pure Ni balls with a diameter of 3 mm were prepared, and they were pressed at 5 kgf to flatten them so that they could be placed on the substrates. The substrate was set on the center bar, and the Ni ball was placed at the center on the upper surface of the substrate. For the measurement of the contact angle at high temperatures, the Ni ball and the substrate were heated by a horizontal furnace. Optical windows permitted the observation of the sample (Ni/substrate). A HDTV camera was utilized for real-time observations of the sample during the experiment. The
experiments were carried out in an argon atmosphere. Each experiment lasted 5 min and was performed at 1823 K. After wet testing, cross sections of the samples were analyzed by X-ray diffraction (XRD) using Cu Kα radiation. They were observed by optical microscopy (OM) and field emission scanning electron microscopy (FE-SEM) with energy-dispersive X-ray spectroscopy (EDS).

3. Results and Discussions

The densities of the titanium carbonitride substrates are shown in Fig. 1, which included the densities of substrates in the previous work.18) The true density of Ti(C0.5N0.5) can be calculated by considering a linear interpolation between the density of TiN (5.44 g/cm³) and that of TiC (4.92 g/cm³) as demonstrated by Vegard law, which is 5.18 g/cm³. The experimental density of Ti(C0.5N0.5) is 5.17 g/cm³, 99.8% as a relative density, sufficiently sound sintered compact. It is unknown exactly how much full densities for the solid solute titanium carbonitrides are. However, Chen and Zhao calculated the densities of (Ti0.75X0.25)C by Ab initio calculations (X indicated the solute atoms, such as Mo, Nb and so on), and these increased with the atomic weight for the solute atoms.13) The densities of the solid solute titanium carbonitrides were larger than that of Ti(C0.5N0.5) and increased with Mo and Nb contents. This trend is same to the Ab initio calculations. The substrates prepared may as well be sound sintered compacts.

Images of Ni on (Ti0.85Nb0.1Mo0.05)(C0.5N0.5) recorded during the wetting test are shown in Fig. 2. When a Ni ball in contact with (Ti0.85Nb0.1Mo0.05)(C0.5N0.5) was heated up to 1823 K, melting started at the interface around 1723 K; the metal completely melted at 1773 K. The contact angles were measured after the completion of melting. It is shown that the contact angles decrease with an increase in the temperature and holding time.

In Fig. 3, the contact angles are shown as a function of the temperature and holding time for Ni on (Ti0.95Mo0.05)(C0.5N0.5), (Ti0.85Nb0.1Mo0.05)(C0.5N0.5), and (Ti0.9Nb0.1)(C0.5N0.5); the previous data for Ni on TiMoCN are superimposed.18) Compared Ni/(Ti0.85Mo0.05)(C0.5N0.5) with Ni/(Ti0.85Nb0.1Mo0.05)(C0.5N0.5), contact angles of Ni/(Ti0.85Nb0.1Mo0.05)(C0.5N0.5) were lower than that of Ni/(Ti0.95Mo0.05)(C0.5N0.5). (Ti0.85Nb0.1Mo0.05)(C0.5N0.5) correspond to displacement of Ti to Nb from (Ti0.95Mo0.05)(C0.5N0.5). Therefore, Nb is one of effective elements to improve wettability between Ni and substrates.

Optical micrographs of sample cross sections recorded after the wetting tests are shown in Fig. 4. Three distinct regions could be observed on the cross sections: an upper region, a middle region, and a lower region. XRD patterns of cross sections of Ni on (Ti0.85Mo0.05)(C0.5N0.5), (Ti0.85Nb0.1Mo0.05)(C0.5N0.5) and (Ti0.85Nb0.1)(C0.5N0.5) are shown in the figure.
(C_{0.5}N_{0.5}) are shown in Fig. 5. These peaks indicate TiCN structure and Ni structure, and no new structure is observed.

A schematic illustration, scanning electron micrographs, and EDS mappings of the cross sections, obtained after the wetting tests for Ni/(Ti_{0.85}Nb_{0.1}Mo_{0.05})(C_{0.5}N_{0.5}) are shown in Fig. 6, where the observed area is middle region. There are two phase: the dark color phase and the light color phase. The dark color phase has high Ti, Mo and Nb concentrations, on the other hand, the light color phase has high Ni concentration. In spite of slight strange shape compared ordinary solid solution cermets, microstructures are likely to be composed of (Ti,X)(C,N) phase and Ni phase. On the basis of the XRD results, it is suggested that substrate atoms entered the Ni region and that (Ti,Mo,Nb)(C,N) were formed during cooling without new phase nucleation. It can be noted from the experimental results, the wetting behavior of Ni on (Ti_{0.95}Mo_{0.05})(C_{0.5}N_{0.5}), (Ti_{0.85}Nb_{0.1}Mo_{0.05})(C_{0.5}N_{0.5}) and (Ti_{0.9}Nb_{0.1})(C_{0.5}N_{0.5}) is reactive wetting accompanying with a dissolution as well as the previous work. The upper, middle and lower regions are Ni-rich, reactive and substrate regions, respectively.

The ratio of the depth of the reactive region (b) to the height of the Ni region (a) for Ni/(Ti_{0.95}Me_{1−x}) was measured. The results are shown in Fig. 7. The (b/a) ratio correspond to the reactive quantity. In the viewpoint of Mo content, the (b/a) ratio increased with increasing Mo contents. The (b/a) ratio for (Ti_{0.9}Nb_{0.1})(C_{0.5}N_{0.5}) was larger than those for them containing Mo. Additionally, (Ti_{0.85}Nb_{0.1}Mo_{0.05})(C_{0.5}N_{0.5}), replaced Ti to Mo in (Ti_{0.9}Nb_{0.1})(C_{0.5}N_{0.5}), was the largest ratio in all the samples. It is indicated that Mo and Nb play a role in rapid reaction between Ni and titanium carbonitrides and Nb is more effective. What is more mixed Mo with Nb, the effect abides by the quantity of solid solute contents.

4. Conclusion

Wetting tests of (Ti_{0.95}Mo_{0.05})(C_{0.5}N_{0.5}), (Ti_{0.9}Nb_{0.1})(C_{0.5}N_{0.5}) and (Ti_{0.85}Nb_{0.1}Mo_{0.05})(C_{0.5}N_{0.5}) substrates with Ni at 1823 K were carried out and contact angles between Ni and substrates were measured. After the wetting tests, the microstructures of cross sections of the samples were observed and compared to the previous work. The results can be listed as follows.

(1) The contact angles decreased with increasing Mo content, and the contact angle for (Ti_{0.9}Mo_{0.1})(C_{0.55−N_{0.45}}) was smaller than that for (Ti_{0.9}Nb_{0.1})(C_{0.5}N_{0.5}).
The contact angle for \((\text{Ti}_{0.85}\text{Nb}_{0.1}\text{Mo}_{0.05})(\text{C}_{0.5}\text{N}_{0.5})\) was smaller than that for \((\text{Ti}_{0.95}\text{Mo}_{0.05})(\text{C}_{0.5}\text{N}_{0.5})\), indicating that Nb is one of effective element to improve wettability.

2) Three distinct regions were observed in the microstructures of the sample cross sections. In reaction phase i.e., middle region, there are two phase: TiXCN and Ni. Further, no new phase was observed after the wetting test.

3) The depth of reactive region/height of Ni-rich region ratios for titanium carbonitrides containing Nb were larger than those for them containing Mo, and \((\text{Ti}_{0.85}\text{Nb}_{0.1}\text{Mo}_{0.05})(\text{C}_{0.5}\text{N}_{0.5})\) had the largest ratio in all the samples.

Acknowledgments

The authors gratefully acknowledge the financial support provided by a project (P08023) of the New Energy and Industrial Technology Development Organization (NEDO).

REFERENCES