Effect of Ni Contents on Microstructures and Mechanical Properties for (Ti_{0.8}Mo_{0.2})C-Ni Cermets

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The (Ti_{0.8}Mo_{0.2})C-Ni cermets (x = 10, 20, 30 and 40 mass%) were prepared by two milling processes; first, the (Ti_{0.8}Mo_{0.2})C produced by mechanical alloying of Ti, Mo and C powders (Process I). Second, mechanical alloyed (Ti_{0.8}Mo_{0.2})C and commercial Ni powders mixed by tumbling ball milling (Process II) for 72 h. On (Ti_{0.8}Mo_{0.2})C-40Ni, the milling time of Process II was 96 h in addition of 72 h. The Vickers hardness with fracture toughness and the quantitative microstructural parameters were measured and analyzed. The relationship between fracture toughness and hardness for the cermets was on the fitted curve derived from the previous data for the cermets, except for the case of (Ti_{0.8}Mo_{0.2})C-40Ni for 72 h, which is lower fracture toughness than that for the previous works and (Ti_{0.8}Mo_{0.2})C-40Ni for 96 h. The contiguity of the samples tend to increase with increasing hard phase contents except for the case of (Ti_{0.8}Mo_{0.2})C-40Ni for 72 h, which is higher than those of (Ti_{0.8}Mo_{0.2})C-40Ni for 96 h. On the other hand, the coefficient of variation for hard phase of the both (Ti_{0.8}Mo_{0.2})C-40Ni were almost same. 


(Received March 10, 2014; Accepted June 11, 2014; Published July 18, 2014)

Keywords: cermet, microstructure, hardness, fracture toughness

1. Introduction

Ti(C,N)-based cermet is one of the candidates for alternative materials to WC-Co, because they have high hardness, wear resistance and oxidation resistance. Therefore, the cermets have been investigated to improve the properties. The mechanical properties of TiC–Ni cermet was reported in 1960s\(^1\) and transverse rupture strength (TRS) and hardness were as low as about 1 GPa and 600 HV. Humenik and Parikh report\(^2,3\) that molybdenum enhances the wettability between hard phase and binder phase. Actually, TRS and the hardness of cermets including molybdenum in TiC or TiC–TiN were improved as above 1.5 GPa and 1000 HV.\(^4\) In addition, the various elements were added to improved various properties, for instance, WC to improve the wetting densification and fracture toughness\(^5,7\) and NbC and TaC to improve the hot hardness and thermoshockresistance.\(^7\) Resulting in the additive elements, the hard phase of the Ti(C,N)-based cermets become core-rim structures such as a Ti(C,N) core and a (Ti,X,Y)(C,N) rim (X and Y denote the additive metallic elements).

It is thought that microstructural features strongly influence to mechanical properties and microstructural homogeneity leads to improvement of the mechanical properties. In the case of the cermets, however, relationship between microstructural homogeneity and mechanical properties has been unclear so far. The complicated microstructures, such as core-rim structures, is one of the main causes of that.

Recently, the cermets with simple chemical compositions are refocused and reported as a result of resource problem.\(^8–16\) In this matter, (Ti,X)C or (Ti,X)(C,N) solid solution cermets\(^10,14–16\) have attracted attentions. However, there were few information about microstructural features and mechanical properties of solid solution cermets. In addition, besides these cermets have only solid soluted hard phases, the characteristics of them enables us to estimate microstructural features quantitatively and correlate with mechanical properties.

In the present work, (Ti_{0.8}Mo_{0.2})C-Ni solid solution cermets with 10–40 mass% Ni contents were prepared, and mechanical properties and the microstructures parameters were analyzed.

2. Experimental Procedures

The five (Ti_{0.8}Mo_{0.2})C-Ni cermets were prepared via two processes, hereafter they were called as Process I and Process II, respectively. Details of these processes are as follows:

Process I: titanium (99.9%, 45 µm), carbon (99.9%, 20 µm), and molybdenum (>99.9%, 3 µm) powders were used as raw powders. These powders were sealed in a 500 ml hardened steel pot together with WC/Co ball and then were dry-mixed by a planetary ball milling machine for 250 h in an Ar atmosphere with 20 : 1 of the ball-to-powder weight ratio (BPR).

Process II: The powder produced by Process I and nickel (>99.9%, 5 µm) powder were sealed in a 420 ml stainless steel pot together with WC-Co balls were mixed in 100 ml ethanol by tumbling ball milling for 72 h with 15 : 1 of BPR. (Ti_{0.8}Mo_{0.2})C-40Ni produced by tumbling ball milling for 72 h indicate relatively higher contiguity of hard phase. Therefore, (Ti_{0.8}Mo_{0.2})C-40Ni were also produced with 96 h of milling time in addition of 72 h. After that, they were pressed under a pressure of 100 MPa and then sintered at 1673 to 1723 K for 1 h under vacuum.

The microstructures of the sintered compacts were observed by field-emission scanning electron microscopy (FE-SEM). The image-processing software was used to measure the microstructural parameters. The hard phase mean grain size, \(d_{\text{hard}}\), is calculated as

\[
d_{\text{hard}} = D \sqrt{\frac{3}{2}}
\]

where \(D\) is the projected grain size actually measured on images. The perimeter of the carbonitride grains, \(L_{\text{hard}}\), and
that of the binder pockets, $L_{\text{binder}}$, can be measured and the contiguity, $C_{\text{hard}}$, is defined as:

$$C_{\text{hard}} = \frac{L_{\text{hard}} - L_{\text{binder}}}{L_{\text{hard}}}$$  \hspace{1cm} (2)

The coefficient of variation, $CV$, which is regarded as the hard phase size distribution, and is defined as:

$$CV = \frac{\sigma}{d_{\text{hard}}}$$  \hspace{1cm} (3)

where $\sigma$ is standard deviation of the hard phase size distribution, which is calculated from all hard phase grain size data.

The densities of the sintered compacts were measured by Archimedian method. The sintered compacts were analyzed by XRD using Cu Kα radiation. Young’s modulus, $E$, was obtained by ultrasonic pulse echo method, which provides velocities of longitudinal and shear waves in the specimen. The Vickers hardness tests were conducted with 294 N. The fracture toughness, $K_{IC}$, was calculated from the length of the radial cracks originating in the corners of the Vickers indentations according to the formula proposed by Niihara et al. (IF method, Palmqvist-type).\textsuperscript{17}

### 3. Results and Discussion

Relationships between density and sintering temperature for the cermets are shown in Fig. 1. These densities increase with increasing Ni contents. Compared the (Ti$_{0.8}$Mo$_{0.2}$)C-40Ni for 72 h milling time to the (Ti$_{0.8}$Mo$_{0.2}$)C-40Ni for 96 h milling time, these are almost same densities. The densities of all samples are constant in the sintering temperature range, indicating that all samples are sufficiently dense.

The XRD patterns for the cermets are shown in Fig. 2. The all cermets indicated typical XRD patterns for the cermets, which means the peaks of TiC structure and nickel existed for them, although there are slight unknown peak at 39 degree in all the cermets. The angles for the nickel peaks trended toward a lower angle. It is considered that some Mo and Ti caused the shift of the nickel peak in this work as well as the other cermets.\textsuperscript{18}

The microstructures of the five cermets were observed by FE-SEM, as shown in Fig. 3. It is known that the core-rim structure of the hard phase shows a contrast between core Ti(C,N) and rim (Ti,X)(C,N) in SEM observation.\textsuperscript{5,6,9,11,12} However, the hard phase of the prepared cermets consisted of
no contrast meaning solid soluted hard phase. The hard phase grain size of (Ti0.8Mo0.2)C-40Ni for 96 h milling time was smaller than that for 72 h milling time. It is indicated that milled powders became smaller with increase of milling time.

The Vickers hardness and sintering temperature is plotted in Fig. 4. The Vickers hardness decreased with increasing sintering temperature and Ni contents. Compared (Ti0.8Mo0.2)C-40Ni with 72 h milling time to (Ti0.8Mo0.2)C-40Ni with 96 h milling time, it with 96 h milling time were higher than that with 72 h milling time. The smaller hard phase grain size of it with 96 h milling time contributed to higher hardness.

The fracture toughness and sintering temperature of each cermets is plotted in Fig. 5. Fracture toughness for them basically increase with increasing sintering temperature and Ni contents. It is seen from Figs. 4 and 5 that the cermets with higher Vickers hardness indicated lower fracture toughness.

The relationship between fracture toughness and Vickers hardness for the cermets is shown in Fig. 6, where the data for TiCN-Mo2C-Ni cermets in the previous works are superimposed. The line is the fitted curve for the data in the previous works.

The fracture toughness and sintering temperature of each cermets is plotted in Fig. 7. The fracture toughness vs hard phase content for the cermets is shown in Fig. 7. The hard phase contiguity increases with increasing hard phase content, except for the case of (Ti0.8Mo0.2)C-40Ni. This trend is the same to it for WC-Co. The levels of contiguity for the cermets are higher than those for WC-Co. There is unclear whether the contiguity for the cermets in this work is the best levels, however, the same to them in the previous work. The hard phase contiguity of the both (Ti0.8Mo0.2)C-40Ni with different milling time were visible difference, it of the (Ti0.8Mo0.2)C-40Ni with 72 h milling time was 30% up, compared to that of the (Ti0.8Mo0.2)C-40Ni with 96 h milling time.

The coefficient of variation for hard phase of the (Ti0.8Mo0.2)C-Ni is shown in Fig. 8. The coefficient of variation for hard phase of the cermets were almost same, but slight different. In the high Ni content, they decrease with decreasing Ni content, on the other hand, below the
(Ti0.8Mo0.2)C-20Ni, the value of the (Ti0.8Mo0.2)C-10Ni is higher than that of the (Ti0.8Mo0.2)C-20Ni. Unfortunately, this trend is appropriate or not, because there are no report for the mechanical alloyed (Ti0.8Mo0.2)C powder and commercial Ni.

4 Conclusion

Five cermets were prepared via two processes, which are mechanical alloyed (Ti0.8Mo0.2)C powder and commercial Ni powder with tumbling ball mill, and the microstructures and the mechanical properties of them were observed and analyzed. The results can be listed as follows.

1) The hard phase of the all prepared cermets consisted of two phase, i.e., hard phase and binder phase, and hard phase were a solid solved phase.

2) The hardness increased with decreasing Ni content, on the contrary, the fracture toughness increased with increasing Ni content for the prepared cermets. Relationship between hardness and fracture toughness for the cermets in this work is on the line deriving from the cermets in the previous works, except for the case of (Ti0.8Mo0.2)C-40Ni with 72 h milling time. The fracture toughness of (Ti0.8Mo0.2)C-40Ni with 72 h milling had lower fracture toughness than that with 96 h milling time.

3) The hard phase contiguity of the cermets decreased with decreasing hard phase contents, except for the case of (Ti0.8Mo0.2)C-40Ni with 72 h milling time. (Ti0.8Mo0.2)C-40Ni with 72 h milling time was clearly higher that with 96 h milling time. On the other hand, the coefficient of variation for hard phase of the both (Ti0.8Mo0.2)C-40Ni were almost same.

Acknowledgement

This research was supported by The Amada Foundation.

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