Effect of Ni and Mo contents on microstructure, magnetic and mechanical properties of Ti(C, N)-based cermets

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Abstract. Ti(C,N)-based cermets were prepared by vacuum sintering. The effect of Ni and Mo contents on microstructure, magnetic and mechanical properties of cermets were investigated using XRD, SEM, EDS, and VSM. The results showed that the proportion of ceramic hard phase decreased gradually, and the core-rim structure became incomplete with Ni content. However, with an increase in Mo content from 6 to 18 wt. %, the thickness of rim phase slightly increased. The complete core-rim structure refined the grain size of cermets, and the particles became the finest when Mo content was about 14 wt. %. The magnetization of cermets increased with Ni content, while their magnetization gradually weakened with Mo content. The deterioration of magnetic properties was caused by the high total content of Mo and Ti alloying elements in the binder phase. Meanwhile, the hardness of cermets decreased, while the TRS initially increased, followed by a gradual decrease with content of Ni. With an increase in Mo content, the hardness and TRS of Ti(C,N)-based cermets increased firstly and then decreased. The fracture toughness of cermets increased with Ni content, while the increasing Mo content reduced the fracture toughness. Due to grain refinement and solid-solution strengthening of the binder phase, the optimal composition of cermet was Ti(C,N)-14Mo-25Ni, whose hardness, TRS, and KⅠC values were ~90.3 HRA, 2340 MPa and 11.7 MPa·m²/2, respectively.

1. Introduction

Ti(C, N)-based cermets are used for the fabrication of cutting tools, Due to their excellent wear resistance, high-temperature hardness, perfect chemical stability, and low friction coefficient [1-3], they attracted the global attention over the past decades. Additionally, they have other applications, such as seal rings, molds, micro mills and so on [4-6]. However, in some working conditions such as the forming of magnetic powder pressing, the mold needs to be non-magnetic at room temperature to ensure the dimensional accuracy of the forming parts and improve the surface quality of the formed parts and the service life of the mold [7]. Therefore, it is important for expanding the potential applications to prepare Ti(C, N)-based cermets with great room-temperature magnetic and mechanical properties.

As Ti(C, N)-Ni based cermets consist of Ti(C, N) hard ceramic grains, which are embedded into the metallic nickel (Ni) matrix, However, poor wettability between Ni-based binder and Ti(C, N) ceramic particles makes it difficult to densify the sintered body, resulting in a low strength and toughness [8]. For improving the wettability and enhancing the mechanical properties of Ti(C, N)-based cermets, such ingredients as Mo and Mo²C are often added to them. Such addition can not only
improve the wettability of metal binder and ceramic particles of Ti(C, N)-based cermets, but also inhibit the growth of ceramic particles during the liquid phase sintering and refine the particles. The latter can significantly improve the mechanical properties of cermets, especially, their transverse rupture strength (TRS) [9-11]. Moreover, the composition of Ni phase is a significant factor affecting the magnetic properties of Ti(C, N)-Ni based cermets [12]. As Ni is the ferromagnetic element whose saturation magnetization and Curie temperature at room temperature of are about 55 emu/g and 770 °C, respectively. Thus, Ti(C, N)-Ni based cermets tend to be ferromagnetic if the influence of the composition of cermets is neglected at ambient temperature [13]. The Mo addition can improve the mechanical properties of cermets and significantly influence the magnetic properties of cermets, which can decrease the Curie temperature and saturation magnetization of Ni. For instance, Babu et al. reported that the magnetization of Ni-Mo alloys decreased due to the solid solution of Mo atoms in the Ni-based binder phase [14]. Zhang et al. have also concluded that the magnetization of Ti(C, N)-Ni based cermets decreased with the Mo content, which mainly caused by the increasing content of Mo atoms in the Ni binder phase [7]. Furthermore, Li et al. have found that the magnetic properties of TiC-xTiN-15(Mo;C/WC)-yNi cermets deteriorated when the content of Ni increased from 20 to 40 wt. %, which was caused by the increasing content of metallic solutes in the Ni phase [15]. These research results strongly indicate that it is possible to produce paramagnetic Ti(C, N)-based cermets at ambient temperature by changing the contents of Mo and Ni, which also influence the mechanical properties of these cermets. However, to the best of the authors’ knowledge, the comprehensive effect of Mo and Ni additions on both magnetic and mechanical properties of Ti(C, N)-Ni based cermets was not reported yet. The aim of this study is to reveal the combined effect of Ni and Mo contents on magnetic and mechanical properties of Ti(C, N)-Mo-Ni cermets.

2. Experimental
The Ti(C, N)-Mo-Ni cermets used in this work were fabricated from commercial Ti(C, N), Mo, Ni and C powders by the powder metallurgy method. The characteristics of the raw powders are summarized in Table 1.

| Powders | Ti(C, N) | C | Mo | Ni |
|---------|----------|---|----|----|
| Oxygen content /wt. % | 0.65 | 0.38 | 0.13 | 0.15 |
| Particle size /μm | 1.5 | 3.20 | 2.85 | 2 |

Table 2 shows the nominal composition of samples under study. The raw powders were mixed with cemented carbide milling balls in ethanol via using a planetary ball mill. The milling procedure involved a milling for 24 h with a rotation speed of 300 rpm at a 7:1 ball-to-powder mass ratio. Then, mixtures were dried in an infrared stove for 1 h at 75 °C and sieved through 80 mesh. Next, the assieved powders were compacted into green compacts at the pressure of 250 MPa and sintered under vacuum at 1450 °C for 1 h in a graphite crucible.

| Cerments | Ti(C, N) | C | Mo | Ni |
|----------|----------|---|----|----|
| A1 | 70 | 1 | 14 | 15 |
| A2 | 60 | 1 | 14 | 25 |
| A3 | 50 | 1 | 14 | 35 |
| A4 | 40 | 1 | 14 | 45 |
| B1 | 68 | 1 | 6 | 25 |
| B2 | 64 | 1 | 10 | 25 |
| B3 | 56 | 1 | 18 | 25 |
The hardness test was conducted using a Rockwell hardness tester, and the TRS was measured using a three-point bending test equipment. The indentation method derived by Shetty et al. was used to determine the fracture toughness (KIC) of cermets [16].

The phase composition was identified via an X-ray diffractometer (Rigaku, Ultima IV, Japan) with the Cu-Kα radiation. The microstructure was analyzed via a scanning electron microscope (Hitachi, S-3400N, Japan) in the backscattered electron (BSE) mode. The elemental distribution was measured by an energy dispersive spectrometer (EDS) equipped with the scanning electron microscope (SEM). The magnetic measurements was carried out with the magnetic field intensity from -10,000 to 10,000 Oe by using a vibrating sample magnetometer (LakeShore, Model 7303 series, USA) at the temperature of 300 K.

3. Results and discussion

3.1. Phase composition

Figure 1 shows the X-ray diffraction (XRD) patterns of the as-sintered Ti(C,N)-Mo-Ni cermets, with various nickel content (15 wt. %, 25 wt. %, 35 wt. %, 45 wt. %) and various molybdenum contents (6, 10, 14, and 18 wt. %), respectively.

![Figure 1. XRD patterns of Ti(C,N)-Mo-Ni cermets: (a) Ti(C,N)-14Mo-xNi (x wt. %) (x = 15, 25, 35, 45) and (b) Ti(C,N)-yMo-25Ni (y wt. %) (y = 6, 10, 14, 18).](image)

All cermets under study presented the diffraction peaks of Ni and Ti(C,N) phases, and the peak of Mo did not appear. It could be deduced that the Mo atoms dissolved into the Ni phase and also formed the rim phase, which was the solid solution of (Ti, Mo)(C,N) [17]. The diffraction peaks of Ni (111) crystal face shifted to a higher angle as the increasing content of Ni, while the diffraction peaks of Ni (111) crystal face shifted to a lower angle with the increasing content of Mo. The results showed that the total contents of alloying elements (Mo and Ti) solid-dissolved into the Ni phase decreased with the content of Ni and increased with the Mo content.

Since the atomic radii of the major elements included in the cermets, such as Ti (1.432 Å), Mo (1.363 Å), and W (1.371 Å), exceed that of Ni (1.246 Å) [18], the lower diffraction peaks of Ni phase imply that the more alloying elements were solid-dissolved in the Ni phase. The variation of diffraction peaks suggests that the dissolution of alloying elements (Ti, Mo) in the Ni binder gradually increased with the content of Mo. However, as the content of Ni rose from 15 to 45 wt. %, the number dissolved Ti/Mo atoms in the Ni phase decreased because of the increasing Ni content dropped the content of solid-dissolved alloying elements in the unit volume of Ni phase.

3.2. Microstructure

Figures 2 and 3 show the BSE-SEM images of Ti(C,N)-Mo-Ni cermets with various Ni (15, 25, 35, and 45 wt. %) and Mo (6, 10, 14, and 18 wt. %) contents, respectively.
The microstructure of cermets displayed the following two types of core-rim structure: (i) a typical black core-gray rim and (ii) a white core-gray rim. The black core of cermets were formed as the remaining undissolved Ti(C, N) particles, whereas the (Ti, Mo)(C, N) solid solution rim phase was formed through the Ostwald ripening. The rim phase (Ti, Mo)(C, N) reprecipitated on Ti(C, N) grains due to the dissolution of small grains and reprecipitation on large ones during sintering on Ti(C,N) grains, which produced to the black core-gray rim [19]. As heavier elements led to a brighter image contrast in the BSE mode [20], the white core contained more Mo atoms than that of the gray rim. As observed in figure 2, the proportion of ceramic hard grains gradually decreased, and the proportion of metallic Ni binder increased gradually with the Ni content. As for cermets with a relatively low Ni content, their microstructure were relatively uniform, and the hard phase particles basically showed the typical core-rim structure in cermets. whose rim phase was relatively complete. However, as for the cermets with high Ni content, the particles with core-rim structure decreased dramatically. Meanwhile, most of the hard phase particles surface have no obvious rim or with incomplete rim phase and part of the hard phase particles have agglomerated. As is seen in figure 3, with the Mo
content increased, the thickness of rim phase precipitated on black core slightly increased. Meanwhile, the core-rim structure gradually became more completely, and the uniformity of the binder phase distribution also improved. As the Mo content changed from 6 to 14 wt. %, the average size of the hard phase grains gradually refined. However, when the Mo content further increased to 18 wt. %, the rim phase became significantly thicker, thus the grain size increased. In contrast, the cermet with Ni content of 25 wt. % and Mo content of 14 wt. % had the most uniform microstructure and the hard phase particles were the finest. This was mainly because that even if the liquid phase accelerated the dissolution of hard phase particles, it was difficult to saturate the binder phase when the Ni content exceeded a certain range. Therefore, the precipitation of the alloying elements was inhibited, manifesting as the obstruction of the rim phase formation. Also, increasing the Mo content within a certain range was advantageous for forming the rim phase with a complete structure and a moderate thickness. But when the Mo content was too high, not only the dissolution of the large particle was suppressed, but also increased the thickness of the rim phase.

3.3. Magnetic properties

Figure 4 shows the hysteresis loops of Ti(C, N)-based cermets with various Ni (15 25, 35, and 45 wt. %) and Mo (6, 10, 14, and 18 wt. %) contents, respectively.

![Hysteresis loops of as-sintered cermets](image)

**Figure 4.** Hysteresis loops of as-sintered cermets: (a) Ti(C,N)-14Mo-xNi (x wt. %) (x = 15, 25, 35, 45) and (b) Ti(C,N)-yMo-25Ni (y wt. %) (y = 6, 10, 14, 18).

As observed in figure 4(a), magnetization of cermets increased with Ni content increasing and only when the Ni content was 45 wt. %, the cermet exhibited obvious ferromagnetic behavior. When the Ni content was less than 45 wt. %, the M-H curves of cermets presented approximate straight line, which indicated paramagnetic of cermets. On the other hand, figure 4(b) shows that with the Mo content increasing, the magnetization of cermets gradually weakened. Moreover, only when Mo content was 6 wt. %, magnetic hysteresis appeared and the saturation magnetization was 0.28 emu/g.

As the Ti, Mo and C are paramagnetic or diamagnetic elements, and ferromagnetic nickel was not presented in ceramic grains of cermets [21]. Thus, the composition of the nickel phase as well as the lattice structure of Ni binder determined the magnetic properties of as-sintered Ti(C, N)-Ni based cermets [22]. Moreover, Ti and Mo atoms existed in the Ni phase in the form of substitutional solid solutions. It has been reported that binary Ni-Mo (Mo ≥ 6 at. %) and Ni-Ti (Ti ≥ 8 at. %) solid solution alloys exhibited paramagnetic behavior at room temperature, and the magnetic properties decreased with increasing of these binary solid solution alloys [14, 23]. The reason why alloying elements weakened the magnetic properties of cermets was that the existence of Mo and Ti alloying elements changed the electrons’ distribution around these dissolved atoms [24], as well as weakened the magnetic exchange between Ni and Ni atoms because of the partial transferring of valence electrons of alloying elements into the empty 3d orbitals of Ni atoms [12, 23, 25]. Consequently, the decrease in
magnetic properties of cermets at room temperature was attributed to the increasing solid solution of alloying atoms (Ti and Mo) into the Ni binder phase. Figure 5 shows the EDS results of as-prepared cermets which exhibited the relative contents of Ti and Mo elements in the nickel binder. N and C contents were ignored due to the deficiency of SEM/EDS analysis. The results show that the total contents of alloying elements (Mo/Ti) in binder phase decrease with Ni content, while the contents of alloying elements in the Ni binder increase with the Mo content. This can be attributed to changes in the magnetic properties of cermets.

![Figure 5. EDS analyses of cermets: (a) Ti(C,N)-14Mo-xNi (x wt. %) (x = 15, 25, 35, 45) and (b) Ti(C,N)-yMo-25Ni (y wt. %) (y = 6, 10, 14, 18).](image)

### 3.4. Mechanical properties

Table 3 shows the mechanical properties of Ti(C,N)-Mo-Ni cermets with various nickel molybdenum content.

| Cermets | TRS (MPa)     | Hardness (HRA) | K<sub>IC</sub> (MPa·m<sup>1/2</sup>) |
|---------|---------------|----------------|-----------------------------------|
| A1      | 1415±25       | 91.2±0.2       | 8.2±0.7                           |
| A2      | 2340±79       | 90.3±0.2       | 11.7±0.3                          |
| A3      | 2194±56       | 87.5±0.1       | 14.8±0.5                          |
| A4      | 1503±49       | 85.5±0.1       | 20.2±0.4                          |
| B1      | 1739±99       | 88.9±0.2       | 13.2±0.6                          |
| B2      | 2100±68       | 89.8±0.1       | 12.1±0.5                          |
| B3      | 2056±80       | 90.1±0.2       | 10.7±0.3                          |

As shown in table 3, the hardness of as-sintered cermets decreased, while the TRS initially increased, then gradually decreased with Ni content. With the Mo content increasing, the hardness and TRS of as-sintered cermets both increased firstly and then decreased. Meanwhile, K<sub>IC</sub> of cermets increased with Ni content, while K<sub>IC</sub> exhibited a gradual drop with Mo content. The improvement of microstructure, especially the formation of a complete rim phase with moderate thickness and uniform distribution of Ni-based phase among the hard phase particles improved the TRS of cermets. However, as the Ni content exceeded 35 wt. %, the microstructure of cermets was no longer uniform, and the number of hard particles with core-rim structure was significantly reduced, which led to the decrease of TRS. Moreover, a certain share of Mo was beneficial to refine grains and improve the TRS of cermet. When the Mo content reached 18 wt. %, large particles in the microstructure of cermet...
increased significantly and the rim phase became thicker, thus decreasing the TRS of cermet. Furthermore, the hardness and fracture toughness (K_{IC}) of cermet showed a reverse trend with the Ni content, which was mainly related to the intrinsic characteristics of Ni and its volume percentage in cermet. With the Ni content increasing, the volume percentage of nickel binder of cermet also increased, that led to the gradual decrease of hardness and increase of fracture toughness. If the content of Ni binder remained nearly unchanged, the fracture toughness was mainly positively correlated with the average size of the hard phase grains. This was because large hard-phase particles were more prone to deflect and consume more energy during the transgranular fracture. Moreover, fine particles also reduced the mean free path of Ni phase that declined the K_{IC} during the intergranular fracture. As the Mo content changed from 6 wt. % to 14 wt. %, the particles of hard phase gradually refined, resulting in a gradual decline in the K_{IC} of the cermet. However, as the Mo content increased to 18 wt. %, although the average size of the hard particles slightly increased, the K_{IC} of the cermet decreased due to the poor uniformity of the binder phase.

4. Conclusions

(1) Magnetization of cerments increased with Ni content and gradually weakened with Mo content. The M-H curves of as-sintered cermet presented an approximately straight line, which suggested paramagnetic properties of cermet. Only Ti(C,N)-6Mo-25Ni and Ti(C,N)-14Mo-45Ni cermet exhibited ferromagnetic properties.

(2) As the content of Ni increased from 15 to 45 wt. %, the TRS of cermet firstly increased, then decreased, and the hardness of the cermet gradually decreased, while K_{IC} rose. With the Mo content increase, hardness and TRS of Ti(C, N)-Mo-Ni cermet both increased initially and then decreased, while the fracture toughness gradually dropped. The optimal composition of cermet was Ti(C, N)-14Mo-25Ni, whose hardness, TRS, and K_{IC} were ~90.3 HRA, 2340 MPa and 11.7 MPa·m^{1/2}, respectively.

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References

[1] Mari D and Gonseth D 1993 Wear. 165 9-17
[2] Matsubara H 1990 Jpn. Int. Met. 29 1008-18
[3] Ettmayer P, Kolaska H, Lengauer W and Dreyer K 1995 Int. J. Refract. Met. Hard Mater. 13 343-51
[4] Clark E and Roebuck B 1992 Int. J. Refract. Met. Hard Mater. 11 23-33
[5] D’Errico G, Bugliosi S and Guglielmi E 1998 J. Mater. Process. Technol. 77 337-43
[6] Wang Y, Zou B and Huang C 2019 Tribol. Int. 134 60-76
[7] Zhang M, Yang Q, Xiong W, Zheng L, Huang B, Chen S and Yao Z 2015 J. Alloys Compd. 650 700-4
[8] Cardinal S, Malchère A, Garnier V and Fantozzi G 2009 Int. J. Refract. Met. Hard Mater. 27 521-7
[9] Park J and Park S 1999 Int. J. Refract. Met. Hard Mater. 17 295-8
[10] Wang N, Tong Y and Fang M 2012 Adv. Mater. Res. 602-4 530-5
[11] Yang Q, Xiong W, Zhang G, Huang B and Wakai F 2015 J. Am. Ceram. Soc. 98 1005-12
[12] Yang Q, Xiong W, Zhou S, Zhang M, Huang B and Chen S 2017 Mater. Des. 115 255-61
[13] Elumalai P, Vasan H, Verelst M, Lecante P, Carles V and Tailhades P 2002 Mater. Res. Bull. 37 353-63
[14] Babu V, Pavlovic A and Seehra M 1996 J. Appl. Phys. 79 5230-2
[15] Li S, Yang Q, Xiong W, Wang S, Mao Q and Zhang M 2018 J. Alloys Compd. 765 1119-26
[16] Shetty D, Wright I, Mincer P and Clauer A 1985 J. Mater. Sci. 20 1873-82
[17] Zhou W, Zheng Y, Zhao Y, Ma Y and Xiong W 2015 Ceram. Inter. 41 5010-6
[18] Laoui T and Biest O 1994 J. Mater. Sci. Lett. 13 1530-2
[19] Córdoba J, Chicardi E and Gotor F 2013 J. Alloy Compd. 559 34-8
[20] Jung J and Kang S 2004 Acta Mater. 52 1379-86
[21] Gee M, Reece M and Roebuck B 1992 J. Hard Mater. 3 119-42
[22] Zhang M, Yang Q, Xiong W, Zhou S, Wang S, Luo H and Ruan L 2018 Metall. Mater. Trans. A 49 3550-5
[23] Stover E and Wulff J 1959 Trans. TMS-AIME 215 127-36
[24] Zhou S, Peng W, Wang S and Wang L 2006 Powder Metall. Technol. 24 243-7
[25] Moriwake H, Kato T, Kuwabara A, Fisher C and Hirayama T 2009 Jpn. J. Appl. Phys. 48 083003