Effects of Different Mo Addition on the Microstructure and Mechanical Properties of Tic Cermets Material

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***Abstract* - Four kinds of composition ratio of (Ti1-xMox)C samples were prepared by conventional powder metallurgy method. In this paper, the impact of the different proportions of Mo on the organization structure and mechanical properties of (Ti1-xMox) C(x=0.1,0.2,0.3,0.4) was investigated by strength, hardness and XRD and SEM analysis. The experimental results show that, (Ti1-xMox)C based cermets have a core-shell structure similar with TiC based metal after addition of Mo. Its core is (Ti1-xMox) which shell is the binder phase of Co. It can be confirmed in XRD analysis. It can be seen from the SEM Scanning, (Ti1-xMox) C-based cermet's microstructure is smaller and it has a t smooth fracture, it's a typical transgranular fracture. After an initial decreasing, the flexural strength increased with the addition of Mo, up to 104Mpa. As for binder Co, in a certain extent, it gave an increase of the mechanical properties of the material.**

Keywords - TiC-based cermets, sintering, wettability, mechanical properties

I. INTRODUCTION

Nowadays, TiC cermets cutting tools are typically used for high hardness, high melting point, excellent electrical, thermal conductivities, and good corrosion resistance of both carbon and stainless steels. The sintering behavior, microstructure and properties of cermets fabricated from an ultrafine TiC (0.2 mm) powder in several sintered forms are investigated widely previously by many authors from different countries in the world [1-2]. Molybdenum is generally added in the form of Mo powders in order to obtain a good wetting of the ceramic by metallic binder [3-5].

Recently, binary transition metal carbides such as (Ti1-xMox)C have attracted much attention for use in increasing the strength of steels. This study aims to understand the ground state structure of various compositions of that carbide.

The additions are for the increase in the properties of combination between TiC grains and Co-binding phase by the formation of a solid solution in (Ti1-xMox) C. Because the metal cermets (Ti1-xMox) C have good performance, and Mo has good wettability of (Ti1-xMox)C [6], so in this experiment, Co was choosed as binder phase. The TiC-based cermets with addition of Mo were fabricated by a conventional powder metallurgy process [7-8]. Micron grade TiC powder was main ingredients, cobalt (Co) was adhesives, and powder metallurgy products were sintered in the vacuum furnace or hydrogen reduction furnace. So, this experiment mainly study the different proportion of Mo to TiC belong to the influence of the cermets mechanical properties, compared to the existing data, find out the best result, for future thorough research of the fine composite materials to lay a certain theoretical basis.

II. EXPERIMENTAL DETAILS

Commercial Ti, Mo, Co and C powders were used in this experiment, they were all above 99.9% purity and 400 mesh particle size [9]. Four kinds of composition of (Ti1-xMox)C samples were prepared by conventional powder metallurgy method. Fig. 1 shows the Ti-Mo alloy phase diagrams, first the alloy composition of titanium and molybdenum were respectively smelted in vacuum arc furnace according to the mole ratio as showed in Tab.1, the proportion of the total quality was 30g.

TABLE.1 COMPOSITIONS OF THE TI/MO ALLOY

Sample	Molecular formula	Weight of Ti/g	Weight of Mo/g
1	Ti0.9Mo0.1	24.5	5.5
2	Ti0.8Mo0.2	20.0	10.0
3	Ti0.7Mo0.3	16.2	13.8
4	Ti0.6Mo0.4	12.9	17.1

The four Ti-Mo Alloys were put into an airtight container in which filled with the high pressure hydrogen (about 4MPa) and heating (usually 400℃) for hydride process. the condition of high temperature and high pressure hydrogen can promote the alloys take absorption reaction, leading to the alloys became embrittlement, then Ti-Mo alloys powder were prepared by ball-milling. The four kinds of Ti/Mo alloy powders were respectively mixed

with graphite powder in the mole ratio 1:1, 6.5% Co powder was added as adhesives.

According to Ti-Mo phase diagram, Ti1-xMox and C is easy to form stable compounds, the sintering process is heat above 400℃ and 10 min heat preservation, the highest sintering temperature is 1800℃ for 3 hours to ensure the decomposition of forming agent and the residual water eliminated. When second sintering were taken due to considering the elements Co's melting point is 1493℃, so the sintering temperature was 1500℃, near its melting point, so that the hardening phase was formed eutectic bonding metal with Co.

III. RESULTS AND DISCUSSION

A. Microstructures of the Alloys

Four samples containing different amounts of Mo were selected to observe the microstructural change with the increase in Mo by SEM. After sintering specimens appeared similar TiC based cermets core shell structure, but it was different in essence. As shown in Fig.1, black part is (Ti1-xMox) C which similar to the TiC hard phase of TiC based cermets; white part is the binder phase Co, also similar to the coating phase of TiC based cermets. Some researches also proved that adding Mo would form the surrounding structure of (Ti,Mo)C solid solution phase outside the TiC phase [10-12]. With the increase of the content of Mo, (Ti1-xMox) C grain size has been on the increase, so that Mo can be a good solid solution with Ti, and (Ti1-xMox) C is also stable. Four specimens are all typical transgranular fracture because of the relatively smooth fractures. Consequently, the more the addition of Mo, the more the precipitation of Mo on the TiC particles and the more the thickness of (Ti,Mo)C formed outside the TiC particles [13-14].

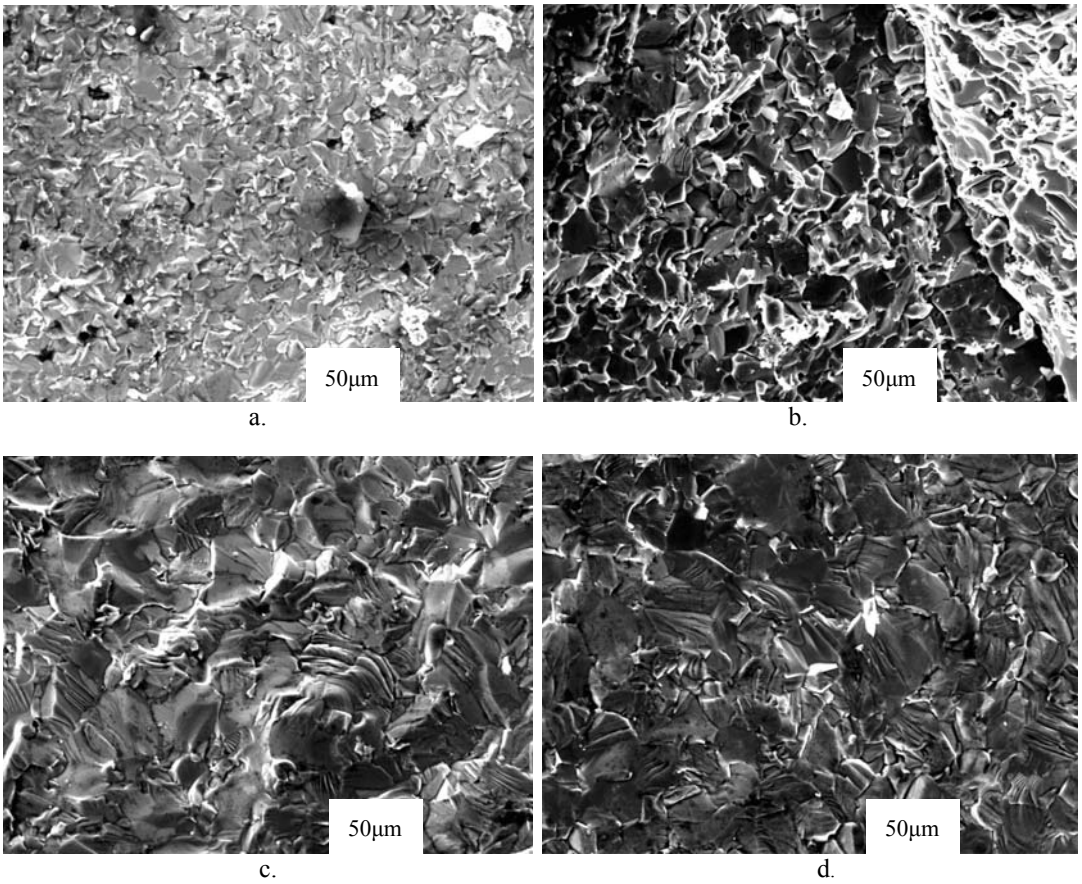


Fig 1. Microstructures of TiC-based cermets with different contents of Mo by SEM:
(a) Ti/Mo=0.9:0.1; (b) Ti/Mo=0.8:0.2; (c) Ti/Mo=0.7:0.3; (d) Ti/Mo=0.7:0.3

Fig.2 shows that there were a lot of transgranular cleavages in (Ti1-xMox)C phase and torn edges resulted by Binder phase torn apart. It is suggested that the interfacial adhesion strength is sufficient high between (Ti1-xMox)C and binder phase. In addition, there are a large of number of slip systems existed in (Ti1-xMox)C particles, so (Ti1-xMox)C cermets particles were easily break away from the slip plane of slip systems when the material

fracture occur. Especially in the (Ti1-xMox)C coarse grains when the material fracture occur complete crystal face and crack may appear, and then ridge shape were formed gradually (as shown in fig.6-b). As the Mo content increased, the trend of crack gradually reduce when (Ti1-xMox)C cermets fracture occurs. As Co was dissolved in (Ti1-xMox)C, the binder phase was decreased. Small plastic deformation was occurred or the plastic deformation is not obviously before (Ti1-xMox)C cermets fracture, bending strength increased greatly.

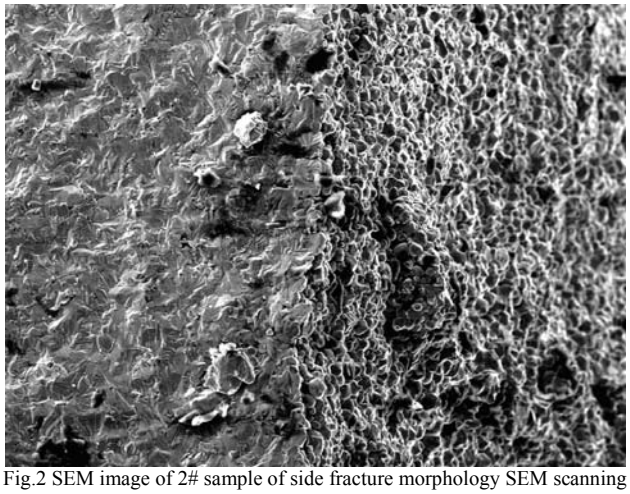


Fig.2 SEM image of 2# sample of side fracture morphology SEM scanning

Four samples' XRD diffraction pattern is shown in fig. 3. From fig. 3 it can be seen that the intensity of the diffraction peak was in 38°, 42°, 61°, 76°, 61°, the main components in the experimental samples are (Ti1-xMox) C. With the increase of Mo, the trend of the diffraction peak is offset to the left, due to the fact that Mo's atomic radius is larger (Mo atomic radius is 1.39×10-10 m). When Mo dissolved into the TiC, lead to TiC interplanar spacing increases, which means the value of d was increased. According to Bragg equation, when d increases, the diffraction series n and diffraction wave were unchanged, so the diffraction Angle theta must be decrescent, leads to the diffraction peak move to the left. Mo was dissolved into the TiC phase gradually and new phase Another Mo gradually dissolved into the TiC phase and the new phase (Ti1-xMox) C was generated.

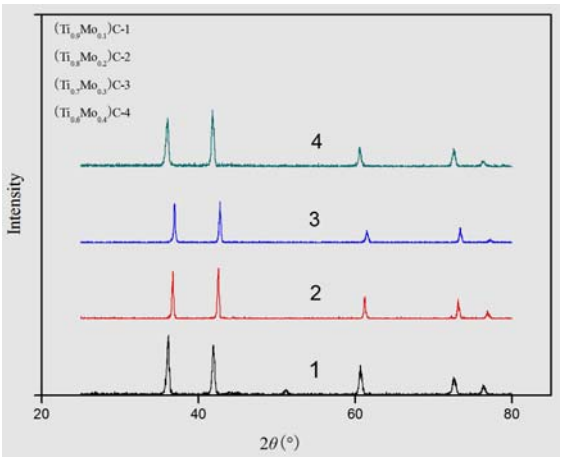


Fig. 3 X-ray diffraction analysis of experimental samples.

B. Effect of Mo on the Mechanical Properties

The addition of Mo would decrease the relative content of the hard phase, which would cause a decrease of hardness a little. As a result, the hardness was not increased obviously with the increase in Mo content [15]. According to engi 200μ cermets bending test method (GB6569-6569) the bending strength was tested. Three point bending test (showed as fig.4) was used for samples with the universal mechanical testing machine. Sample sizes are shown in table 3, the span is 30mm, and loading rate is 0.5mm/min.

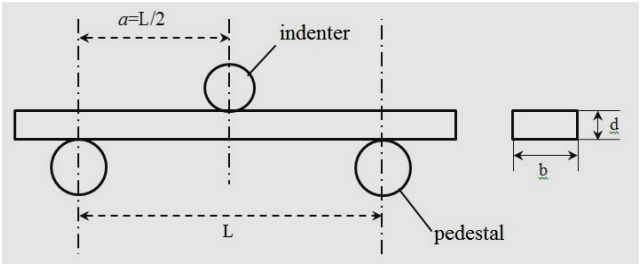


Fig. 4 Bending strength test structure diagram.

TABLE.2 THE SIZE AND SPAN OF SAMPLES

Sample	Support span(L)/mm	length /mm	Width(b) /mm	Thickness(d) /mm
1	30.00	32.46	12.48	4.32
2	30.00	32.36	12.56	4.26
3	30.00	32.74	12.00	4.40
4	30.00	32.00	12.10	4.32

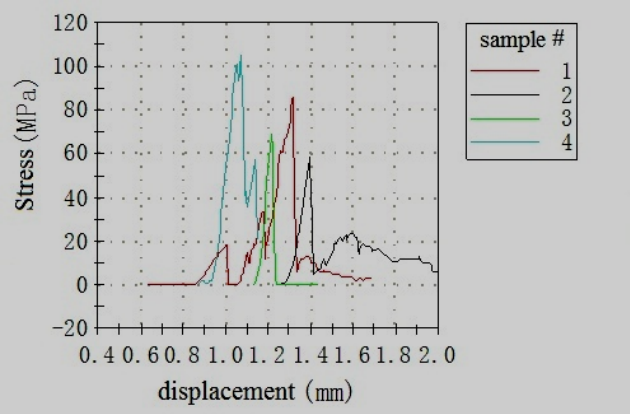
Three-point bending strength design formula is as follows:

$$\sigma_b = \frac{3PL}{2bh^2}(MPa) \quad (1)$$

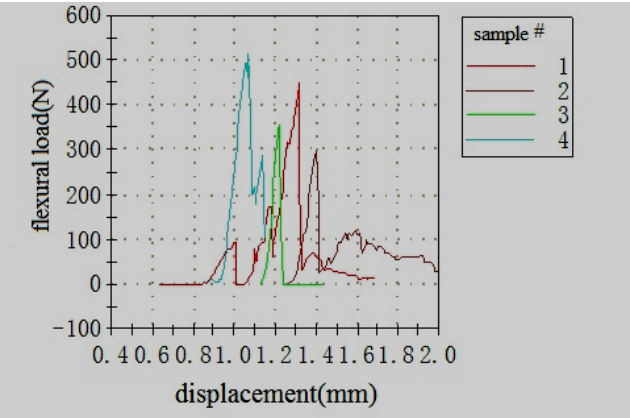
P is the maximum value of breaking load.

Fig.5 shows the relationship of the stress and bending load with the displacements. The bending strength of

experimental material shown in table.4 was calculated by the formula (1) and figure 3. The calculating results were agreed with fig.2.



(a)



(b)

Fig.5 The relationship of the stress and bending load with the displacements.

TABLE.4 BENDING STRENGTH TEST DATA

sample	Support span(L) /mm	Width(b) /mm	Thickness(d) /mm	Bend load /N	Bend stress /MPa
1	30.00	12.480 00	4.320 00	448.748 10	86.702 79
2	30.00	12.560 00	4.260 00	296.610 55	58.558 54
3	30.00	12.000 00	4.400 00	356.376 19	69.029 48
4	30.00	11.880 00	4.320 00	516.874 95	104.909 32

To intuitively show the influence of Mo addition on bending strength of the specimen, with the atomic ratio of Mo/Ti as abscissa and bending strength as the ordinate to draw materials of bending strength with the Mo content variation, as shown in fig. 5.

As shown in fig.6 is the bending strength of different components (Ti1-xMox)C cermets. Mo content had a great effect on the bending strength of (Ti1-xMox)C cermets. With the increase of the content of Mo, the bending strength decreases after increasing first. The reason that the bending strength reduced and then increased is mainly related to its microstructure.

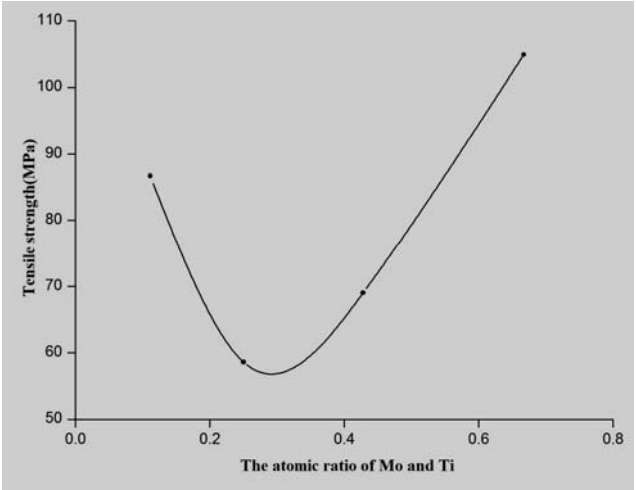


Fig. 6 bending strength trend

When Mo content of (Ti1-xMox)C cermets is relatively small, for example Mo:Ti=0.1:0.9, according to the thermodynamics reaction equation of Ti with C or Mo, it can be found that Ti react with C more easily than Mo. So, when there was a little Mo addition, Ti and C react first, a small amount of brittle TiC was created and the material mechanics performance degradation. When atomic ratio Mo/Ti is 0.25 (i.e., Mo/Ti = 0.2:0.8), the bending strength of specimen appeared a minimum value. This is may be due to the amount of generated TiC in the cermets has reached the maximum value, TiC hard phase was dispersion distribution in metal cermets, make the toughness of the material is greatly reduced, under the action of a small force it will fracture. With the increase of content of Mo, the atomic ratio of Mo/Ti increased from 0.42 to 0.67, bending strength of (Ti1-xMox)C cermets also was increased. There are various causes of this result, one of the most likely is with the increase of Mo addition, a lot of Mo and Ti was formed (Ti1-xMox)C solid solution, enhances toughness and bending strength. Another possibility is that too much Mo was dissolved into the binder phase Co. Mo's atomic radius is 1.39×10-10m, Co's atomic radius is 1.16×10-10m, redundant Mo can be a very good solute dissolved in Co, the effect of Mo is solid solution strengthening binder phase. At the same time, (Ti1-xMox)C grains have been further increased. Generally the WC bending stress is 131MPa. Compared with the bending strength in tab.5, bending strength of the tungsten carbide are larger than the (Ti1-xMox)C sample, but the maximum bending strength of the sample is 104MPa that is closed to the WC. This shows that the Mo addition can effectively improve bending performance of (Ti1-xMox)C cermets, witch is closed to the bending capacity of the WC. It is clear that the strength was

increased by the addition of Mo and further increased with the increase in Mo content. Because of wettability improvement of the liquid to the solid phase by the addition of Mo, the binding strength would increase between the binder phase and the solid phase. In addition, pores will give a very big effect on the strength.

IV. DISCUSSION

The Mo addition has great influences on the mechanical properties of (Ti1-xMox)C cermets, the bending strength maximum value of samples is close to the bending strength of WC. If further improvement taken, it will have good application prospect as a substitute of WC tool material.

The mechanical properties of (Ti1-xMox)C cermets is best when the Mo/Ti ratio is 2:3. It is possible that Mo and Ti was dissolved into Co with the increase of Mo addition and (Ti1-xMox)C was increased gradually, adhesives Co reduced at the same time. (Ti1-xMox)C adhesives bond more closely with binder phase, it needs to be further experimental research.

The results of the experiments can The results of the experiments can be well in conformity with the conclusion that previous studies of (Ti1-xMox)C cermets structure and wettability of Mo. The influence of Co on the wettability and binding strength will be a priority over Ni [16]. Mo addition has improved the wettability of binder phase, and Co has important influence on the performance of the cermets.

V. CONCLUSIONS

(1) The fracture morphology of (Ti1-xMox)C based cermets is mainly large (Ti1-xMox)C particles transgranular cleavage fracture.

(2) Ti and Mo can be a good solution and form stable (Ti1-xMox)C during sintering. Mo's addition changed the wettability of Co, and Co has formed a good binder phase to have very great effect to improve the intensity of (Ti1-xMox)C based cermets. It is due to improve wettability of the binder phase to the hard phase by formation of (Ti, Mo)C solid solution which is wetted easier by Ni and Co liquid than TiC.

(3) The addition of Mo in (Ti1-xMox)C based cermets, enhances the mechanical properties of the metal cermets. When atom ratio of Mo/Ti is 2:3, the bending strength can reach the maximum that is close to the bending strength of WC. The influence of Mo on the hardness of TiC-based cermets was not evident, but on the strength, it was very evident.

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