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Microstructure and Mechanical Properties of Ti(C,N)-based Functional Gradient Cermets Nitriding by Microwave Heating

Abstract: The interaction between nitrogen and titanium carbonitride (Ti(C,N))-based cermets by microwave heating was applied to develop functional gradient cermets. Ti(C,N)-based cermets was densification and nitrided simultaneously above the eutectic temperature, which greatly shortens the sintering time. Experimental results show that a face centered cubic (fcc) rich surface layer was formed at the surface of the cermets. Meanwhile, a new three layers core/rim structure was found in the cermets and its formation mechanism was proposed in this study. The functional gradient material exhibits excellent comprehensive properties.

Keywords: microwave, sintering, microstructure, titanium carbonitride, functional gradient cermets

PACS® (2010). 81.05.Mh, 81.40.-z

DOI 10.1515/htmp-2014-0075
Received May 4, 2014; accepted August 1, 2014;
published online September 18, 2014

1 Introduction

Cutting tools are required to meet higher standards for anti-wear ability as they are being used in more complex thermal-mechanical coupling environments with the development of machining, especially for high-speed machining [1]. Several studies [2, 3] have shown that functional gradient hard materials (FGHMs) with an fcc rich layer can be formed on the surface of hard metal tools by nitriding, and such a process can improve the wear resistance of homogeneous hard metal. Traditional process to fabricate these FGHMs is heating hard metal through the combination of radiation and convection of heat and nitriding in a resistance furnace, and the heat flow is outside-in. Therefore, nitriding should be carried out after the material densified, otherwise when binder melts, the access of the internal pore gas to the outside is blocked and densification will stop, and the mechanical properties will be degraded. The traditional nitriding process to fabricate FGHMs is a two steps process: (1) dense-sintering the hard metal by state-of-the-art industrial sintering methods and (2) nitriding at solid phase [4]. However, diffusion at a solid phase has a much lower rate than at a liquid phase.

Microwave heating is more energy and time efficiency than traditional heating since heat is produced in the bulk of a compact. In addition, there is an inverse thermal gradient takes place at the compact, with a higher temperature in the core than at the surface [5]. So, when microwave sintering materials, the densification of bulk material is inside-out, which provides a potential way to fabricate FGHMs through one process. In this process, densification and nitriding will be achievable simultaneously conducted at the liquid phase since the binder of outside material melts fall behind the inside.

Although substantial work has been done in developing functional gradient hard metals it deals with traditional sintering with a solid phase sintering condition [3, 6–8]. Therefore, in this work, one aim is to nitriding sinter cermets at the liquid phase by microwave heating. Additionally, microstructures and mechanical properties of the samples are investigated.

2 Experimental methods

The raw material with chemical composition of $TiC_{0.7}N_{0.3}$-15WC-10Mo_2C-10Ta/NbC-15Co/Ni (in mass%) was mixed in an industrial state-of-the-art procedure, pressed to green bodies at 300 Mpa, dewaxed at 673 K for 1 hour. The dewaxed sample was placed in a vacuum microwave oven

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saturated in 99.9% pure nitrogen at temperature of 1773 °C for 15 minutes and a frequency of 2.45 GHz. In order to accelerate the heating rate at medium temperature, a nitrogen pressure of 0.2 bar was achieved at 573 K to form microwave plasma heating, and the nitrogen pressure reached 0.8 bar at soaking time. Temperature measurements are taken with a pyrometer.

The strength and hardness of the cermets were measured by three point bending tests and a Rockwell indenter with a load of 60 kgf and dwell time of 5 s, respectively. The microstructure of polished specimens was observed on the cross-section by field emission electroprobe micro-analyzer (FE EPMA, JEOL, JXA-8530F) in back-scattered electron (BSE) mode.

3 Results and discussion

Fig. 1 illustrates the micrograph of the cross-section along with the elements distributions in the gradient zone of the cermets nitriding sintered at 1773 K for 15 min by microwave heating. It can be seen from Fig. 1 that the surface zone exists a 13–15 μm thick layer rich of Ti and N, which is a layer rich in fcc phase. The W and Mo contents decrease from the interior zone to the gradient zone border and then sharply increase just outside the fcc zone border.

When sintering at the nitrogen atmosphere, Ti migrates to the surface due to high affinity of N and Ti; at the same time, W and Mo migrate to internal supplement

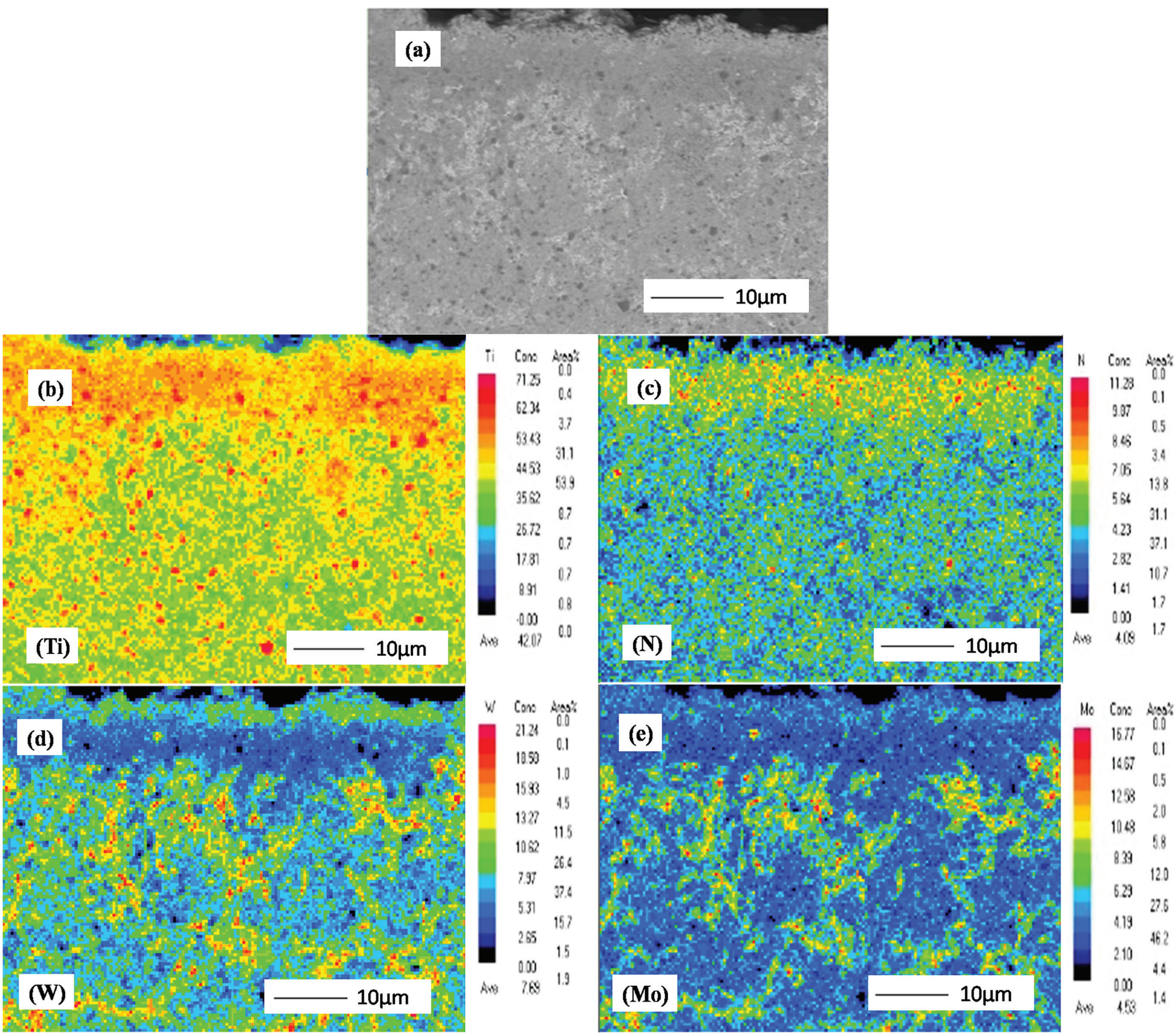

Fig. 1: (a) Micrograph of the cross section and the distribution of the elements, (b) Ti, (c) N, (d) W, (e) Mo in the gradient zone of Ti(C,N) based cermets sintered by microwave heating.

where the vacancy was left by out diffusion of titanium, so the fcc rich outer layer formed. However, in this study, outside the fcc rich layer there is a thin irregular layer about 3–6 μm thick formed, in which Ti and N contents are lower than that of fcc zone, and the W and Mo contents are higher than that of fcc zone but lower than that of the interior zone. This is different from the gradient structure formed by the conventional nitriding sintering. The exact formation mechanism of this kind of layer is still unknown, but it might be reasonably speculated. Since the nitriding is starting from the green bodies, which has a lot of small pores, nitrogen goes into the pores and forms microwave plasma under microwave irradiation at high temperature. Under the effect of high-energy plasma, nitriding reaction occurred on the billet surface. Because the reaction is quick and occurs on certain depth, the fcc phase is formed before the W and Mo on the surface zone diffuse to internal, which hinders the inward diffusion of W and Mo. In addition, the strong coupling effects of Ti and N on the surface zone makes W, Mo migrate outward and formed the outermost layer of the material. The outermost layer has irregular thickness because it is free surface.

Fig. 2 presents the core/rim microstructure of the cermets observed using EPMA/BSE, it can be seen that white core and grey rim (white array in Fig. 2, for simplicity, named S_1) are the major microstructure. There is also a white irregular phase (black array in Fig. 2) and two kinds of core/rim structure being observed: (a) black core, white inner rim and grey outer rim (yellow array in Fig. 2, for simplicity, named S_2); (b) grey core, white inner rim and grey outer rim (red array in Fig. 2, for simplicity, named S_3). S_2 is a typical structure in Ti(C,N)-based cermets with big hard phase particles. The black core is undissolved raw Ti(C,N) hard phase particles. The white

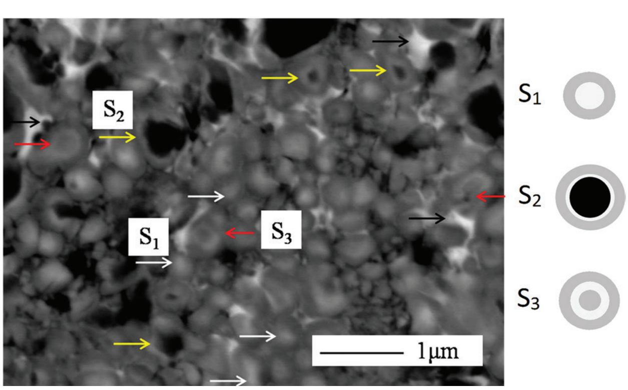

Fig. 2: EPMA (BSE) micrographs of Ti(C,N) based cermets and schematic of the three core-ring structures

inner rim, rich in W and Mo, is formed during the solid-state sintering, and the grey outer rim is formed during the liquid-state sintering. S_1 mainly exists in fine grain TiCN based cermets [9].

It should be noticed that S_3 is clearly found for the first time to the best of our knowledge [9, 10]; obviously its formation mechanism is also unknown. As one can see from Fig. 2, the particle size (including core and inner rim) of S_3 is between that of S_1 and S_2, and also S_2 and S_3 have similar three layers structures. Furthermore, original mixture is made up of ball-milled products of micron Ti(C,N) and other additives, and the distribution of particle size is continuous. Therefore, presumably the S_3 is the product of medium sized particles through dissolving precipitation mechanism. Accordingly, the formation mechanism of S_3 might be described as follows: When the particle size is medium, elements W and Mo infiltrate into Ti(C,N) particles during the solid sintering stage, but migration of elements is a diffusion process and microwave sintering process is very short, W and Mo elements have concentration difference in the inner and outer layers of the Ti(C,N) particles in this stage. In liquid phase sintering stage, although diffusion is enhanced, the W, Mo still cannot penetrate into the Ti(C,N) due to the short sintering time. Therefore, these inner and outer layers of the Ti(C,N) particles with different W and Mo elements contents become the grey core and white inner rim of S_3, respectively. The grey outer rim of S_3 should be formed during liquid sintering, similar to the grey outer rim of S_2.

Ti(C,N)-based functional gradient cermets sintered by microwave heating exhibit excellent comprehensive properties: the transverse rupture strength of 1456 MPa, Rockwell hardness of HRA 90.7, respectively. It is apparent that these properties are even superior to similar composition Ti(C,N)-based cermets reported in the literature [11, 12]. The superior strength and hardness can be attributed to the formation of ultra-fine core/rim structure such as S_1. Additionally, the formation of a new core/rim structure S_3 may enhance the mechanical properties. Although S_3 has three layer structures, the gradual change of composition can reduce the interface stress, which is beneficial to mechanical properties.

According to Janisch [6], When nitrogen in liquid phase, due to the channel of element inward diffusing is blocked, nitride will occur in the surface layer, and presumably porosity cannot shrinkage timely, the mechanics properties of the material will be reduced. However, in the case of microwave sintering, this phenomenon does not occur, the samples have inverse temperature gradient during sintering, therefore, densifying and nitriding occurred in the whole sample, this also contribute the high mechanical properties of the cermets.

4 Conclusions

In this work, Ti(C,N)-based cermets with fcc rich surface layer are successfully fabricated by microwave sintering at 1773 K for 15 minutes at the nitrogen pressure of 0.8 bar. A little W and Mo contained irregular thin layer formed outside the fcc rich layer due to the special mechanism of microwave heating. The cermets are composed of three types core/rim structures. White core and grey rim structure is the main microstructure in the cermets among the three type. Grey core, white inner rim and grey outer rim structure was first found in cermets, which may contribute to excellent mechanical properties.

Funding: This work was financially supported by the Chinese Important National Science and Technology Specific Project (No. 2012ZX04003051) and National Natural Science Foundation of China (No. 51305134 and No. 51275168).

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