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Formation of wear-resistant graded surfaces on titanium carbonitride-based cermets by microwave assisted nitriding sintering

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ABSTRACT

Microwave assisted nitriding sintering was used to form a wear-resistant graded surface on titanium carbonitride (Ti(C, N))-based cermets. The influence of processing parameters on the formation of wear-resistant graded surface layers on cermets was investigated. The nitriding process was carried out at liquid phase sintering temperature and with a maximum nitrogen pressure of 0.08 MPa. The formation of the wear-resistant graded surface layers depended on the temperature. Nitriding at 1430 °C formed a graded structure in which a (Ti, W, Mo, Ta) (C, N) governed microstructure changed into a hard metallic bulk structure with microscopic non-uniformities present in the matrix. A graded structure with only a (Ti, W, Mo, Ta) (C, N) layer was formed when nitrided at 1500 °C and 1530 °C. The microwave assisted nitriding sintering yielded greater nitride efficiency than the traditional sintering. At applied constant nitrogen press, the nitriding rate of the surfaces of samples decreased with increasing temperature, however, that of the bulk of the sample had the opposite tendency.

1. Introduction

Ti(C, N)-based cermets was prepared by a powder metallurgy process, which include mixing, pressing, and sintering. Ti(C, N)-based cermet is a promising material for some industrial applications, such as semi-finishing and finishing work [1,2]. However, their lower wear-resistance limits their further application, i.e. it would prevent its use in high-speed cutting. Due to the higher hardness and absence of a ductile binder phase compared to bulk cermets, a surface layer rich in cubic carbides (fcc-rich layers) formed by nitride treatments yields an improved cutting performance from such cermets: these are referred to as wear-resistant layers [3,4]. General nitride treatments are carried out by resistance heating, for which the heating mechanisms are radiation and convection.

Microwave sintering has several unique characteristics such as: volumetric heating, rapid heating and selective heating [5]. Microwave sintering also shows some advantages compared to traditional sintering [6–8]: enhanced diffusion processes, a reduction in processing time and energy required, inhibition of grain growth, improved mechanical properties, and reduced environmental hazard levels. However, most of the materials have a low capacity to absorb microwave energy at low temperatures [6], in most cases SiC was used to cause hybrid heating during microwave heating [9], but it wastes energy and damages the thermal insulation structure. Tap et al. [10] report a microwave sintering process under a reactive atmosphere to form functionally graded cemented carbides, the process combines simultaneous sintering and nitriding, but they also used SiC as an auxiliary heating unit.

The aim of this work was to form wear-resistant surfaces on Ti(C, N)-based cermets by microwave assisted nitride sintering without an auxiliary heating unit, based on the results of the influence of sintering temperature on the formation of a gradient microstructure on the surfaces of the cermets. To overcome the low heating speed of the cermets at low temperatures, microwave plasma was ignited by microwave irradiation of a rarefied nitrogen, which heated the samples until the samples themselves became heat-absorbent.

2. Experimental work

Ti(C, N)-based cermet samples from a mixture of $TiC_{0.7}N_{0.3}$, WC, TaC/NbC, Mo_2C, Co and Ni were prepared by standard powder metallurgy methods. The composition of the powdered mixture of the cermet is listed in Table 1. The green compacts were sintered in a vacuum furnace heated to 400 °C for 1 h to remove the wax. Finally, the pre-sintered sample was placed in a vacuum microwave oven saturated in 99.9% pure nitrogen at a maximum pressure of 0.08 MPa, a temperature of 1430 to 1530 °C, and a frequency of 2.45 GHz for 15 min. Schematics of the microwave sintering furnace and a typical heating process therein are shown in Figs. 1 and 2. There was no auxiliary heating unit in the heating structure. To accelerate the rate of heating at low temperatures,

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Table 1
Composition of the alloy for nitriding (wt.%).

Component	$TiC_{0.7}N_{0.3}$	WC	TaC/NbC	Mo_2C	Co	Ni
Alloy	Balance	15	10	10	10	5

a nitrogen pressure of 0.02 MPa was achieved at 573 K to induce microwave plasma heating; the nitrogen pressure reached 0.08 MPa by soaking time. Temperature measurements were taken with a pyrometer (Raytek Corp., USA).

The microstructures of the polished specimens were observed, in cross-section, by scanning electron microscopy (SEM, Philips Corp., The Netherlands) and electro-probe micro-analyser (EPMA, JEOL Corp., Japan) in back-scattered-electron (BSE) mode. The phase compositions were detected by an X-ray diffract-meter (XRD, Bruker Corp., Germany). The sintered samples was cut into 1 mm × 3 mm × 3 mm pieces taken from the surface and 3 mm × 3 mm × 3 mm cubes taken from the centre by wire-electrode cutting to measure their nitrogen content with a nitrogen/oxygen analyser (Leco Corp., USA).

3. Results

3.1. Temperature characteristics

Fig. 2 shows the heating characteristics of microwave nitriding sintered cermet in a pure N_2 atmosphere. This can heat the material rapidly at low temperatures through the plasma formed by microwave irradiation ignition of rarefied nitrogen gas in the absence of SiC and other auxiliary heating elements, but the temperature fluctuations were greater than those experienced when using hybrid heating at low temperatures [9]. There were two causes of these temperature fluctuations: the plasma produced was uneven, and the temperature measurement points changed between the Al_2O_3 crucible and the samples with the rotation of the turntable. With increasing temperature, the capacity of a material to absorb microwave energy increased, and the Al_2O_3 crucible heated under thermal radiation from the plasma and the sample; the temperature field became uniform and the rate of heating tended to be stable until a temperature of 1100 °C was reached. When the temperature field tended to a uniform state, microwave plasma and its effects could be suppressed by increasing the nitrogen pressure until pure microwave heating occurred. Cermet remains in its solid phase sintering stage and material shrinkage begins at 1100 °C [11]. The existence of an inverted temperature gradient during microwave heating, which is not present in conventional heating [12], implied

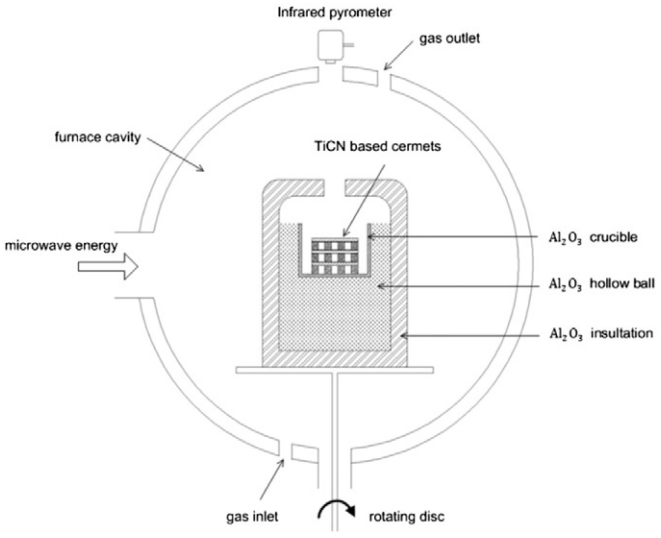

Fig. 1. Schematic of the microwave sintering furnace.

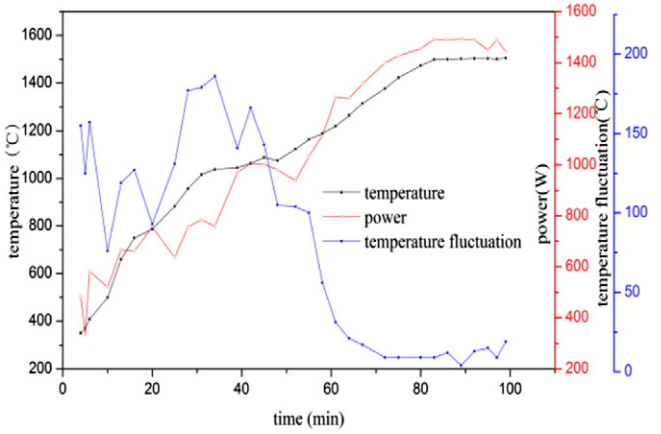

Fig. 2. Heating characteristics of TiCN-based cermets nitrided by microwave heating.

that increasing the nitrogen pressure at temperatures greater than 1100 °C to induce pure microwave heating would be conducive to internal pore eduction during liquid phase sintering, and the mechanical properties of the material will be improved accordingly.

3.2. Surface topography

Fig. 3 shows digital photographs of the prepared samples. The cuboidal samples fabricated by microwave assisted nitriding sintering maintained their original shapes well and neither bubbling nor distortion occurred; the surfaces appeared light yellow in colour. There were no visible flaws in the samples sintered by microwave heating, thanks to the optimisation of their thermal insulation structure and pressure controlled preparation regime. At the same time, micro-cracks caused by uneven temperature distribution at low temperatures were reduced due to the formation of liquid phase during the later stages of sintering.

3.3. Formation of surface gradient layer

Fig. 4 shows the cross-section SEM/BSE images of Ti(C, N)-based cermets sintered at different temperatures. After nitriding at 1430 °C for 15 min (Fig. 4a), the surface of the cermet formed two layers: a grey surface layer, and a bright white transition layer. There were micro-segregations in the substrate, and greyish white, island-like matter distributed throughout the matrix. When the temperature was increased to 1500 °C (Fig. 4b), the grey surface layer grew and the bright white transition layer disappeared. In the substrate, the greyish white, island-like matter disappeared and the colour became a mixed bright white and grey combination. The cross-sectional morphology, when sintered at 1530 °C for 15 min (Fig. 4c), was similar to that observed at 1500 °C. Since these images were obtained under SEM–BSE mode, the brighter colour of the white material indicated that they must contain more heavy metallic elements than its darker counterpart [13].

To further understand the elemental distribution over each different area of the samples shown in Fig. 4, electron microprobe analyses were used to examine the cross-section after treatment at 1430 °C and 1500 °C, respectively. As shown in Figs. 5 and 6, the grey matter contained high elemental Ti and N contents, the greyish white material contained high elemental W and Mo contents, and the bright white material contained the highest elemental W and Mo contents. It was consistent with the results of Fig. 4.

An analysis of the EPMA micrographs in Figs. 5 and 6 pointed to the fact that the surface layer, and transition layer presented noticeable N-enrichment when nitriding sintered at 1430 °C, and the thickness of concentrations exceeding 10% was approximately 35 to 45 μm; however, there were only sporadic elemental Ti enrichment regions, together with the aforementioned elemental W and Mo components. The surface