Preparation of Ultrafine Ti(C,N) Based Cermet Constructed by β-Co and Research on Its Toughening Mechanism

Ying DENG[1,2,a], Xiao-Long JING[1,b], Bing LIU[1,c], Hui CHEN[1], Zhong-Tao JIANG[1] and Xiang XIONG[2,d,*]

[1]Research Institute for New Materials Technology, Chongqing University of Arts and Sciences, Chongqing 402160 , PR China

[2] State Key Laboratory of Powder Metallurgy, Central South University, Changsha 410083, China

[a] dengying.163@163.com, [b] 513730656@qq.com, [c] 846239587@qq.com, [d] xiong228@sina.com

* Corresponding author: E-mail: xiong228@sina.com

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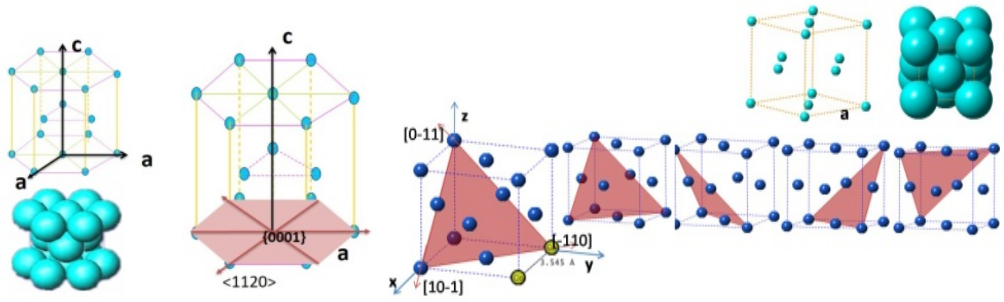
Abstract. Ti(C,N) based cermet material which composed by hard phase and binder phase, has excellent performance, is the best choice for manufacturing industry and military product etc.. However, it's application areas has been limited due to the shortcoming of toughness of hard phase, and a study in this area has important scientific theoretical value and practical significance. The project intends to design a new high tough Ti(C,N) based cermet material through the face-centred cubic cobalt β-Co building reinforced cermet structure and starts a systematic research on the binder phase mechanism. This study base on the toughening mechanism of ultrafine β-Co in cermet materials, the ultra-fine mix-powders 50Ti(C,N)-15WC-10Mo_2C-8TaC-17Co were used as basic ingredients, using high-energy ball milling, spray drying, low pressure sintering technology, Ti(C,N) based cermet of excellent performance was successfully prepared.

Introduction

With the rapid development of the aerospace, military, energy and other modern industry, has put forward higher requirements to the manufacturing and processing technology. Ti (C, N) based cermets material having a low density, high hardness, high wear resistance, etc., is the best choice for modern tool materials[1]. Cermet is a composite material of hard phase and binder phase structure. Wherein the hard phase is of brittleness, lacks toughness. Therefore, the cermet toughening has become one of the main directions of today's cermet material studies.



a b

Fig 1 Crystal structure of cobalt: a.α-Co b.β-Co

As a source of the toughness of cermets, the binder phase is the most critical part of the cermet toughening research. In previous reports, Ti(C,N) based cermets mostly has Ni as binding phase [2-4], but too high Ni content will form a brittle phase Ni_3M [3]. Ni and Co have similar mechanical properties [5]. Co toughness is better because of its wettability to hard phase is better than that of Ni and has a good solid solution effect. But some reports found that excessive Co in the binder phase will make the atoms of the metal phase and the hard phase mismatching increase[6], and the cermets toughness decrease. But some other studies has found that phase interface doping can

improve the phase interface conjunction of cermet[7-8]. Early tests have confirmed that Ti(C,N) based cermet, by using cobalt as the binder phase, and adding metal elements such as Ta, V, Mo to dop, has solved issues on cobalt and hard phase interfacial bonding, atomic matching, etc..

Cobalt, at room temperature, usually presents two kinds of structures: the hcp (α-Co) and fcc (β-Co) structure [9]. α-Co with only three slip systems has worse toughness than β-Co with 12 slip differential systems (figure 1), and β-Co has an identical structure as Ti(C,N), matching better than α-Co, having obvious structure advantages [10]. In addition, β-Co has unique annealing twins ,and shows better robust performance than α-Co. Annealing twins CSL (coincidence site lattice) grain boundary can effectively block cracks, reducing the grain boundary fracture and improve the ductility of the material [11]. Therefore, from the analysis of the structure and properties of the metals, we know β-Co has better strength and toughness than α-Co.

The laboratory has already prepared single-phase β-Co stable at room temperature, and having integrated the early studies of cermets components and pre-preparation process, this study uses Micro/Nanostructured spherical β-Co to substitute Ni, and uses 50% Ti (C, N)-15%WC-10%Mo2C-8%TaC-17%Co of the total component content as the basic component, and uses Mo_2C- 8TaC to improve phase interface, optimize the overall structure of the cermet. The mechanical properties of different grain cermets have been discussed and good results in cermets toughening have been achieved.

Preparation Procedures

Preparation Technique Design

Studies have shown that different compositing methods of cermet powders affect greatly the material properties [12]. This study does high-energy ball milling the mixed powder and then spray-drying so as to overcome composite powders' agglomeration and obtain mix-powders with excellent performance. Furthermore, this study uses ultrafine spherical Co powder with good dispersion that can be sufficiently filled in ceramic gaps and under sufficient mixing conditions, well-coat hard phase powders and avoid agglomeration and segregation[13].

Sintering methods in preparation of cermet are mainly pulse sintering, microwave sintering, low pressure sintering, hot isostatic pressing (HIP) sintering and vacuum sintering, etc.. Of the cermet, since in the sintering process, Ti(C,N) decomposition causes large porosity, using pressure sintering is the effective means to reduce porosity and get cermet with good density. Numerous studies indicate that, in general, particle Ti(C,N) based cermets can get fully dense body at the sintering temperature between 1450°*C* -1500°*C*,. And of the ultrafine system, due to the high activity of the ultrafine cermet powders, whose solid-state reaction is stronger than that of conventional particles, and whose liquid phase appearannce temperature is low, ultrafine Ti (C, N) based cermets' sinter temperature is lower than that of common particle cermets. The sintering temperature of 1450 °*C* can obtain fully dense sintered body.

After a lot of laboratory tests, the ultrafine metal sintering process routes have been determined: 1450 °*C* holding for 105min(figure 2); the conventional cermet particles use traditional techniques: 1500 °*C* holding for 150min.

Experimental Procedure

The experiment has prepared 3 groups of samples, whose ingredients are 50Ti (C,N) -15WC-10Mo2C-8TaC-17 Co. Sample A's materials are 1μm powders, and the traditional cermet preparation process is used ; Sample B's are commercial Co powders. Sample C's are spherical β-Co powders (products of the present study). Ultrafine ceramic samples B and C's experimental matrix material Ti($C_{0.7}$, $N_{0.3}$) powder has an average particle size of about 0.4μm (Figure 7-12); WC average particle size is 0.4μm (Figure 6-1); the rest of the second category of carbide's mean diameter is 0.4-0.5μm, Metal Co is the product of this experiment whose average particle diameter is 0.2μm and the commercial product Co powder with an average particle diameter of 0.5μm (Figure 6-2). And the particle sizes of the comparative Sample A's mix-powders are all 1μm.

The predetermined ratio of a good mix of powder raw materials are put into high-energy ball mill; the ratio of ball and feed is 1: 5 and add 0.5 ~ 0.6L/ kg(raw materials) of alcohol, and add paraffin wax whose weight is 4% of the raw materials and then the mill pot is vacuumized and filled with nitrogen, and then sealed to do the high-speed milling for 48h; After milling, the slurry is discharged and spray-dried, and then mold the mixture, and put it into pressure sintering furnace to do the overpressure sintering ,and the sintering temperature is 1450-1500 ℃. At 15min before the end of sintering, 4MPa argon is filled in. Complete the. sintering and the target is obtained .

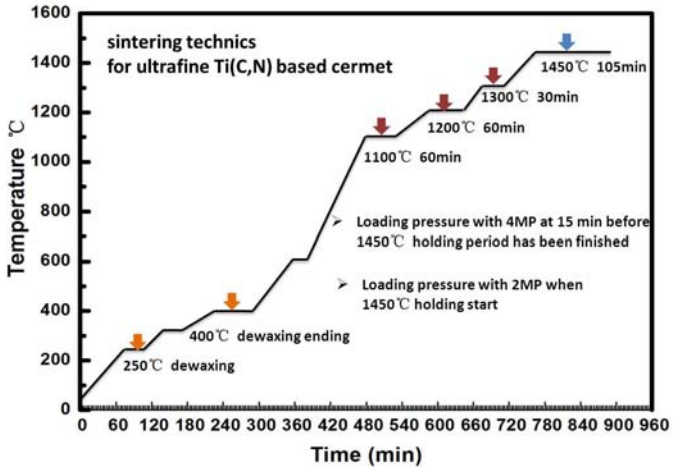


Fig.2 Curve of sintering technics for ultrafine Ti(C,N) based cermet

Morphology Structure Characterization Analysis

Use Japan JEOL-6490LV scanning electron microscope to observe the sample's morphology and grains. Observe Ti(C,N) cermet sample's microstructure in the backscattered electron (back-scattered-electron, BSE) model; Observe the fracture morphology of the sample in the secondary electron mode (Secondary Electron, SE). Use Japan JEOL-2100F field emission TEM to observe the grain morphology, high resolution microstructure and diffraction; the sample is line -cut into sheets of 0.5mm, and is then mechanically thinned to 100μm or less and is then thinned by ion and observed. Use Germany Leica DMI8M microscope to observe the surface porosity of the polished cermet specimen and determine the porosity of the sample according to microstructure map. Use Japanese D / MAX2500VL / PC-type X-ray diffraction (XRD) to do the phase analysis (CuKα, λ = 0.154 nm);

Physical Characterization Analysis

Use WE-100B-type universal material testing machine to test the transverse rupture strength (TRS), using the three-point bending test; the sample size is 35×5.5×5.5 mm, the span is 30 mm, and the loading speed is 0.5mm/min. Use AR- 600 Rockwell hardness to measure the sample's Rockwell hardness(HRA); Use HV-10 Vickers hardness tester to test the material's Vickers hardness(HV), loading 30Kg, and packing 15s.Use the Shetty fracture toughness calculating formula to calculate the fracture toughness values:

$$KIC = 0.0889\ (HV \bullet P / 4L)^{1/2}\ (MPa \bullet m^{1/2}) \quad (1)$$

Wherein, HV is Vickers hardness, P is the applied load value (N), L is the average value of the crack length of the indentation apex (m).

Results and Discussion

Phase Analysis

Figure 3 shows the XRD diffraction patterns of the experimental Ti(C,N) based cermet A, B, C. As shown, the alloy is mainly composed of the two kinds of phase (Ti, Me) (C, N) and Co solid

solution, which explains that after the low pressure sintering all the carbides have been fully soluted into the hard phase Ti(C,N) and the binder phase. Co (111,002) crystal face diffraction peaks shift significantly to the lower angle, which is because Co solid solution has soluted the larger size atoms of W, Mo, Ta, etc.. Wherein A, B have significant hcp Co (101), and its phase fcc crystal plane (200) peak value is significantly lower than the Sample C's, proving that some part of Co in Sample A, B has gone martensitic transformation during cooling process, and has generated hexagonal structure Co. Compared Co crystal face peaks for sample C with PDF15-0806, it can determine that its corresponding crystal planes are (111) (200); both are of fcc structure and their diffraction peaks obviously shift to the lower angles, this proves that in the sintering process of the alloy powders turning into the ceramic body, Co 's crystal structure of sample C has not changed and no martensitic transformation has occurred.

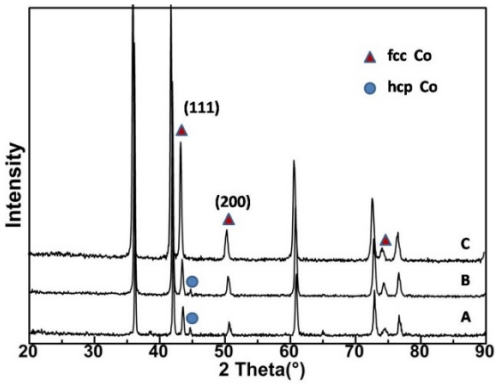


Fig 3 XRD partterns for Ti(C,N) ceramic samples

To sum up, the cermet of using single-phase β-Co as a binder phase, in the entire sintering process (from powders to the liquid and then to the cooled body after sintering), has gone neither forward nor inverse martensite transformation, and the defects due to phase change and defect sources of the sintered body have been reduced, which can effectively improve the overall performance of the cermet.

Microstructural Analysis

Figure 4 is Ti(C,N) based cermet's BSE morphology at 1450℃ sintering temperature. The figure shows Sample A, B, C hard phase microstructures are all typical of core-rim structure, and the hard phase is surrounded by binder phase solid solution. According to the backscatter principle[14], the brighter the area, the higher contents of heavy metal elements (W, Mo, Ta).

Ti (C, N) based cermet's core-rim structure is an important factor determining the quality of the overall performance[15]. In the solid-phase sintering process, with the increase of the sintering temperature, Mo_2C, TaC and WC, and the other second category of carbides are in turn dissolved into the metal Co binder phase, and when the concentration of heavy metals in the binder phase is saturated, (Ti, W, Mo, V) (C, N) precipitates appear, which are coated on the surface of the particles of the undissolved Ti(C,N) of to form a "core-rim" structure[16]. In the subsequent phase sintering process, heavy metal elements are in continuing dissolution - precipitation reaction, but because of lower specific gravity than before, the SEM-BSE precipitation phase morphology appears gray in the outer phase, and its thickness increase with the sintering temperature rising and the holding time increase.

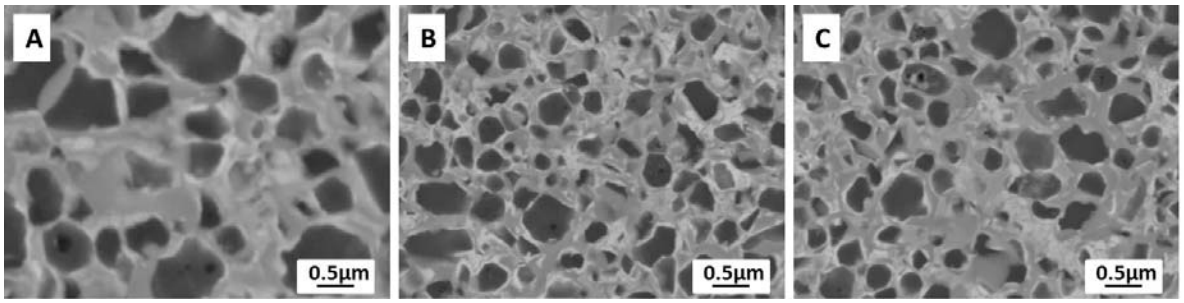


Fig.4 BSE imagines for Ti(C,N)based ceramic under 1450°*C* sintering

The figure shows that in Sample A alloy, the black core size is large (the vast majority of the black core group are undissolved Ti (C, N) particles), and in the sintered body many particles have not formed a complete rim structure, and part of the particles are coated with a thin layer of the ring, and some core ring structures are not fully developed, which explains that, of Sample A, during the sintering, the atomic diffusion, dissolution, precipitation and other processes are not complete, and have been suppressed. In Sample B alloy tissue, large particles of the hard phase core are fine and uniform, whose edges are ball-rounded, and rings fully developed. Meanwhile the relative thickness of the rim phase has increased more than that of Sample B, indicating that of the sample B the liquid phase sintering dissolution- precipitation process is complete. Compared with Sample B, Sample C's rim phase relative thickness is larger. The inner-rim phase (white rim) turns thinner, the outer-rim phase (gray rim) thicker. This suggests that when in liquid phase, W, Mo and other heavy metals diffuse from the inner to the outer, the liquid and the binder phase, layer by layer ,with higher rate and solubility. And in the cooling process, W, Mo, Ta dissolved in Co solid solution are prior again solidified into the liquid-solid interface, resulting in the increase of the thickness of the outer phase. It can be inferred that as the experimental product β-Co has a high surface energy and internal energy, the lattice constant change degree of the binder phase is larger than the average, which result in higher degree of solid solution.

Mechanical Performance Analysis

Take 5 of each of the resulting sintered samples A, B, C, and test the strength, hardness, and fracture toughness and the test values are shown in Table1. As shown in the table, the sample C's overall performance is the best, Sample B follows. Compared to the same grain sample B, Sample C's flexural strength (TRS) has increased by 7%; fracture toughness (KIC) increased by 10%, indicating that β-Co has a robust effect. This is because the fracture mode of sample B, C is mainly intergranular. Meanwhile, the metal binding phase β-Co solid solution strengthening effect is more obvious, and the fracture toughness of the alloy is higher .

Table1 mechanical properties for Ti(C,N) based cermet samples A,B,C

Sample		Mechanical properties		
		TRS(MPa)	HRA	K_{IC}(MPa·$m^{1/2}$)
A	1	1890	90.5	8.97
	2	1834	90.3	8.69
	3	1867	90.7	8.71
	4	1860	90.2	8.76
	5	1866	92.8	8.82
	average	1863.7	90.5	8.79
B	1	1998	91.9	9.97
	2	2033	92.1	10.11
	3	2013	92.2	9.83
	4	2009	91.9	9.75
	5	2019	92.3	10.09
	average	2014.7	92.1	9.97
C	1	2130	92.9	11.82
	2	2180	92.6	11.58
	3	2166	93.0	11.89
	4	2141	92.4	11.68
	5	2155	92.8	11.97
	average	2155	92.7	11.79

Conclusion

The results of the mechanical property analysis support the microscopic structure analysis. Core-rim structure of sample C is optimal with uniform particle dispersion , proving β-Co can effectively improve the overall performance of the cermet body.

(1) β-Co has a 12- slip system, with good toughness, and its sub-structure twins after annealing can stop crack propagation.

(2) Cermet by usingβ-Co as binder phase, due to its good solid phase diffusion rate, at the same sintering temperature, the ring phase is thicker, thus greatly improving the wettability between the hard phase and binder phase, and thereby improving the toughness and strength of the cermet.

(3) During the preparation of the cermets, there is no positive or negative martensitic phase transformation occurred for the single-phase β-Co, and the dislocations and twins produced by the phase change no longer form, thereby the defects have reduced, and the mechanical properties of the cermet has been improved.

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