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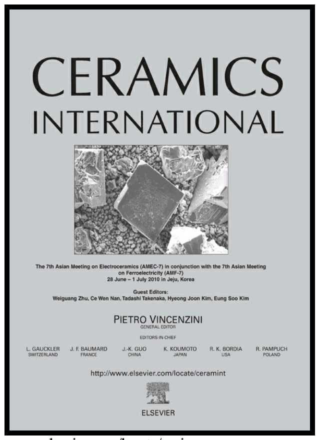

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Enhanced mechanical properties and oxidation resistance of tungsten carbide-cobalt cemented carbides with aluminium nitride additions

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Abstract

Tungsten carbide-cobalt cermets respectively doped with 0, 0.5, 1.0, 1.5 and 2wt.% aluminum nitride were fabricated by the sintering process at 1400℃. The existence of aluminum nitride in the binder phase could refine tungsten carbide grains and reinforce the obtained cermets. The cermets with 1.0wt.% aluminum nitride exhibited the higher hardness of 17.1GPa and transverse rupture strength of 3120MPa, compared with 15.6GPa and 2500MPa of the pure cermets. Owing to the addition of aluminum nitride, a high oxidation resistance was measured in cermets with 2.0wt.% aluminum nitride, which is nearly 1.9 times than that in the pure cermets.

Keywords: Cermets; Ultrafine-grained microstructure; Aluminum nitride; Mechanical properties; Oxidation

1. Introduction

Cemented carbides are multiphase materials composed of a metal ceramic and a cobalt binder. Tungsten carbide cermets are widely used in the machining, drilling, cutting, forming and mining tools fields where the high hardness, wear resistance and good strength are required [1-3]. Refining tungsten

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carbides grain size can significantly improve the mechanical properties of the hardmetals [4,5]. The most effective way of inhibiting the ultrafiner WC grain growth in the sintering process have usually depended on the addition of VC, Cr_3C_2. However, the degradation of mechanical properties at high operating temperatures is mainly due to the oxidation resistance of WC-Co, which is a property for ensuring an adequate cutting performance in metal cutting operations at temperatures above 600℃[6]. Moreover, the addition of VC, Cr_3C_2 can't enhance the oxidation resistance of cemented carbides. The oxidation behavior and mechanism of WC–Co hardmetals were investigated at temperatures between 600 and 1000℃, which can obtain a linear correlation between mass gain and time for WC-Co alloys in the oxidation process, and the oxide layers of WC-Co cemented carbides exhibit a compact structure, mainly consist of WO_3 tungsten oxide and $CoWO_4$ tungstates[7,8]. The most effective ways of controlling the oxidation of WC-Co alloys at the elevated temperature have depended on the addition of carbides powders. The additions of cubic refractory carbides (TiC and TaC) have been observed to improve the oxidation resistance of WC-Co grades owing to the presence of TiO_2 and Ta_2O_5 in the oxide layers. However, an amount of added TiC or TaC in WC-Co cemented carbides can induce that dissolved TiC or TaC separates out mainly as the brittle honeycombed (Ti,W)C or (Ta,W)C cubic solid solution depending on the dissolution-reprecipitation in the sintering process [9,10], which can lead to an inhomogeneous microstructure and damage the mechanical properties of the cemented carbides.

Herein we present a new approach to improve the oxidation resistance and enhance mechanical properties of WC-Co cemented carbides simultaneously. The aluminium nitride is resistant enough to high-temperature oxidation and can be used as a refractory material up to 1100℃[11]. The addition and mechanism of aluminium nitride in the WC-Co cemented carbides has not been reported. By a combination of experimental work and measurement, the main mechanisms in WC-Co cemented carbides affecting the mechanical properties and oxidation resistance of aluminium nitride could be revealed. With the existence of aluminium nitride, a dramatically improved combination of mechanical properties and oxidation resistance of WC-10Co-1.0AlN (in wt.%) materials was obtained.

2. Experimental procedures

The WC-10Co cemented carbides, containing 0, 0.5, 1, 1.5 and 2 wt.% AlN, were prepared in the present work. WC (0.2 µm average size), Co (0.8µm average size) and AlN (0.3µm average size) powders were used as the base materials, which were mechanically milled in a planetary high-energy ball mill with four jars in methanol under argon atmosphere, using WC-8 wt% Co milling vial and media for 24 hours at the milling speed of 250r/min and the ball-to-powder weight ratio of 5:1. The composite powder was mixed with 1 wt.% paraffin, granulated and compressed into a rectangular plate under a uniaxial pressure of 200 MPa. Sintering was carried out by a sinter-HIP at 1400 °C for 60 min in Ar atmosphere with a gas-pressure of 5 MPa. After sintering, the alloys were cooled to room temperature at the speed of 25 °C/min in the vacuum furnace. Alloy samples having dimensions of 20×6.5×5.25 mm^3 were prepared for microstructural analysis and mechanical properties measurement.

The density of the sintered alloys was measured by Archimedes method. The sintered alloys were grinded and polished with diamond pastes. The microstructure observation of the alloys as well as the compositional analysis of some certain phases was conducted using a FEI Nano230 scanning electron microscope (SEM). The carbide grain sizes and the mean free path of the sintered specimens were determined using photoshop software based on the SEM images. More than 300 carbide particles and binder phase were measured to obtain statistically meaningful results. Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) observations were carried out in JEM-2100 microscope at 200 kV. The hardmetals foils for TEM were prepared by the ion milling. The microstructural morphologies and the phase compositions were characterized by a JEOL JXA8530F electron microprobe analyser (EPMA). The hardness was measured by the Vickers indentation with a load of 30 kg. The transverse rupture strength was tested by the 3-point bending method with INSTRON 3369. The thermal tests were performed and recorded during isothermal treatments at 800℃ for a series of dwelling time.

3. Result and discussion

The microstructures of the WC-Co-AlN cermets, which were prepared by the sinter-HIP densification of the composite powders, were shown in Fig. 1. The WC average grain size of WC-Co cemented carbides was about 750 nm, which has a relatively inhomogeneous distribution in the binder phase and the abnormal grain growth in the microstructure without the AlN addition. Moreover , the WC grain size of alloys decreased obviously with the increase of AlN content. The WC grain size reduces to 720 nm when 0.5 wt.% AlN content was added. After adding 1.0 wt.% AlN, the mean grain size was decreased to 650 nm. The mean free path of binder phase in WC-Co hardmetals is 150nm, which has a relatively inhomogeneous distribution in the microstructure. With the increase of AlN content, the mean free path of hardmetals with 0.5 wt.% AlN addition reduces to 140nm. When 1.0 wt.% AlN content was added, the mean free path was 95nm. After adding 1.5 and 2.0 wt.% AlN, the mean free path was increased to 105nm and 120nm. The hardness and transverse rupture strength values of the alloys with AlN addition were higher than that of the base alloy. The measured mechanical properties of the prepared WC-10wt%Co cemented carbides with AlN additions were listed in Table 1, together with comparisons from the literatures whose additives were TiC or TaC added by the ball milling. The hardness and transverse rupture strength values of the sintered WC-10wt%Co-1.0wt%AlN cemented carbides was obviously higher, as compared with the values reported in the references 12 and 13, which can use TiC or TaC as the oxidation resistant additives. Traditionally, the addition of TiC and TaC was the most effective method to inhibit the oxidation phenomenon of WC-Co cemented carbides in the high temperature applying process. However, the existence of TiC and TaC could induce the formation of the brittle honeycombed (Ti,W)C or (Ta,W)C cubic solid solution, which could damage the mechanical properties of the cemented carbides and restrict the robustness and application fields of WC-Co cermets. Fig. 2 showed the evolution of the specific mass gain with time observed during oxidation at 800℃, which revealed that the oxidation kinetics follows a linear law independent for the WC-Co-AlN cemented carbides. The mass gain rate could depend on the composition of the cemented carbides [14]. The existence of AlN could reduce the weight gain rate obviously, which meant a tremendously increase in oxidation resistance of WC-Co cermets. Moreover, the oxidation resistance was higher for the cemented carbides with higher AlN content. The high oxidation resistance was measured in WC-Co cermets with 2.0wt.% aluminum nitride, which is nearly 1.9 times than that in the pure cermets.

To clarify the distributions of various alloying elements in the cemented carbides and investigate the microstructure of the WC-Co-AlN cermets, EPMA of cemented carbides were performed. Fig. 3 showed the elemental distributions of W, C, Co, Al and N atoms in the microstructure of WC-Co-1.0%AlN. In the microstructure of WC-Co-1.0%AlN, two types of phases with different BSE contrasts and atomic concentrations were reveal as W,C-rich and Co-rich areas. Moreover, Al and N atoms were mainly concentrated on the Co-rich areas. The EPMA mappings in the WC-Co-1.0%AlN indicated that the Co binder phase were rich in Co, Al, N atoms.

The morphology and the structure of the WC-Co-AlN cermets were further characterized by intensive HRTEM analyses. Fig. 4a showed a typical WC-Co microstructure. Combined with Fig. 3

that Al and N overlap with Co, HRTEM of Co binder phase was performed in Fig. 4b. Further TEM analysis (Fig. 4b) proved that Al,N-rich particles mainly could exist inside the Co binder phase grains. It could be seen from Fig. 4b that the nanoparticles have formed the phase interface with Co matrix phase in semicoherent interface and there are a mass of edge dislocation around the nanoparticle. According to the analyse of crystal structure, the HRTEM image of the binder phase indicated that the matrix phase was Co (fcc structure) and the nanoparticles was AlN (fcc structure). Moreover, the grain size of AlN nanoparticles was 8-10nm.

It can be seen from Fig. 1 and Table 1 that the existence of AlN can refine the microstructure of WC-Co cemented carbides and improve the mechanical properties of cermets. In the sintering process of cermets, WC dissolves in the binder phase which is presumably spread around the WC grains at the elevated temperature, and W and C can reprecipitate as WC from the oversaturated binder phase onto existing during isothermal holding and cooling [15]. The conventional method of inhibiting the WC grain growth is adding VC and Cr_3C_2 into the raw powder mixtures as grain growth inhibitors [16]. However, the addition of VC, Cr_3C_2 can't enhance the oxidation resistance of WC-Co alloys. The addition of TiC or TaC can induce that the formation of brittle honeycombed cubic solid solution in the sintering process, which can improve the oxidation resistance of cermets and reduce the mechanical properties of the cermets. Fig. 3 and 4 show that the AlN nanoparticles can exist in Co binder phase. According to the mechanism of inhibiting the WC grain growth, the dissolution of AlN in the cobalt binder phase may produce a rich AlN layer in the binder phase and inhibit the growth of finer WC particles depending on the dissolution-reprecipitation mode. The existence of AlN can hinder the growth of WC grain and the densification process of cemented carbides. It can be seen from Fig. 2 that the existence of AlN can reduce the weight gain rate at 800℃ and improve the oxidation resistance of WC-Co cermets. The oxide layers of WC-Co oxidized at 800℃ can exhibit a compact structure, mainly consisting of WO_3 and $CoWO_4$ [17]. Owing to the fact that the surface of AlN can form a compact Al_2O_3 layer at the elevated temperature and inhibit the diffusion of oxygen element, the AlN nanoparticles existed in the Co binder phase uniformly can hinder the oxidation process of binder phase and reduce the diffusion rate of oxygen element. Therefore, WC-Co cemented carbides with the AlN addition can obtain the ultrafine WC grains, obviously higher mechanical properties and oxidation resistance.

4. Conclusions

In summary, a new approach to control the growth of WC grain, improve the mechanical properties and oxidation resistance of cermets simultaneously was developed in the present work. By a combination of experimental work and measurement, a dramatically improved combination of mechanical properties and oxidation resistance of WC-10Co cemented carbides with the AlN additions was obtained. In the sintering process, the less AlN in the WC-Co cermets can inhibit the growth of finer WC particles depending on the dissolution-reprecipitation mode. WC-Co-AlN cermets with the homogeneous and fine microstructure, can exhibit the higher hardness and transverse rupture strength. The AlN nanoparticles existed in the Co binder phase uniformly can hinder the oxidation process of binder phase and reduce the diffusion rate of oxygen element in high temperature circumstance. Using this method, the homogeneity of the microstructure, excellent mechanical properties and oxidation resistance in cemented carbides can be achieved synchronously.

Acknowledgments

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References

[1] D.D. Phuong, P.V. Trinh, L.V. Duong, L.D. Chung, Influence of sintering temperature on microstructure and mechanical properties of WC-8Ni cemented carbide produced by vacuum sintering, Ceramics International, 42(2016) 14937-14943.

[2] V. Bonache, M.D. Salvador, V.G. Rocha, A. Borrell, Microstructural control of ultrafine and nanocrystalline WC-12Co-VC/Cr3C2 mixture by spark plasma sintering, Ceramics International, 42(2011) 1139-1142.

[3] J. Xiong, Z.X. Guo, M. Yang, W.C. Wan, G.B. Dong, Tool life and wear of WC-TiC-Co ultrafine cemented carbide during dry cutting of AISI H13 steel, Ceramics International, 39(2013) 337-346.

[4] A. Petersson, J. Agren, Constitutive behaviour of WC – Co materials with different grain size sintered under load, Acta. Mater. 52 (2004) 1847-1858.

[5] X. Wang, H. Wang, R. Moscatelli, X. Liu, X. Song, Cemented carbides with highly oriented WC grains and formation mechanisms, Materials Science Engineering A659 (2016) 76-83.

[6] X. Shi , H. Yang , G. Shao ,X. Duan ,S. Wang, Oxidation of ultrafine-cemented carbide prepared from nanocrystalline WC-10Co composite powder, Ceram. Int. 34 (2008) 2043-2049.

[7] F. Lofaj, Y.S. Kaganovskii, Kinetics of WC-Co oxidation accompanied by swelling, J. Mater. Sci. 30 (1995) 1811-1817.

[8] M. Aristizabal, J.M. Sanchez, N. Rodriguez, F. Ibarreta, R. Martinez, Comparison of the oxidation behaviour of WC-Co and WC-Ni-Co-Cr cemented carbides, Corrosion Science 53 (2011) 2754-2760.

[9] G. Ostberg, K. Buss, M. Christensen, S. Norgren, H.O. Andren, D. Mari, G. Wahnstrom, I. Reineck, Effect of TaC on plastic deformation of WC-Co and Ti(C, N)-WC-Co Int. J. Refract. Met. Hard Mater. 24 (2006) 145-154.

[10] C. Barbatti, J. Garcia, P. Brito, A.R. Pyzalla, Influence of WC replacement by TiC and (Ta,Nb)C on the oxidation resistance of Co-based cemented carbides, Int. J. Refract. Met. Hard Mater. 27 (2009) 768-776.

[11] V.A. Lavrenko, A.F. Alexeev, Oxidation of sintered aluminium nitride, Ceramics International, (9) 1983, 80-82.

[12] N. Li, W. Zhang, Y. Du, W. Xie, G. Wen, S. Wang, A new approach to control the segregation of (Ta,W)C cubic phase in ultrafine WC-10Co-0.5Ta cemented carbides Scr. Mater. 100 (2015) 48-50.

[13] S. Huang, J. Xiong, Z. Guo, W. Wan, L. Tang, H. Zhong, W. Zhou, B. Wang, Oxidation of WC-TiC-TaC-Co hard materials at relatively low temperature, Int. J. Refract. Met. Hard Mater. 48 (2015) 134-140.

[14] S.N. Basu , V.K. Sarin, Oxidation behavior of WC-Co, Mater. Sci. Eng. A 209 (1996) 206-212.

[15] X. Wang, Z.Z. Fang, H.Y. Sohn, Grain growth during the early stage of sintering of nanosized WC-Co powder, Int. J. Refract Met Hard Mater. 26 (2008) 232-241.

[16] C.B. Wei, X.Y. Song, S.X. Zhao, L. Zhang, W.B. Liu, In-situ synthesis of WC-Co composite powder and densification by sinter-HIP, Int. J. Refract Met Hard Mater. 28(2010) 567-571.

[17] M. Jafari, M.H. Enayati, M. Salehi, S.M. Nahvi, C.G. Park, Comparison between oxidation kinetics of HVOF sprayed WC-12Co and WC-10Co-4Cr coatings, Int. Journal of Refractory Metals and Hard Materials 41 (2013) 78-84.

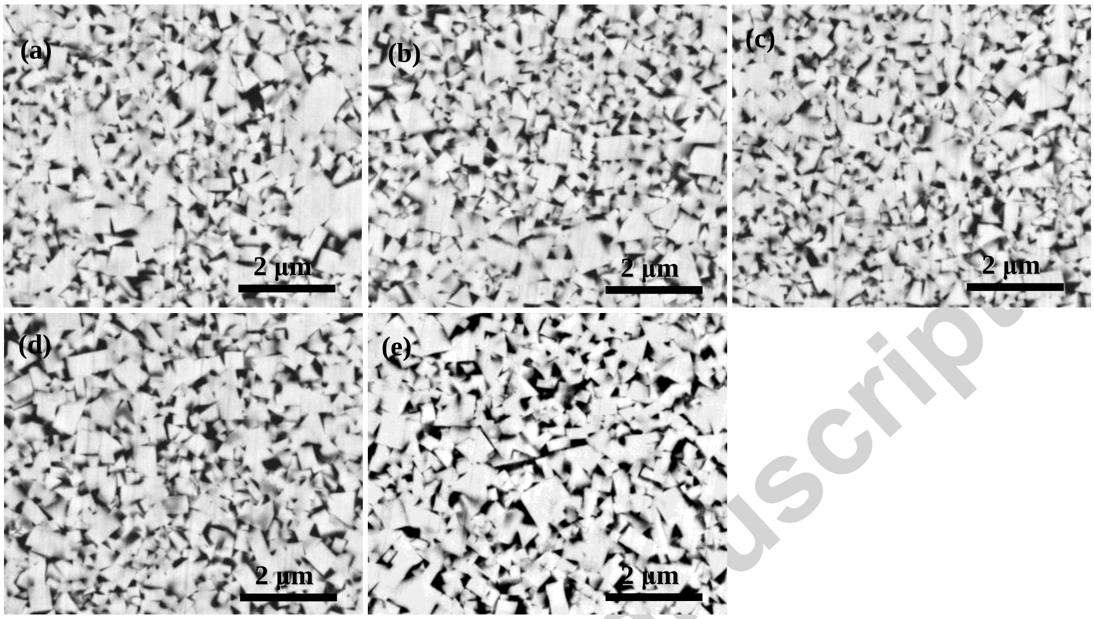

Fig. 1. SEM images of WC-10wt%Co alloys with different AlN content:

(a)0%AlN,(b)0.5% AlN,(c)1.0% AlN (d)1.5% AlN (e)2.0% AlN

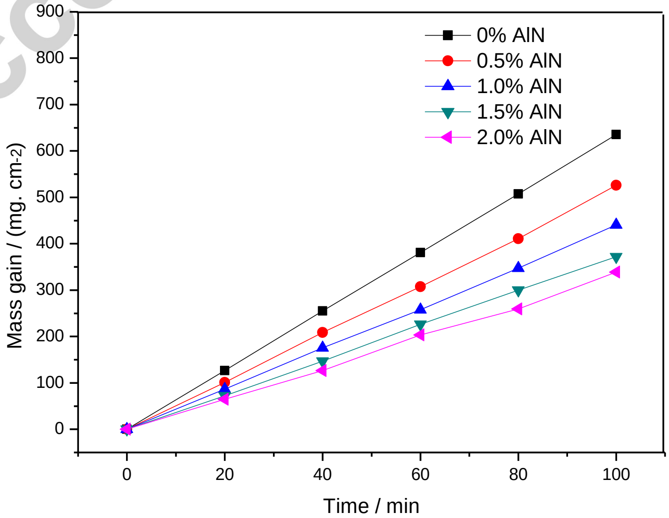

Fig. 2. Specific mass gain vs. time corresponding to WC-Co-AlN cemented carbides

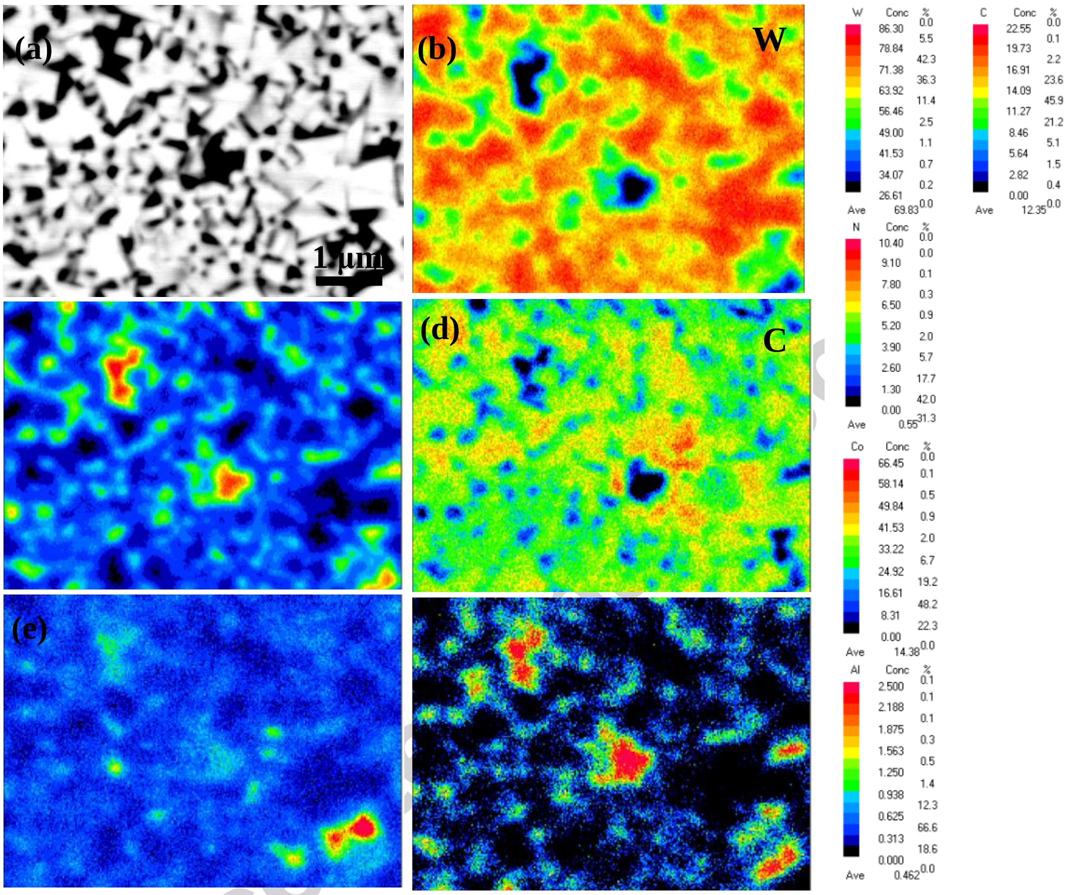

Fig. 3. Section-distribution of the elements in WC-Co-1.0AlN: (a) SEM image，(b) W element，(c) Co element，(d) C element，(e) Al element，(f) N element

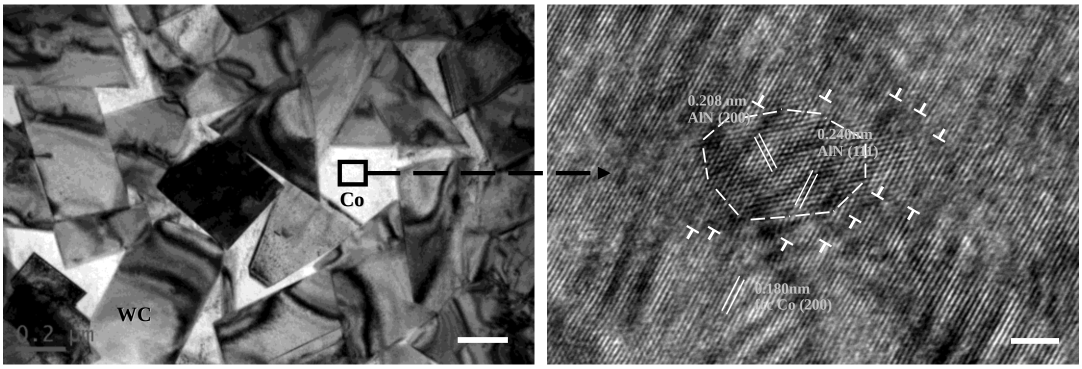

Fig. 4. TEM image of WC-Co-1.0AlN(a) and the corresponding high resolution TEM (HRTEM) image of binder phase(b)

Table 1. Properties of the WC-10wt%Co alloys with different AlN content prepared by sinter-HIP

Properties	Relative density(%)	Average grain size (nm)	Mean free path (nm)	Vickers hardness (GPa)	Transverse rupture strength (MPa)
WC-10Co	99.3	750	150	15.6	2500
WC-10Co-0.5AlN	99.2	720	140	16.6	2630
WC-10Co-1.0AlN	98.9	650	95	17.1	3120
WC-10Co-1.5AlN	98.2	650	105	16.8	2820
WC-10Co-2.0AlN	97.9	660	120	16.3	2560
WC-10Co-0.5Ta [12]	-	-	-	14.6	1760
WC-10Co-4.28TiC-12TaC [13]	-	-	-	15.5	2200