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TiTaCN-Co cermets prepared by mechanochemical technique: microstructure and mechanical properties

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Abstract

Microstructure and mechanical characterization of (Ti,Ta)(C,N)-Co based solid solution cermets prepared by two mechanochemical synthesis processes (one- and two-step milling) and a pressureless sintering in protective helium atmosphere. Materials with composition of $Ti_xTa_{1-x}C_{0.5}N_{0.5}$-20%Co with two different Ti/Ta ratios (x = 0.9 and x = 0.95) were developed to prepare four groups of experimental materials. Microstructures were observed using confocal microscopy and grain size was evaluated using image analysis. Mechanical testing was carried out using nanoindentation equipment and nanohardness and indentation Young´s modulus were obtained. Mechanical properties of individual phases were measured using single load/unload method with 20 mN maximum load (40 mN/min loading rate and maximum 10 s holding time for each indent). Mechanical properties of each material as a bulk were obtained also by single load/unload method with 300 mN maximum load (600 mN/min loading rate and maximum 10 s holding time). The resulting mechanical properties were comparable to that of typical industrial hardmetal cermets. Two-step milling resulted in finer microstructure but a wider range of grain size distribution. No significant dependence between mechanical properties and number of milling steps was found. However, the materials with higher amount of Ta showed slightly higher indentation elasticity modulus.

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Keywords: cermet; hardmetal; mechanochemistry; hardness, indentation

1. Introduction

Modern hardmetals used to machine demanding materials such as steels with high strength and/or hardness, complex alloys, and similar, rely on very hard, usually some sort of ceramic, particles placed inside or bond together by metal based matrix, often some solid solution. A typical example is WC-Co cermet, used for cutting, machining, and other type of tools. Hard components there are made of tungsten carbide with very high hardness and excellent abrasion resistance [1]. The soft Co based binder provides sufficient fracture toughness. Suitable stiffness can in the WC-Co be controlled by the binder content - less Co makes the composite stiffer and vice versa [2]. Recently there has been an effort to replace the tungsten based materials with other alternatives. Metal-ceramic composite materials made from Ti(C, N) are currently being introduced as cutting tool materials because of their good lifetime, slow wear and good chemical stability at high temperatures [3,4]. Titanium carbonitride, Ti(C,N), is a solid solution of the TiC-TiN system. It has high melting point, high thermal and electrical conductivities, good thermal and chemical stability [5-7]. These materials are potentially lighter and more environmentally friendly than WC-Co. A major problem in the use of metal-ceramic composite materials of Ti(C, N) type as replacement for the WC-Co in large scale industrial market is their lower strength. This lower strength is attributed to the ceramic particles. It can be improved at the expense of either hardness, which increases with the increasing volume fraction of hard particles, a reduction in size of these grains and the distance between them. Heavy metals improve the surface quality allowing excellent cleavage resistance, machinability and

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dimensional accuracy of the workpiece. Regarding the hard grains, their core is usually composed of dissolved Ti (C, N) particles in the original pre-sintered metal-ceramic composites [8]. Boundary phase is formed during the liquid phase sintering when the complex carbonitride solid solution containing titanium and other transition metals precipitates from the supersaturated binder phase, which consists of Ni, Co or their alloys and undissolved core particles. The transition between the core and the edge can generate residual stresses that promote cracking and consequent reduction in toughness of materials [8]. For further improvement of their properties, other binary carbides (e.g. NbC, TaC, Mo_2C) are usually added. TaC is often used to enhance stability at higher temperatures, hardness, thermal shock and creep resistance [3,9,10].

Mechanochemistry is an interesting method of chemical synthesis in solid state materials. It usually uses high energy milling [11-13]. It is potentially cheap and easily scalable technique where dissolution or melting of the reactants is not required.

The aim of this work was to prepare a series of alternative hardmetal systems by means of high energy milling and to characterize them from the point of view of microstructure, hardness and modulus of elasticity.

2. Experimental procedure

2.1. Materials

The experimental materials were prepared by high energy milling which utilizes mechanically induced self-sustaining reaction (MSR) from commercially available pure powders [9,14,15]. The starting materials were: Titan powder (purity 99%, grain size < 44 μm, StremChemicals); Tantalum powder (purity 99,6%, grain size < 44 μm, Alfa-Aesar); Graphite powder (grain size < 53 μm, Fe ≤ 0.4%, Merck); Cobalt powder (purity 99.8%, grain size < 150 μm, StremChemicals).

Milling and homogenization was realized in a modified planetary ball mill (Planetary Mill Pulverisette 4, Fritsch). 46.5 g of an elemental powder mixture together with tempered steel balls (15, d=20 mm, m=32.6 g) used as milling medium were placed in a 300 ml tempered steel vial (67Rc) and milled under 0.6 MPa of high-purity nitrogen gas (H_2O and $O_2 \leq 3$ ppm, Air Liquide) The powder-to-ball mass ratio (PBR) was ~1/10.5, and a spinning rate of 400 rpm for both the rotation of the supporting disc and the superimposed rotation in the direction opposite to the vial was employed. High energy input activated chemical processes and that lead to MSR and consequently to creation of titanium and tantalum carbonitrides.

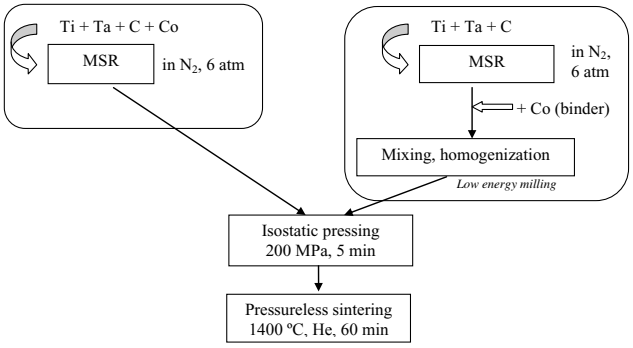

Fig. 1. Schematic of preparation of experimental materials – one step (left) and two-step milling (right).

The final mixtures for sintering were prepared by two ways – one step and two step millig, Fig. 1. In one step milling all starting powders were milled together from start together with cobalt binder. In two-step milling first Ti, Ta, and C powders were milled in nitrogen atmosphere, and only after the MSR had taken place and (Ti,Ta)(C,N) had synthesized, the Co powder was added.

The prepared mixtures were isostatically pressed at 200 MPa for 5 mins. Then they were pressurelessly sintered at 1400 ºC for 60 min in protective He atmosphere.

Resulting samples were discs of 20 mm diameter and height around 5 mm. Four different experimental states of $Ti_xTa_{1-x}CN$-20%Co were prepared with two different Ti/Ta ratios and two ways of milling, as it is summarized in Tab. 1.

Table 1. Experimental materials: notation, composition, milling type.

Material	Ti / Ta ratio	Milling
90/10-1	0.9 (Ti) / 0.1 (Ta)	1 step
90/10-2	0.9 (Ti) / 0.1 (Ta)	2 steps
95/5-1	0.95 (Ti) / 0.05 (Ta)	1 step
95/5-2	0.95 (Ti) / 0.05 (Ta)	2 steps

2.2. Experimental methods

The chemical composition was studied by X-ray diffraction and reported in detail elsewhere [8]. The microstructures were observed on polished surfaces using light microscopy where clear contrast between carbide / carbonitride grains and cobalt binder could be seen. Microstructure parameter such as volume fraction of phases, grain size and shape, were evaluated using image analysis by means of analytical software ImageJ 1.47e.

Mechanical properties were measured by means of instrumented indentation. Instrumented indentation represents a modern technique which, unlike the traditional hardness testing, does not rely on observation of the indent made by hard tip on the surface of the tested material. It rather continuously records the depth of penetration (h) into the material with respect to the actual applied load (P). The result is a loading, or P-h, curve as it is schematically shown in Fig. 2. From the known geometry of the tip and its material properties a number of data about the tested material can be inferred.

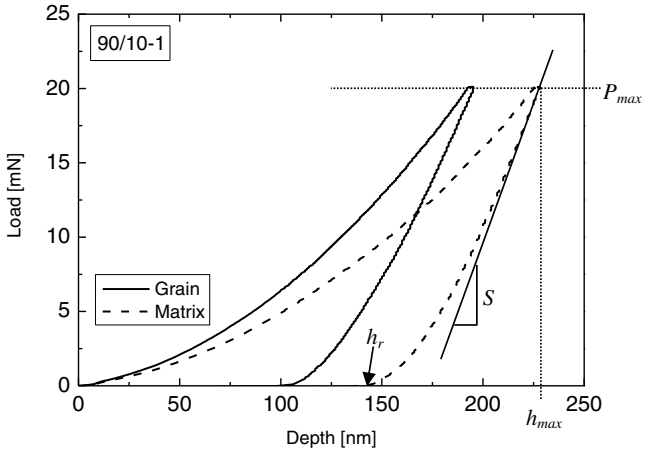

Fig. 2. Typical load (P) vs. penetration depth (h) curves of a load-unload instrumented indentation tests for ceramic grain and metallic binder (material 90/10-1), where the designation of various quantities is illustrated: the maximum load (P_{max}), maximum penetration depth (h_{max}), residual depth (h_r), and contact stiffness (S). After [16].

Indentation hardness, H_{IT}, is calculated as the mean pressure over the contact area

$$H_{IT} = \frac{P_{\max}}{A(h_c)} \tag{1}$$

where $A(h)$ is the contact area as function of depth of penetration (h), which for Berkovich tip is:

$$A(h) = 24.5h^2 \tag{2}$$

From the unloading part of the P-h curve the so-called contact stiffness S is calculated

$$S = \frac{dP}{dh}, h = h_{\max} \tag{3}$$

The contact depth, h_c, is estimated as

$$h_c = h_{\max} - \varepsilon \frac{P}{S} \tag{4}$$

where ε is a geometric factor, which for Berkovich indenter tip is 0.74. Based on these results also elastic response of the system can be evaluated as

$$E^* = \frac{\sqrt{\pi}}{2}\frac{S}{\sqrt{A(h_c)}} \tag{5}$$

where E^* is a system composite modulus of elasticity whose value is

$$\frac{1}{E^*} = \frac{\left(1-\nu_i^2\right)}{E_i} + \frac{\left(1-\nu_s^2\right)}{E_s} \tag{6}$$

E and ν are the elasticity modulus and Poisson´s ratio, respectively. Subscripts i and s refer to indenter and sample, respectively. From the known parameters for the indenter, the elasticity modulus of the material E_s is calculated and referred to as E_{IT}.

In present work nanoindentation equipment TTX-NHT, CSM instruments, was employed. Diamond Berkovich indenter (three sided pyramid) tip was used and the results were evaluated using the Oliver-Pharr method [17]. Mechanical properties of the individual cermet constituents were measured in two ways. In the first case, the individual sites were selected manually to get data for individual phases contained in the microstructure (grains and binder). The maximum load was 20 mN. Single loading/unloading profile was used, loading rate was 40 mN/min, and holding time at maximum was 10 s. Five to ten indents were made into each of the principal phases.

In the second case the grid nanoindentation technique was used [18,19]. This method is based on large matrices of indentations (~several hundred) and subsequent statistical analysis of the indentation results [19]. Basically, a large number of indentations is performed and automatically analyzed to obtain hardness, elastic modulus and eventually other mechanical properties. Such property (for example hardness) is then plotted in form of a frequency plot (normalized histogram), which is then fitted by a probability density function. In the case of multi-phase systems the resulting distribution is usually a superposition of results belonging to the individual phases which can be mathematically separated. In the present study the grid indentations were performed in each material on randomly selected representative areas by 10 × 10 rectangular matrix (100 indentations) with 5 μm spacing. The maximum load was set to 20 mN which yielded maximum indentation depth of ~150-250 nm. To eliminate creep the maximum load was held constant for 10 s. The results were fitted by Gaussian distributions and mechanical properties were inferred.

The mechanical properties of each material as a whole were measured at higher load of 300 mN as maximum. The loading rate was 600 mN/min and holding time at the maximum was 10 s. In this case arrays of 9 indents were made in each material. The indents were separated by at least 20 μm so that they were not influencing one another.

3. Results and Discussion

3.1. Composition and microstructure

The phase compositions of the resulting materials were studied in detail in ICMS (Sevilla) using analytical methods – X-ray diffraction and energy dispersive spectroscopy (EDS) [8,14,15]. It was shown that the method of high-energy milling resulted in all cases in the formation of complex carbonitrides of Ti and Ta. The overall microstructure consists of these ceramic particles distributed in a complex intermetallic matrix of (Ti, Ta)-Co type [8,14,15,20].

The micrographs in Fig. 3 illustrate the microstructures of all experimental material together with the Berkovich indenter impressions made by 300 mN load. The image analysis showed clear differences between the materials milled in one and two steps, mainly in the size and distribution of grains. It can be immediately seen in Fig. 3 that the materials prepared in one step milling had grains of more uniform size. The results of statistical treatment of the grain size distribution in terms of grain diameters are in Figure 4. According to these results the materials prepared in one step milling had much narrower grain size distribution than those prepared in two steps. Moreover, the material 95/5 (higher amount of Ti) had significantly larger grains than the system 90/10. This can be appreciated also intuitively from Fig. 3. The materials that were milled in two steps had many more very small grains; in Fig. 4 we see that the material 90/10-2 had much more than 50 % of grains smaller than 1 μm. On the other hand, also much larger grains in these systems exist and the distributions are quite wide. Similarly as in the systems prepared by one step milling, also here the material with higher amount of Ti (95/5-2) tended to have larger grains than the other one (90/10-2). It seems that the milling in the absence of the soft binder phase (step one in the two-step milling) lead to much more severe break-up of the hard carbonitride particles during their hard localized contacts. The presence of Co seems to protect the created hard particles which have more regular and rounded shape with a more uniform size distribution.

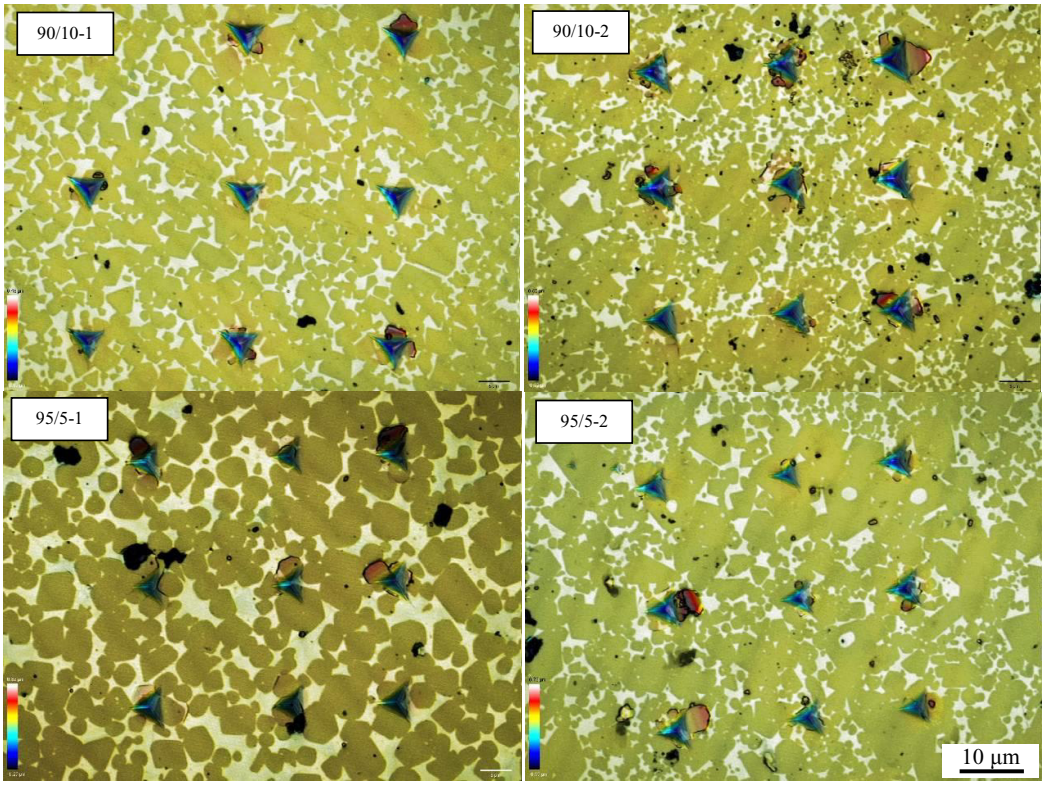

Fig. 3. Microstructure of the experimental materials showing grain size, shape and distribution together with typical Berkovich indents made by 300 mN load. Confocal microscopy.

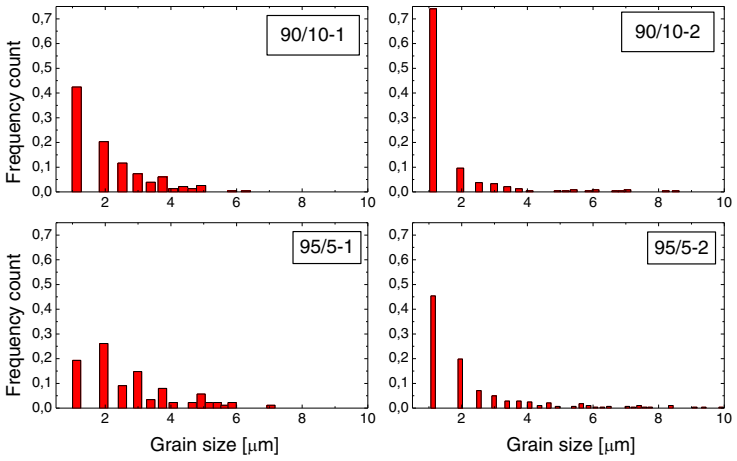

Fig. 4. Grain diameter distributions of the experimental materials

3.2. Nanoindentation of individual constituents

Table 2 shows the results of the nanoindentation experiments performed by targeted indentation of individual microstructure features (grains and binder). Clear difference between the values is present, where hardness of grains was 26.0 – 30.5 GPa while that for the matrix was 15.5 – 18.9 GPa. An example of this difference can be also appreciated on the load vs indentation depth plot in Fig. 2 where averaged loading curves of the two main constituents for material 90/10-1 are shown.

Further examination of the results in Tab. 2, however, does not show any obvious tendency in hardness with regard to Ti/Ta ratio nor with regard to the milling method.

Table 2 Properties of the experimental materials measured by targeted nanoindentation.

	Carbide grains		Binder matrix	
Material	H_{IT} [GPa]	E_{IT} [GPa]	H_{IT} [GPa]	E_{IT} [GPa]
90/10-1	28.6 ± 3.1	416 ± 6	18.7 ± 1.8	405 ± 20
90/10-2	26.0 ± 3.5	414 ± 19	17.4 ± 1.6	384 ± 17
95/5-1	27.4 ± 0.4	430 ± 10	15.5 ± 2.0	350 ± 15
95/5-2	30.5 ± 0.5	428 ± 21	18.9 ± 0.5	392 ± 6

3.3. Grid nanoindentation

As the image analysis showed, the characteristic dimensions of each phase (grain size and binder layers) were in the finer microstructures approximately 1 μm. For grid indentation, in general, the maximum indentation depth should be set so that $h/D < 0.1$ where h is the indentation depth and D is characteristic dimension of the phase or grain. Higher indentation depth can result in mechanical answer of the feature surroundings and to deduce the correct value can be difficult. On the other hand, the indentations had to be sufficiently deep to reduce the negative effect of surface roughness on the scatter of the data.

At maximum loads of 20 mN the indentation depths in our materials were 150-250 nm, so the aforementioned rules were respected in the one-stage milled materials. In the other two they were satisfied for the hard carbide grains where the indentations are shallower. The values for the binder phase in these samples can be influenced by the grains below the indent which has to be taken to account.

After collecting the data, these were statistically evaluated and normalized frequency histograms were plotted. An example is given for both hardness and elasticity in the material 90/10-1 in Fig. 5. The histograms were then fitted with bimodal Gaussian distributions (as illustrated also in Fig. 5) and the resulting values are summarized in Tab. 3 (together with the data measured by 300 mN indentations, see further in Section 3.4). The results of the grid indentation are in a very good agreement with the values found by individual indenting, which are shown in Tab. 2. The scatter of these values tends to be significantly higher than in Tab. 2 which could be expected given the random nature of placing of indents.

Similarly as in the previous case, no clear tendency in hardness or elasticity is observable and the values of different materials are similar within the standard deviation.

Table 3 Grid nanoindentation results.

Material	Grain		Matrix		Composite	
	H_{IT} [GPa]	E_{IT} [GPa]	H_{IT} [GPa]	E_{IT} [GPa]	H_{IT} [GPa]	E_{IT} [GPa]
90/10-1	28.8 ± 3.6	426 ± 32	20.5 ± 8.9	372 ± 50	21.0 ± 1.6	404 ± 23
90/10-2	32.0 ± 10.0	428 ± 70	20.4 ± 16.2	364 ± 102	19.9 ± 2.0	392 ± 9
95/5-1	27.3 ± 2.3	424 ± 112	19.9 ± 12.7	350 ± 110	19.3 ± 1.7	366 ± 36
95/5-2	30.5 ± 1.9	428 ± 15	18.9 ± 3.2	392 ± 65	20.5 ± 2.0	397 ± 10

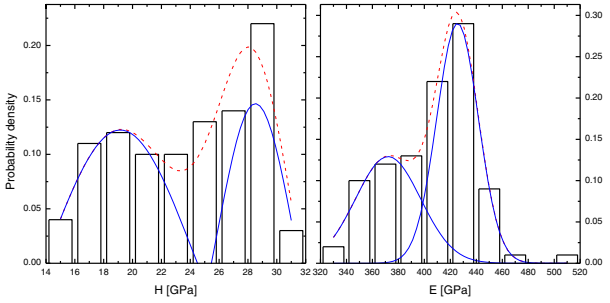

Fig. 5 Hardness and elasticity modulus distributions for the material 90/10-1 measured by grid nanoindentation at max load 20 mN.

3.4. Mechanical properties of the composites

The results of indentations with maximum loads of 300 mN are given in Tab. 3. These values reflect the overall response of the experimental materials and their low scatter suggests that they reliably represent the properties of the whole composites. The hardness values tend to be lower than one would expect from the values obtained at low loads but this is a consequence of the

indentation load size effect (dependence of hardness on the applied load) which has been reported in ceramics [21] and hardmetals [22] before. The results of all experimental materials are comparable to typical values found in industrial hardmetals.

4. Conclusions

Four (Ti,Ta)(C,N)-Co hardmetals were prepared by mechanochemistry. They were based on two compositions ($Ti_{0.9}$ $Ta_{0.1}$ and $Ti_{0.95}$ $Ta_{0.05}$) which were high energy milled in two different ways (single-stage and two-stage) and subsequently pressurelessly sintered. Their mechanical properties were investigated using nanoindentation methods. The results can be summarized as follows:

- The two-stage milling usually leads to a finer microstructure but with much wider grain size distribution.
- The suitability of instrumented indentation to measure the mechanical properties of the different constituent phases as well as properties of material as a whole was demonstrated.
- The low load indentation (20mN) was used to measure hardness and elasticity modulus of individual microstructure constituents. Both targeted and grid indentation yielded consistent and comparable results which allowed to clearly distinguish between the grains and binder. The grid technique lead to higher scatter of data. It was found that the hardness of a ceramic component was in the range 26.3 to 31.6 GPa, the highest values were observed in carbonitride grains in the material 95/5-2 (31.6 ± 0.7 GPa). The hardness of binder was typically in the range from 15.7 to 21.1 GPa.
- Characterization of the composites was carried out using a higher load (300 mN), hardness values ranged from 19.3 to 21.0 GPa, modulus 287-374 GPa. The experimental materials have similar values of hardness and modulus within the experimental error of measurement.
- The results show that the methods of one stage and two stage milling lead to small differences on the micro-level but the materials had comparable macroscopic values of hardness and modulus, i.e. the single step milling produced sufficiently good quality microstructures.

Acknowledgments

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References

[1] Exner HE. Physical and chemical nature of cemented carbides. Int Met Rev 1979; 4: 149-73.
[2] Roebuck B, Almond EA. Deformation and fracture properties and the physical metallurgy of WC – Co hardmetals. Int Met Rev 1988; 33: 90–110.
[3] Ettmayer P, Kolaska H, Lengauer W, Dreyer K. Ti(C,N) cermets—metallurgy and properties. Int J Refract Met Hard Mater 1995; 13: 343-51.
[4] Rabezzana F, Calzavarini R, Chiara R. Machining tests with cermets for turning and milling operations. Industrial Ceramics 2001; 21: 182-4.
[5] Pastor H. Titanium–carbonitride-based hard alloys for cutting tools. Mater Sci Eng 1988; 105–106: 401–9.
[6] Zhang S. Titanium carbonitride-based cermets: processes and properties. Mater Sci Eng A 1993; 163: 141–8.
[7] Clark EB, Roebuck B. Extending the application areas for titanium carbonitride cermets. Int J Refract Met. Hard Mater 1992; 11: 23–33.
[8] Chicardi E, Torres Y, Córdoba JM, Hvizdoš P, Gotor FJ. Effect of tantalum content on the microstructure and mechanical behavior of cermets based on $(Ti_xTa_{1-x})(C_{0.5}N_{0.5})$ solid solutions. Mat Design 2014; 53: 435–44.
[9] Córdoba JM, Sánchez-López JC, Avilés MA, Alcalá MD, Gotor FJ. Properties of Ti(C,N) cermets synthesized by mechanically induced self-sustaining reaction, J Europ Ceram Soc 2009; 29: 1173–82.
[10] Manoj Kumar BV, Kumar JR, Basu B. Crater wear mechanisms of TiCN–Ni–WC cermets during dry machining. Int J Refract Met Hard Mater 2007; 25: 392–9.
[11] Beyer MK, Clausen-Schaumann H. Mechanochemistry: the mechanical activation of covalent bonds. Chem Reviews 2005; 05: 2921-44.
[12] Fernández-Bertran JF. Mechanochemistry: an overview. Pure Appl Chem 1999; 71: 581–6.
[13] Baláž P, Choi WS, Fabián M, Godočíková E. Mechanochemistry in the preparation of advanced materials, Acta Montanistica Slovaca 2006; 11: 122-9.
[14] Chicardi E, Córdoba JM, Sayagués MJ, Gotor FJ. Inverse core–rim microstructure in (Ti,Ta)(C,N)-based cermets developed by a mechanically induced self-sustaining reaction. Int J Refract Met Hard Mater 2012; 31: 39–46.
[15] Chicardi E, Córdoba JM, Sayagués MJ, Gotor FJ. Absence of the core–rim microstructure in $Ti_xTa_{1-x}C_yN_{1-y}$-based cermets developed from a pre-sintered carbonitride master alloy. Int J Refract Met Hard Mater 2012; 33: 38–43.
[16] Fischer-Cripps AC. Nanoindentation. Springer 2011.
[17] Oliver WC, Pharr GM. An improved technique for determining hardness and elastic modulus using load and displacement sensing indentation experiments. J Mater Res 1992; 7: 1564-83.
[18] Constantinides G, Ravi Chandran KS, Ulm F-J, Van Vliet KJ. Grid indentation analysis of composite microstructure and mechanics: Principles and validation. Mat Sci Eng A 2006; 430: 189-202.
[19] Nohava J, Hausild P, Randall NX., Favaro G. Grid nanoindentation on multiphase materials for mapping the mechanical properties of complex microstructures. in IMEKO 2010 TC3, TC5 and TC22 Conferences, Metrology in Modern Context, November 22−25, 2010, Pattaya, Chonburi, Thailand, 195-8.
[20] Chicardi E, Torres Y, Córdoba JM, Sayagués MJ, Rodríguez JA, Gotor FJ. Effect of sintering time on the microstructure and mechanical properties of (Ti, Ta)(C,N)-based composites. Int J Refract Met Hard Mat 2013; 38: 73-80.
[21] Csehová E, Andrejovská J, Limpichaipanit A, Dusza J, Todd R. Indentation load-size effect in Al_2O_3-SiC nanocomposites. J Elec Eng 2010; 61: 305-7.
[22] Duszová A, Halgaš R, Priputen P, Bľanda M, Hvizdoš P, Lofaj F, Dusza J. Nanohardness of individual phases in WC–Co cemented carbides, Key Eng Mat 2014; 586: 23-6.