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ELECTRO CONDUCTIVE ALUMINA NANOCOMPOSITES FROM DIFFERENT ALUMINA-CARBIDES MIXTURES

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Abstract. This work presents the results of an electro-discharge machined ceramic composites consisting of a base non-conductive ceramic component such Al_2O_3, to which is added sufficient amounts of an electro-conductive ceramic nanoparticles such as TiC, TiNC, NbNC, TaNC, and SiC (whiskers) to achieve an electrical resistance of less than about 100W.cm. With these compositions intricate geometries and features as holes, chamfers, slots, angles, changing radii and complex curves can be electro-discharge machined (EDM) into the ceramic body after Pulsed Electrical Current Sintering (PECS) to achieve maximum density and mechanical properties. In EDM, the electrically conductive workpiece or ceramic blank is eroded by electric discharges or sparks which on a small scale generate localized shock waves and intense heat.

The four compositions studied were in the same proportion for all raw materials: alumina 42 (vol %) + conductive material (TiC, TiNC, NbNC, and TaNC) 22 (vol %) + SiC_w 36 (vol %). Processing was carried out mixing raw materials in the suitable proportions in a polypropylene container with zirconia balls and isopropanol media for 72 hours in order to guarantee the homogeneity of the final compositions. The powders were dried and introduced into a PECS furnace for sintering to 1650ºC (100 MPa/2 min). The diameters of the pieces obtained were 20 and about 40 mm and 7 mm thickness.

SiC whiskers reinforced electrically conductive ceramic compositions provide a fully dense material with optimal mechanical properties. The capability of electro-discharge machining obtains good surface quality, chip-free edges, dimensional accuracy and complex shapes. The fracture toughness is improved two to three fold over individual ceramic components. Strength and hardness is also increased.

Some composites were tested as a cutting tool to machine IN-718 nickel-base superalloy industrial laminating cylinders. The composites were formed and electro-discharge machined to a standard size cutting insert.

Keywords: Alumina, Silicon carbide whiskers, PECS, SPS - EDM, TiCN-NbCN-TaCN, Titanium carbide

1 Introduction

Materials for cutting tools inserts fall into several well-known categories. These include high speed steels, cast alloys of cobalt and chromium, sintered carbides and ceramic materials such as alumina.

Ceramic tool materials with oxide matrices, particularly alumina, Al_20_3, are of increasing interest, asthey exhibit high hot-hardness and very high abrasion resistance, thus making it suitable for high speed machining. Ceramic materials are used in especially difficult applications. They have high hardness, chemical inertness and wear resistance even at elevated temperatures. Ceramic cutting tools made of ceramic+carbide, as alumina-titanium carbide composites, have been successful in machining ferrous and non-ferrous alloys. The utility of the ceramic materials may be limited by its low fracture toughness in application where tools tend to foil by fracture, say, in milling or high speed roughing. Main trends in research of ceramic materials are shifting from high purity single phase like Al_20_3 to multiphase composite ceramics, and nowadays extensive research is done to identify all the combinations which would satisfy the requirements: high hardness, high toughness, high temperature resistance and inertness toward machining part.

The development of new cutting tool inserts is continuous and remains an issue. In particular, great efforts are being made to improve the fracture toughness by the addition of hard particles of silicon carbide whiskers to the Al_20_3 matrix and the introduction of Ti(CN), Ta(CN), Nb(CN), etc., cermets as an alternative to WC-Co hard metals [1] to enhance its mechanical properties considerably. Themechanochemical process called mechanically induced self-sustaining reaction (MRS), as proposed by Yen et al., [2], is a novel method to produce high purity transition metal carbonitrides from mixtures of elemental transition metal and carbon in nitrogen atmosphere [3-6].The mechanical milling has shown to be a powerful powder processing technique that allows production of cost-effective ultrafine products and extremely homogeneous composite materials [7].

Electro Discharge Machining (EDM) is a good choice when it comes to machining of very hard materials, provided that they have enough electrical conductivity. The main advantage of EDM is the machining of ceramics is its ability to produce high-complexity shapes, independently of the mechanical properties of the material (hardness, brittleness, flexural strength, etc.). In the case of non-conductive ceramic components it is necessary to add sufficient amounts of an electro-conductive ceramic above the percolation threshold such as metallic carbides, nitrides, etc., to achieve its electrical conductivity and so that it becomes susceptible to EDM [8].

The spark-plasma sintering method (SPS), also known as pulsed electrical current sintering (PECS) or field-assisted sintering technology (FAST),can be roughly compared with the conventional hot press. Additionally a pulsed electric current is applied directly to the graphite mold. The SPS method comprises three main mechanisms of action: a) the application of uniaxial pressure, b) the application of pulse voltage, and c) the resistance heating of graphite dies and sample. It is obvious that the efficiency of this method is influenced by electric and thermal properties of the sample. Consequently, to obtain materials that are dense and nanostructured, it is necessary often to use non-conventional sintering techniques. The initial grain size plays a critical role in the microstructure development during sintering, particularly when the grain sizes are of nanoscale.

In this paper, we present results of the mechanical behaviour of several compositions of a base non-conductive ceramic component such as Al_2O_3 to which is added sufficient amounts of several electroconductive ceramic components such as TiC, TiCN, TaCN, NbCN to achieve an electrical resistance of less than about 100 ohm centimeters specific resistance. To improvethe mechanical properties of these compositions (fracture toughness, thermal shock, etc.) a fixed amount of SiC whiskers was added. The combination of mechanical activation and the SPS has been shown to be suitable for the production of materials having nanostructure and a controlled consolidation level.

2 Experimental procedure

The following raw materials were used as starting powders: 1) TM-DAR grade α-Al_2O_3 powder (Taimei Chemicals Co., Japan) with a specific surface area of 14.6 mgr-1 and an average grain size of 150 nm; 2) Titanium carbide (TiC) from Hubei Minmetals Trading Corporation Limited (China) with an average grain size of 40 nm; 3) XCN (X=Ti, Nb, Ta) also of nanometric grain size synthetized by mechanically induced self-sustaining reaction (MSR) following the procedure of Córdoba, et al. [9]; 4) Silicon carbide whiskers (SiC_w) (diameter = 0.6 μm, length = 10-12 μm) from Tokai (Japan). The morphology of the starting carbonitrides powders is shown in Fig.1.

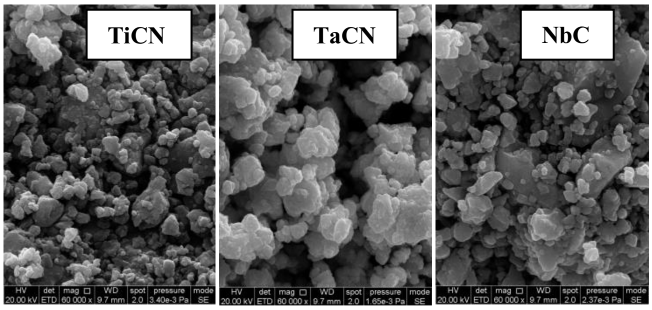

Figure 1. FESEM of the startingTi, Ta, and Nbcarbonitrides powders.

The processing can be divided into two main steps: 1) with corresponding proportions, alumina (42 vol%), TiC, XCN (X= Ti, Ta, Nb) (22 vol%) and SiCw (36 vol%) powders were regardless mixed in a polypropylene container by using zirconia balls for 72 hours in alcohol media (2-propanol, 99% purity, Panreac, Spain), in order to ensure a good homogeneity of the mixtureand 2) alumina powders and the others non-oxide raw materials were mixed together and rolled again in a polypropylene container with zirconia balls in alcohol media for 72 hours. Then the powders were dried first at 60ºC and after at 120ºC and sieved below 63 microns.

The obtained powders were sintered by Pulsed Electrical Current Sintering (PECS) (FCT System GMBH, HPD25, Germany), using a graphite die under vacuum (10^{-2} mbar) at temperature above 1650 ºC. The temperature was measured by using an optical pyrometer focused on the upper part graphite punch, at about 5 mm from the sample, being 100 MPa and 2 min the applied pressure and dwell time, respectively. The tests were carried out at a heating rate of 100ºC min^{-1} to reach the maximum temperature. In this way disks of 20 and 40 mm diameter and about 3 and 7 mm height respectively were obtained.

Density of the composites was measured according to the Archimedes method in deionized water. The microstructure was studied by Field Emission Scanning Electron Microscopy (FESEM) (FEI: Quanta FEG 650). The flexural strength (3-point bending test) and fracture toughness were measured in an Instron 8562 testing machine. These measurements were tested by six beams with 3 mm x 4 mm x 15 mm dimensions for each temperature. K_{IC} measurements were performed using the single-edge-notched-beam technique (SENB) (a/w=0,4 and notch radius ≈ 100 μm) following the guidelines described in the ASTM C1421 standard [10]. Indentation tests with a polished material surfaces were carried out inVickers indenter (Buehler Micronet 5103 equipment) applying a load of 200 g with a dwell of 10 s, performing at least 30 indentations per sample.

Thermal conductivity/diffusivity of the samples was measured using two equipments: Diffusivity measurements were carried out by the laser flash method using LFA 457 Microflash (Netzch, Germany). Experiments were done in nitrogen atmosphere at 25, 300, 600 and 900 ºC, attending the ASTM E-1461 and DIN EN 821 norms. The experimental data were analyzed by the Cape-Lehman model and "Pulse

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Correction" both implemented in the equipment software. The specific heat (Cp) as a function of temperature was calculated using a DSC from TA Instruments (Discovery), equipped with external cooling RCS90 equipment.

The electrical resistivity of the composites was measured by a four–probe method and using the current intensity of 100 mA.

Electrical discharge machining (EDM) tests on composites were carried out by wire EDM, using a tungsten wire of about 0,2 mm diameter and water as dielectric liquid media.

3 Results and discusions

Figure 2 shows FESEM microphographs of the polished surfaces of the sintered conductive-composites.The grain size of each composition is given by the particle size of the starting carbonitridecomponents. The finest microstructures belonging to composition A + TiC + SiCw, while the other carbonitride microstructures with small to large size are those with Ti, Ta and Nb respectively.

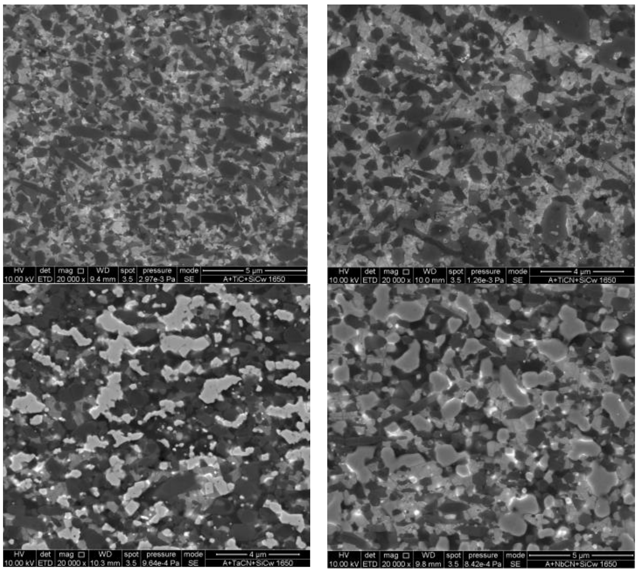

Figure 2. Representative FESEM images of the polished surface of the sintered compositions: A) A+TiC+SiC$_w$, B) A+TiCN+SiC$_w$, C)A+TaCN+SiC$_w$, and D)A+NbCN+SiC$_w$.

The mechanical properties are shown in Table1. Microhardness values for each of the compositions obtained can be observed. The results obtained are correlated to the microstructure obtained and are directly dependent on the particle size.The A+TiC+SiC$_w$composites shown the highest microhardness values whereas lower values occur in the A+NbCN+SiC$_w$composites. As for the flexural strength, higher values are obtained for the compositions of A + TiC + SiC$_w$ (Table 1) and are gradually decreasing with the presence of Ti, Ta and Nbcarbonitridesrespectively. The higher tenacity values are presented in the compositions obtained with alumina, titanium carbide and SiCw. This is linked to the effect produced SiC whiskers distributed on fine matrix of these composites.

Thermal conductivity results are shown in Figure 3.Niobium carbonitrides composites and those with titanium carbide have lower thermal conductivity values at higher temperatures. The values of resistivity and electrical conductivity can be seen in Table 1.

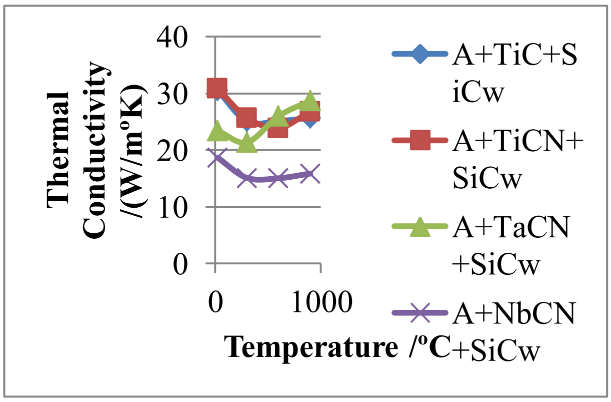

Figure 3. Graphical representation of the thermal conductivities of compositions: A) A+TiC+SiC$_w$, B) A+TiCN+SiC$_w$, C) A+TaCN+SiC$_w$, and D) A+NbCN+SiC$_w$.

Figure 4 shows some of the pieces electro discharge machinedbased on A-TiC-SiC$_w$ and with the Ti and Nbcarbonitrides compositions.

Table 1. Physical properties of the composites elaborates.

Engineering constant		A+TiC+SiC$_w$	A+TiCN+SiC$_w$	A+TaCN+SiC$_w$	A+NbCN+SiC$_w$
Hardness	[GPa]	23,53	22,16	19,34	20,89
Flexural strength (3 points) σ_f	[MPa]	768	451	430	369
Toughness K_{IC}	[MPa.m$^{1/2}$]	7,3	6,57	4,90	6,40
Density	[gr/cm^3]	3,848	3,860	5,427	4,247
Electrical Resistivity	[Ω·m]	9,02E-05	6,66E-05	2,47E-05	1,90E-05
Electrical Conductivity	[S m^{-1}]	1,11E+04	1,50E+04	4,05E+04	1,90E-05

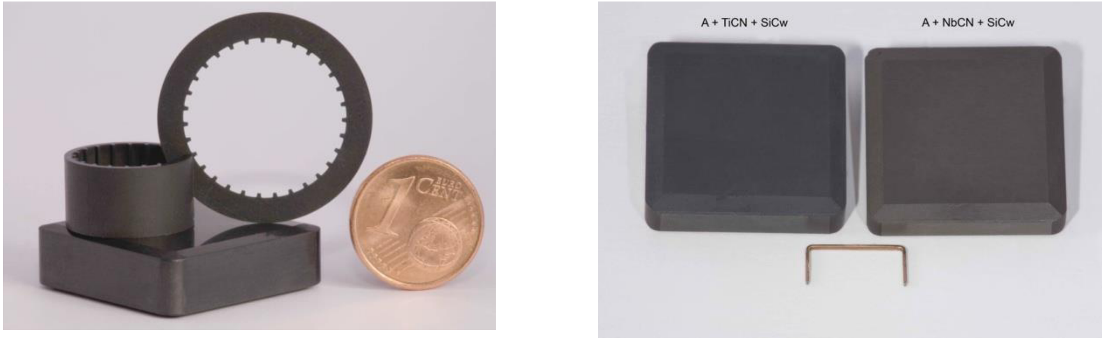

Figure 4. A-TiC-SiCwelectro-discharge machining pieces (left).Cutting tools machined by EDMalumina based Ti, and Nb carbonitrides composites (right).

In Figure 5, the microstructures observed by FESEM of the A-TiC-SiC$_w$ specimens are shown. In this Figure, it can also be seen the excellent surface finish of the piece machined by EDM.

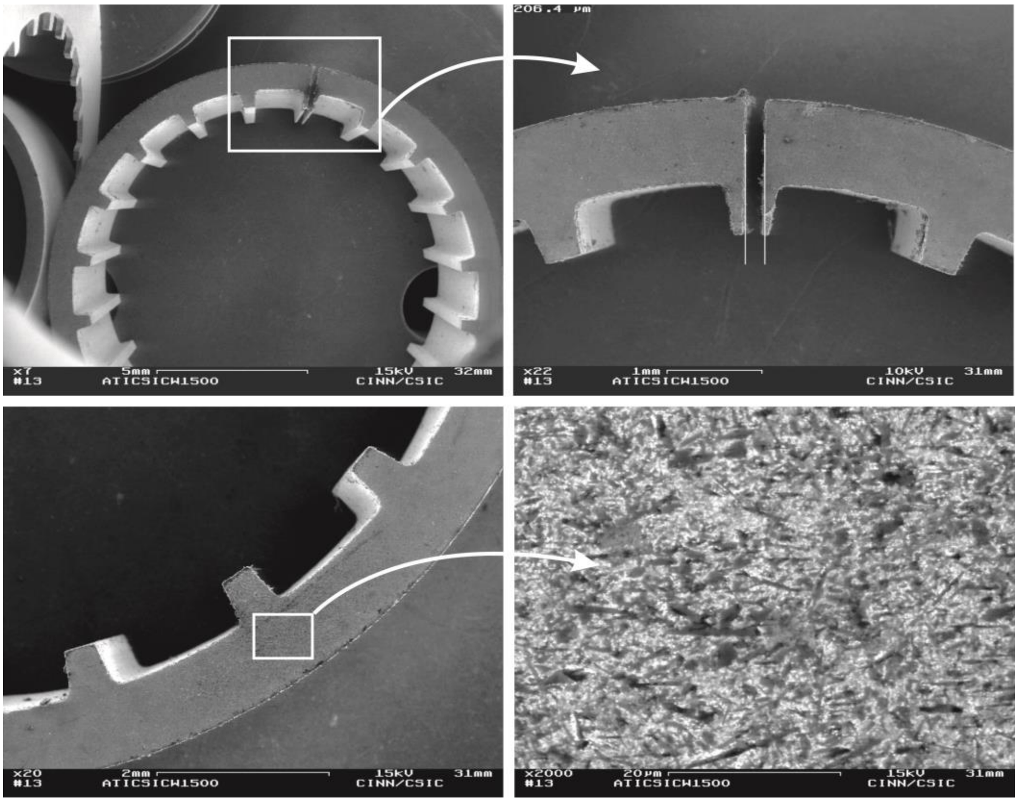

Figure 5. FESEM microphotographies of ATiCSiC$_w$ composition machined by EDM. The thickness of the wire is cutting about 200 microns.

The dimensions of the cutting plates prepared and machined by EDM are shown in Table 2. For engineering evaluation was used to roughing machining TBC cylinders IN-718 nickel-base superalloy, namely type ARAP rolling cylinders (HSS) (Fig.6A), currently being an alternative to high chromium iron (ACRH-N) cylinders because of its better performance, better surface finishes, smaller changes in the mill, and, particularly, reduced machining costs.

The machining of the casting roll was carried out following the same procedure for all the compositions of the prepared plates. Subsequently, rotating the plate and taken other edge, the machining was extended. The aim wastomachineof a length of 250 mm of the roll under these conditions: speed S = 82,5m / min and cutting feed F = 0.55mm / rev. The test performed under these conditions show a different behavior depending on the composition of the plates. Some better than others, and demonstrate good toughness with the continuous presence of continuous metal chips (Fig.6C).

Table 2. Dimensions of cutting plates.

RAW MATERIAL	LENGTH (mm)	WIDTH (mm)	THICKNESS (mm)
Alumina + NbCN + SiC_w	25.40	25.50	5.12
Alumina + TiC + SiC_w	25.34	25.33	7.89
Alumina + TiCN + SiC_w	25.55	25.40	5.96
Alumina + TaCN + SiC_w	26.44	26.60	5.86

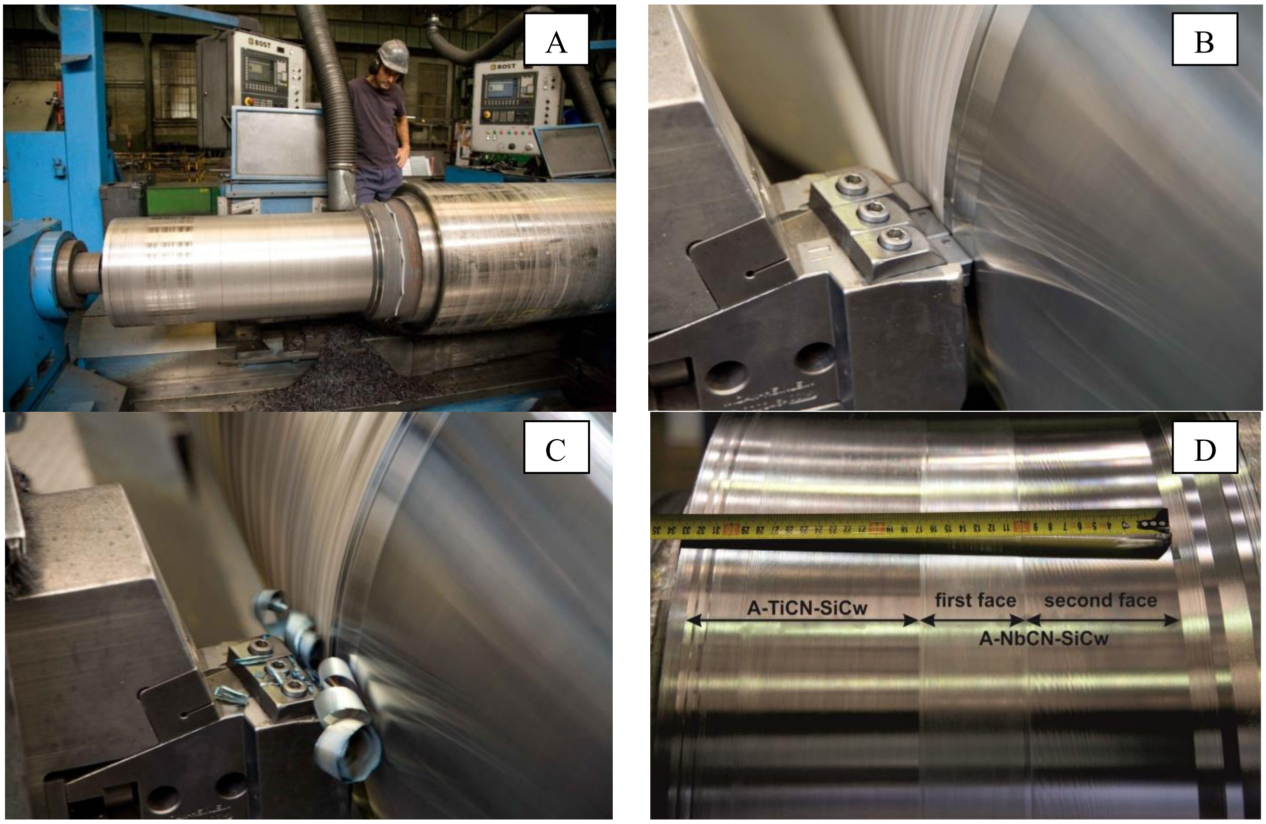

Figure 6. Cilinder rolling tested with the composites elaborated.

In Figure 6, it can be seen different aspects of machining of the cylinder roll tested; it can be observed that the best performances are obtained in the materials developed with titanium and niobium carbonitrides (Fig.6D). In this case, with niobium, it was possible to rotate the specimen and to take advantage, of using another cutting face to continue machining the cylinder avoiding its breakage. This improved behavior could be related to the low thermal conductivity values of both composites. Other compositions showed a quick deteriorationas soon as they suffer a small stroke of the cylinder.

4 Conclusions

Several composites with the same proportions were selected according to the following composition premises: raw materials no conductive (alumina), carbide (Ti) and carbonitride(Ti, Ta, Nb) raw materials and silicon carbide whiskers. The electrical conductivity of the sintered pieces was taken into account in the mixture proportions for composites that could be electro-discharge machined (EDM). The SPS sintering was shown to be an effective method for the fabrication of dense bulk nanostructured materials. The bestmechanical behaviourin the terms offlexural strength and toughness correspond to A-TiC-SiC_w composites and the other compositions have lower values related to their densities.

Alumina-based composites made with TiC and NbCN are the most interesting materials for industrial machining cylinder rolls for steel plants.

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