High Performance Composite Materials Created Through Advanced Techniques

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The paper presents the results of experiments in obtaining some plastic mixtures with high quality characteristics, which should lead to products of complex geometry and improved chemico-structural features, meant to be used in the processing industry-helical milling machining by applying the formation technology in a plastic state. The paper presents the physico-chemical, mechanical and structural features of the mixtures of hard K20 alloys, the compositional networks of the powder making system and of the multi-component organic binder, all these being accomplished according to ICEM's technical view. To improve the toughness, the tenacity and the wear resistance of the parts devoted to metal working industry, the helical mills were coated with some extra-hard layers by TiC, TiN/Ti$_2$N deposits on hard alloy support by a new PVD technique which supposes a combined magnetron sputtering and ion implantation (CMSII).

Keywords: plastic mixtures; helical mills; extra hard layers; magnetron sputtering; ion implantation

The technological development in the field of powder metallurgy is connected to the emergence and development in last 15-20 years, of the Plastically Formed Techniques, aimed products with highly performing characteristics.

The plastically formed techniques are part of the category « near-net-shapes technologies and allow the creation of highly complex geometric shapes by using special "feedstock"materials in a plastic state. The extrusion moulding procedure, as a new technology, was initially regarded as a "tempting choice" for current fabrication procedures, as it constituted the basis for development of technological methods that allow the fabrication of small parts, with complex geometry and high dimensional precision, responding to the current need for miniaturization and high productivity in most industrial fields[1,2].

The extrusion moulding consists in making plastic mixtures made of metallic powders and organic binders, that should have flowing properties appropriate for forced filling of the cavity of a pattern, or for the extrusion moulding of the desired profile. Upon formation, the binder is eliminated, and the remaining metallic skeleton is subjected to a sintering process so to become dense. The procedure derives from the old and quite well-known method of injecting plastic materials. Mainly, the extrusion is a relatively simple process: the plastic material is introduced into a cylinder, at the edge of which there is a cast or mould endowed with an orifice having the shape and dimensions which allow the material to be extruded. The material inside the cylinder is pushed with the help of a piston or of an helicoidal bolt, and is thus forced to pass through the orifice of the extrusion mould.Extruded semi-processed products are then cut at the desired length.

Experimental part

Experimental works have targeted a method of obtaining a binder compatible with the metallic powder, of establishing best rapport between metallic powder / organic binder within the plastic mixture, of producing high-standard plastic mixtures, of describing the physico-mechanical features of plastic mixtures of processed metallic powders, as well as determining the preliminary technological parameters necessary for making highly complex products-helical milling machine made of plastic mixtures of sintered metallic carbides.

We used a metallic carbide powder as part of the research, namely WC-6Co (usage category ISO-K20), produced by the Tizit Plansee company -Austria. We have attempted to produce a significant lot of products, with a complex geometry, namely helycoid milling machine designed for the processing industry. The physical-chemical features of the used powder K20 are shown in table 1.

The organic binder is an agent of temporary action, which ensures the uniform distribution of powder inside the cavity of the shaping mould. It is well known that there is no perfect, universal binder; choosing a binder depends on each particular case or circumstance. The plastic binder is made of, as by its weight, 50-80% petrolatum wax, 5-20% polyisobutylene, 15-20% petroleum wax and maximum 20% kerosene. A multi-component binder endowed with a wax/polymers rapport of 2.5, and an addition of 2% stearic acid-a substance with strain-active properties that helps improve the rheological properties of the plastic mix, was selected for research. Thus, the percentage composition of the binder is: 60% petroleum wax; 10% kerosene; polyisobutylene 28%; 2% stearic acid[2]. The physical properties of the organic binder used to obtain the plastic mix, are as follows (table 2).

Type of powder	Chemical composition			Theoretical density [g/cm^3]	Apparent density [g/cm^3]	Settled density [g/cm^3]	Average diameter [µm]	Specific surface [cm^2/g]	Spherical pointer S
	WC	TaC+ NbC	Co						
K20	93	0.5	6.5	14.65	3.25	4.06	1.50	2366	0.335

Table 1
PHYSICO-CHEMICAL CHARACTERISTICS OF USED POWDER K20

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Table 2
PHYSICAL PROPERTIES OF USED ORGANIC BINDER

Substance	Density [g/cm^3]	Melting point [^{o}C]
Petrolatum wax	0,95	49-52
Kerosene	0.97–0.99	53–58
Polyisobutylene	0.923–0.930	115
Stearic acid	0.95	73–75

In order to obtain the binder, the components have been gravimetrically measured, by weighing them on an analytical scale (± 0,05 g precision) and then slowly heated, under continuous mixing, up to 125–130^{o}C. A double axed mixing device with sigma(Ó) shaped arms was used for experimental works, endowed with a capacity of 2 l. Heating the mixing device was done by using oil – we used a special oil for transformers – heated and re-circulated with the help of a temperature adjuster: Regloplast type 1350 KHL. The temperature of the heating agent was mentained steady a (160^{o}C), while the temperature of the plastic mix varied within the (125–130^{o}C) interval. All the experiments led to the conclusion that the best rapport between the metallic carbide powder and the metallic binder is around 93-93.5% WC-TaC-NbC / 7-6.5% multi-component organic binder.

The theoretical density ($\tilde{n}_p$) of the metallic powder WC-6Co (sort K20), according to ISO specification is: 14.65 g/cm^3. The powder quantity (W_p) introduced for obtaining the plastic mix was of 1850 g. The theoretical density ($\tilde{n}_1$) of the binder was calculated as a weighted average of the binders' components in the mix, as follows:

$$\rho_1 = \rho_{cearapetroleum} \cdot \%cearapetroleum + \rho_{cerezina} \cdot \%cerezina + \rho_{poliizobutilena} \cdot \%poliizobutilena + \rho_{acid\ steric} \cdot \%acid\ steric$$

so:

$$\rho_1 = 0.95 \cdot \frac{60}{100} + 0.98 \frac{10}{100} + 0.926 \cdot \frac{28}{100} + 0.95 \cdot \frac{2}{100}$$

$$\rho_1 = 0.946\ g/cm^3$$

The theoretical density of the plastic mix was calculated as follows:

$$\rho_{am} = \rho_1 + \Phi(\rho_p - \rho_1)$$

The theoretical density of the mix is 6.975 g/cm^3. Three cylindrically-shaped tests were taken from the obtained plastic mixture, in order to determine the real density of the mix. The plastic mix was made even for 8 h in the mixing device, at a temperature of 25-130 ^{o}C and was evicted at the temperature of de 90^{o}C; the mix continued to cool in the air. The material came out as irregularly shaped pieces, of relatively high dimensions, which become solid upon cooling. The mixture was then put through two processes: grinding and filtering. The amount of time allowed for these two processes was of 4 h. A set of 3 filters was used for the filtering operation, with nets dimensions of 1.25 mm; 0.6 mm; 0.4 mm. Three different granulations of the plastic mix have emerged.

The products resulted from plastic mixtures of sintered metallic carbides of the K 20 type have been subjected to a pre-sintering process in a discontinuous oven, electrically heated with resistances, with reduced atmosphere, having hydrogen as reducing agent, with a debit of de 220 l / h. The parameters of the pre-sintering process- have been:* atmosphere: hydrogen (debit 400 l/h);* wrapping/ covering environment: aluminium undergoing calcination in advance at a temperature of l la T= 1400 ^{o}C;* pre-sintering temperature: 1050^{o}C;* maintaining the pre-sintering temperature: 30 min; *breezeway: 200 ^{o}C – 30 min; 250 ^{o}C – 60 min; 350 ^{o}C – 60 min; 450 ^{o}C – 60 min; 550 ^{o}C – 30 min;* average heating speed up to 500 ^{o}C: 0,5 ^{o}C/min;* average heating speed from 500 ^{o}C la 900 ^{o}C: 2.5 ^{o}C/min; *total duration of the pre-sintering cycle: 15h30min.The pre-sintered tests have then been sintered so that to obtain the network of properties required from the material. The operation was performed by void induction heating (10 $^{-3}$ torr), by induction heating with medium frequency currents, Balzers type, while the cooling was performed in stationary hydrogen, having a pressure of about 200 atm[3]. The parameters of the sintering operation that led to the obtaining of the desired physico-mechanical properties have been: *sintering temperature: 1400^{o}C;*maintaining the sintering temperature:1 h;* total sintering duration: 6 h; *average heating speed:5^{o}C/min;* wrapping/ covering environment: aluminium undergoing calcination. The sintered products of the experimental lot made at this stage, had the following physico-mechanical properties: strength HV; *density (g/cm^3); *contraction. The physico-mechanical features are shown in table 3**.**

The microstructural analyses was accomplished by gradually exposing the products to Murakami attack. The analysis of the extruded sintered elements upon optical microscope revealed an uniform repartition of the multi-component binder within the metallic powder, while the elimination of the binder led to the emergence of a porous system, with uniformly distributed pores within the metallic skeleton. The analysis of the sintered samples upon optical microscope conformed the above, indicating a corresponding porosity (A04, 0.06% volume, fig. 1).

The metallographic study points to the existence of phase α in the analysed structure; the α phase is revealed through Murakami attack (20% solution), under the shape of granules of average dimensions, grey in colour, with a polyhedral shape. The study also revealed the existence of the β(Co) phase of white colour (fig. 2). There are no free carbon separations and the η phase is missing (fragile phase), which leads to the conclusion that the technological parameters of the sintering cycle have been properly determined. Deep investigations through electronic microscopy of deflection have been made. The results of examinations have been registered as images of secondary electrons of various sizes. An analysis of the

Table 3
PHYSICO-MECHANICAL FEATURES OF THE SINTERED PRODUCTS FROM PLASTIC MIXTURES OF SINTERED METALLIC CARBIDES, K20 TYPE

Sintered metallic carbide	$\rho_{sint.}$ (g/cm^3)	Transversal breaking point/ strength N/mm^2	HV_{50}
Sort K20	14.90	2100	1577

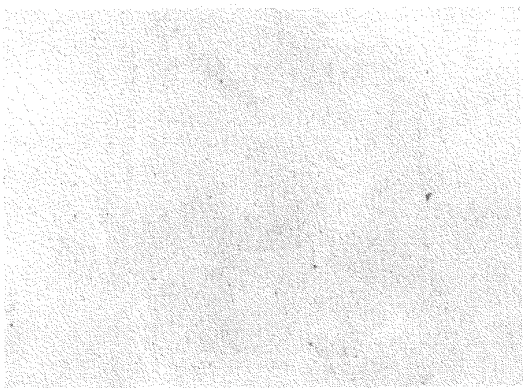


Fig. 1. Porosity of sintered sample -K20 type
State: unattached 100X

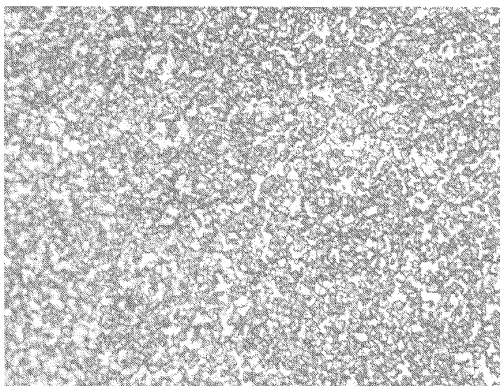
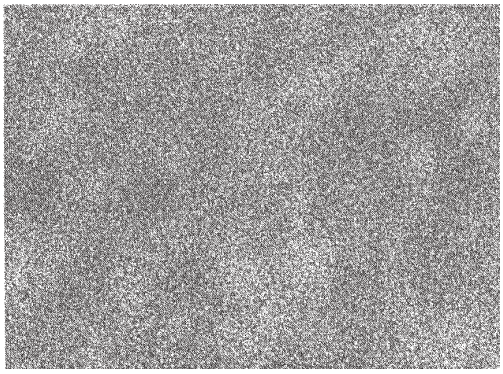


Fig. 2. Microstructure of sintered sample from K20
Attak: Murakami 1500X
phase α-M (WC) angular shape; phase γ (TaC-WC) rounded shape; phase (β)binder



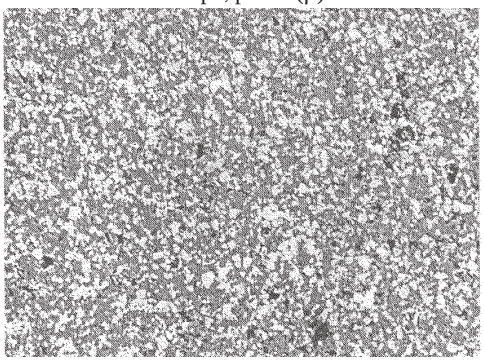


Fig. 3 a,b. Distribution of components in the extruded sintered material
3000X

qualitative chemical composition was performed and the X radiation energy spectrum of the elements within the material. The elements distribution was also registered. (fig. 3a,b).

In figure 4 is showed the representative product from extruded - sintered metallic carbide type K20 – helical mills.

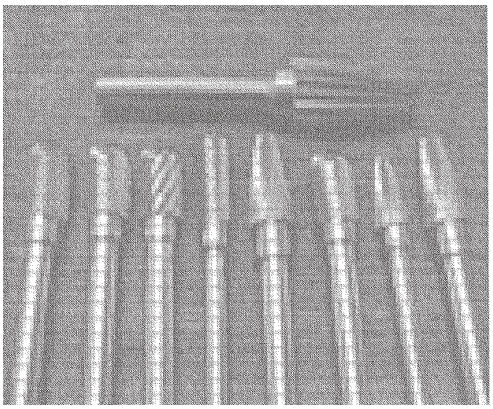


Fig. 4. Helical mills obtained from
extruded - sintered metallic carbide

From plastic mixtures of sintered metallic carbides of the K 20 type it was realized a number of 45 sintered helical mills, that were plated with protective and functional layers type TiC, TiN, Ti_2N.

The coatings with extra-hard layers type TiC, TiN, Ti_2N, on a base of hard alloy K20 type were realized using a new technique PVD supposing a magnetron sputtering combined with an ionic implant. The plasma is produced by a magnetron discharge and the procedure can be defined as a Combined Magnetron Sputtering and Ion Implantation (CMSII). The system combines the advantages of hard coating deposition with those of ion implantation. The deposition of a fine hard layers and ionic implantation represents two tools frequently used in superficial modification of metallic materials.

By the help of that method can be improved the properties depending of micro-hardness, chemical stability and wear or corrosion resistance, to mention only few of them. The first attempts concerning the ionic implantation of plasma were made at the end of past century and since the interest for this type of treatment presents a more and more larger interest. This type of treatment have had however a lack, i.e. the small depth to implant the ionic species (sub-micronic depths). So, the metastable structures resulted following the implantation were located on reduced depths, which was not an appropriate solution for coating the tools devoted to metal cutting. A solution to this problem is the duplex treatment which consists of deposing a hard layer in the same time with ionic implantation.This is in fact the principle of CMSII method, to achieve the deposition of hard layer by magnetron sputtering simultaneously with the ionic implantation[4].

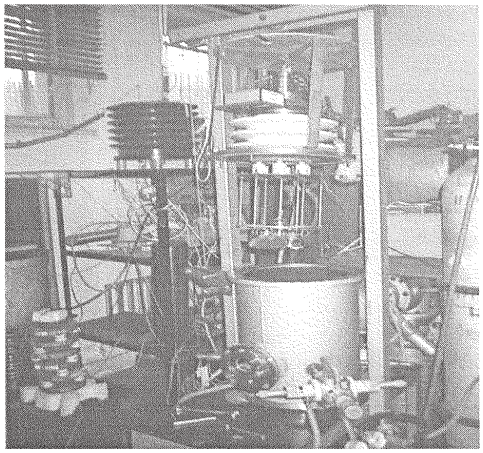


Fig. 5. Image of experimental installation for magnetron sputtering combined with ionic implantation

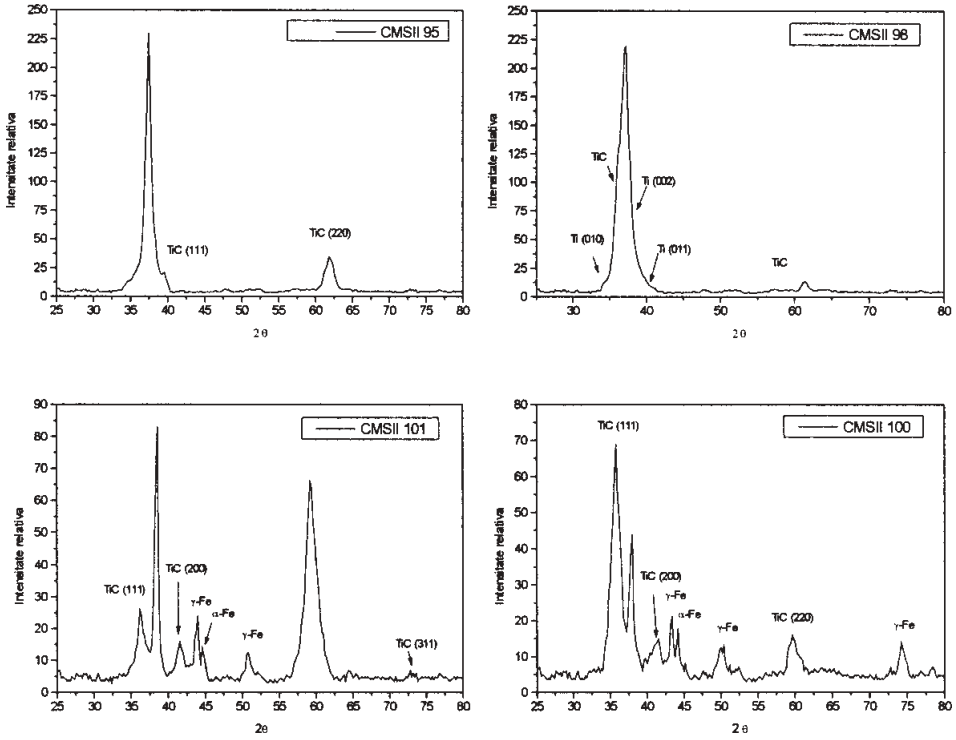


Fig. 6. X-ray diffraction spectra of hard layers of TiC obtained at different flows of reactive gas a)Q_c = 0.67 sccm; b) Q_c = 1.18 sccm; c) Q_c =1.7 sccm; d) Q_c = 2.3 sccm

Table 4
MICRO-HARDNESS VALUES OBTAINED FOR THE TiC, Ti_2N / TiN OF LAYERS

Layer type	$HV_{0,04}$	$HV_{0,1}$
TiC	1800 - 2500	1800 - 2100
Ti_2N/TiN	3116 - 3300	2067 - 2200
Layer material(Comparatively)	1450-1500	1339 - 1559

The ionic implantation is achieved as a result of deposition on the sub-layer (generic name for the compound subjected to treatment) of high tension impulses. In figure 5 can be observed an overall view of experimental installation.

The deposition method CMSII was successfully used to obtain layers from TiN but it can be used also to obtain multiphase layers if during deposition are used two reactive gases. The two types of reactive layers are introduced into the technological enclosure by a distribution system that has calibrated needle valves, mounted on the way of the two gases so that the flows of the two gases can be precisely and independently controlled. The TiC layers were obtained by using as a reactive gas the butane (C_4H_{10}) and to obtain layers of TiCN it was used a gaseous mixture of C_4H_{10} and N_2.The micro-hardness measurements were realized with a metallographic microscope Epytip 2 type having a Hanemann micro-hardmeter[5]. The pressing loads were of 40 respectively 100 gf (400, respectively 1000 mN).

The main tool to investigate the structure of deposited layers was X-rays diffraction (XRD). This analyse was made with a diffractometer DRON with Cu anti-cathode that supplied a radiation with wave length λ = 1.54 A. The X-rays diffraction was realized on samples from stainless steel having deposited the obtained layers. In figure 6 are presented the X-ray diffraction obtained for TiC layers at different flows of C_4H_{10}.

When it is suppressed the C_4H_{10} admission and the N flow is of 6.2 sccm it is obtained a bi-phased structure TiN in a matrix Ti_2N. This is practically the case most favorable from the micro-hardness point of view when are obtained

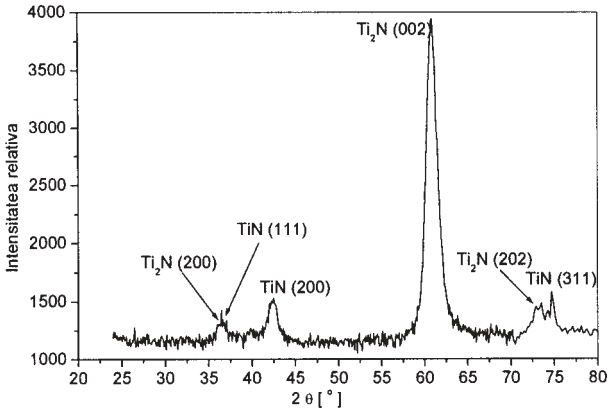


Fig. 7.X-ray diffraction spectra of hard layers of TiN/Ti_2N

the highest values (~ 5500 HV 0.04 at a layer thickness of over 10μm). The X-ray diffraction of such a layer is shown in figure 7. Table 4 presents the micro-hardness values obtained for the two types of layers, the sub-layer material being a plastic mixtures of sintered metallic carbides of the K 20 type compound.

The more reduced values of micro-hardness of layers obtained at 100 gf in respect to those obtained at pressing loads of 40 gf are due to the influence of sub-layer. This influence is obvious at reduced layer thickness and high pressing loads.

The layer depths were measured on cylindrical samples that were coated in the same time with the helical mills. The measurements were done by sample sectioning and measuring with optical microscope. The layers thickness were as follows: - TiC layer 6.6 μm ± 0.2; TiN/Ti_2N 6.9 μm ± 0.2.

Conclusions

Experimental works have established:

- composition and content of the link system (60% petrolatum wax; 10% kerosine; 28% polyisobutylene; 2% stearic acid) – allow the making of an even plastic mix at a temperature lower than the decomposition temperature specific to the binders components;

- the technological parameters involved in obtaining the plastic mix based on metallic powder K20 type : T = 125-130 ^{o}C, t = 8 h.

- the plastic mix was analysed as follows :-determining the density of the components in the mix : ρ = 0.946 g/cm^3;as well as the theoretical densities of the plastic mix: ρ = 6.975 g/cm^3;-determining the link content: an organic link of aprox. 6.5% ;

- setting the thermal, time and pressure parameters, for the pre-sintering and sintering processes;

- the physico-mechanical and structural features of the sintered samples from plastic mixtures based on sintered metallic carbides.

The features of sintered materials made of plastic mixtures from metallic powders are: $\rho_{sint.}$ = 14.90 g/cm^3; $R_{m\ transv.}$ = 2100 N/mm^2; HV_{50} = 1577:

- from plastic mixtures grade K20 it was realized sintered helical mills that were plated with protective and functional layers type TiC, TiN, Ti_2N.

- the coatings with extra-hard layers type TiC, TiN, Ti_2N, on a base of hard alloy were achieved using a new technique PVD supposing a magnetron sputtering combined with an ionic implant;

- the micro-hardness measurements indicated the fact that for the layers with structure predominant of Ti_2N the micro-hardness is large, being around 3000 HV 0.04, in relation to ~ 1700 HV 0.04 when TiC phase is major;

- the more reduced values of micro-hardness of layers obtained at 100 gf in respect to those obtained at pressing loads of 40 gf are due to the influence of sub-layer. This influence is obvious at reduced layer thickness and high pressing loads.

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