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DIAMOND COMPOSITES FOR STONE CUTTING AND DRILLING

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Executive Summary

Metal-bonded diamond composites are widely used in materials processing, especially in cutting, drilling and grinding of hard metals, ceramics and stone. The effectiveness of the performance of metal-bonded diamond tools depend in a great extent on the retention of diamond particles embedded in the metal matrix and on the wear resistance of the matrix. *The main objectives of the project were: 1) to improve bonding integrity of diamond particles and metal matrices; 2) to develop new wear resistant matrices and cost-effective processing routes for fabrication of metal bonded diamond tools.*

To solve the first objective methods were developed for processing of protective coating on the surface of diamond particles which from one side act as diffusion barriers preventing reactions of diamond particles with the metal matrix at processing temperatures and in the same time provide metal-metal type of bonding between coated diamond particles and metal matrix. This was achieved by PIRAC (Powder Immersion Reaction Assisted Coating) developed by PI at the Technion with formation of Cr, Ti or Nb carbide or carbonitride thin conductive coatings, which was followed by electrodeposition of thick (20-200mkm) of metal; Co and Co-W alloy layers.

To solve the second objective compositions were developed with possible precipitation hardening mechanisms as well as with introduced dispersed hard particles such as WC and containing low melting metal phase particles. During fast heating of 70-80% dense compacts above the melting temperature of such low melting phase followed by application of pressure (hot pressing route) the liquid formed is extruded from larger size "lakes" into the pores resulting in rapid consolidation to full density and often in high mechanical properties of the product. Such process developed during research period at the Technion and transferred to UMM, Cracow was called Short Distance Infiltration or SDI. In some cases SDI is accompanied by reactions between the liquid phase and the matrix resulting in formation of new phases, usually intermetallics. In this cases the presence of the liquid phase is very short and the process can be described as *Pressure Assisted Supertransient Liquid Phase Sintering.* Ag-Cu eutectic (T_m = 780^{0}C), Cu-23Mn-17Sn low melting temperature alloy (T_m = 790^{0}C) and Al (T_m = 660^{0}C) were studied as low temperature phases. The best results on a number of compositions were obtained when Cu-23Mn-17Sn was used as a low melting temperature phase.

Collaborating scientist Dr. Joanna Karwan-Baczewska visited Technion three times during period of the research and was trained in number of techniques involved in the project: a) processing: PIRAC coating of diamonds, heat treatments in hydrogen atmosphere, high pressure consolidation (cold sintering), hot pressing employing rapid heating of compositions with low melting phase; b) characterization: SEM with chemical analysis – EDS. High pressure cell and hot pressing cell, and furnace for hot pressing were designed and fabricated at the Technion and sent to UMM, Cracow. There were working contacts between Israel industry – "Toolgal Ind. Diamonds Ltd.", Degania A and Industries in this field in Poland: "Trzhebinia" and "CTD" – Zabrze. During last two years one of the technologies of fabrication of metal bonded diamond tools was transferred to "CTD' as well as laser beam welding apparatus for welding metal matrix segments with diamonds to the body of a cutting blade.

Research Objectives

Metal-bonded diamond composites are widely used in materials processing, especially in cutting, drilling and grinding of hard metals, ceramics and stone. The effectiveness of the performance of metal-bonded diamond tools depend in a great extent on the retention of diamond particles embedded in the metal matrix and on the wear resistance of the matrix. *The main objectives of the project were: 1) to improve bonding integrity of diamond particles and metal matrices; 2) to develop new wear resistant matrices and cost-effective processing routes for fabrication of metal bonded diamond tools.* In both countries Israel and Poland are industries fabricating metal-bonded diamond tools for cutting, drilling and grinding of stone, glass ceramics and hard metals. Israeli industry "Toolgal Industrial Diamonds Ltd." is one of the leading industries in this field in the world and is able to transfer the experience and know-how to the industries in Poland. In both countries there is a large demand in metal bonded diamond tools for stone cutting and drilling for building industry and in Poland also for mining industry. The PI, Prof. E.Y. Gutmanas, has many years of experience in development of advanced techniques and novel metal matrix materials for metal bonded diamond composites and was working in research and development with "Toolgal" for many years.

The present research was on the leading edge of the research and development of metal bonded diamond tools: a) combination of cost-effective PIRAC protective coatings by reactive diffusion with processing of thick electrolytic metal coatings was developed during the present research and resulted in pronounced improvement of bonding integrity of diamond particles in the metal matrix – in the last years CVD coated diamond particles (Cr and Ti coatings) are marketed by both main world companies producing industrial diamonds: General Electric and De Beers, but adhesion of the CVD coating to the diamond surface is relatively poor as compared to PIRAC coatings (Cr, Ti and Nb carbides and carbonitrides); b) a novel rapid processing route of composites was developed – pressure assisted Short Distance Infiltration (SDI): during fast heating of 70-80% dense compacts containing low melting phase above the melting temperature, T_m, of such low melting phase followed by application of pressure (hot pressing route) the liquid formed is extruded from larger size "lakes" into the pores resulting in rapid consolidation to full density and often in high mechanical properties of the product. In some cases SDI is accompanied by reactions between the liquid phase and the matrix resulting in formation of new phases, usually intermetallics. In this cases the presence of the liquid phase is very short and the process can be described as *Pressure Assisted Supertransient Liquid Phase Sintering.* Ag-Cu eutectic (T_m = 780^{0}C), Cu-23Mn-17Sn low melting temperature alloy (T_m = 790^{0}C) and Al (T_m = 660^{0}C) were studied as low temperature phases. Most of the results on development of metal bonded diamond composites is presented in proceedings of International conferences – our results obtained in present research and presented in present report are definitely unique, describing advanced methods of processing as compared to those presented for example in papers of the last International Conference dealing with the topic: "Hard Materials and Diamond Tooling", Euro PM

2002, held on October 7-9th, 2002 in Lausanne, Switzerland [1]. The same applies to papers presented during previous International Conferences in Granada, Spain (1998), Washington, USA (2000) and Nice, France (2002), or papers published in International Journals [2-4]. The PI was invited and published a review paper in ASM Handbook in which processing of metal bonded diamond composites was also considered [5]. In the last years there were attempts to fabricate metal bonded diamond composites employing SHS – Self-Propagating High-Temperature Synthesis [6-7], but in all cases full density of the matrices was not achieved, resulting in poor retention of diamond particles in the matrix. Pressure assisted thermal explosion mode of SHS was successfully used by PI and Dr. I.Gotman (Investigator in current project) for synthesis of dense *in situ* ceramic matrix composites [8-10]. Most recently the approach was successfully applied to metal-ceramic-diamond composites. This results may be a basis for future cooperation between two universities for industrial development of diamond based cutting, drilling and grinding tools in both countries.

"Toolgal Ind. Diamonds Ltd.", Degania A was supplying industrial diamonds for the research on no profit basis and conducted some tests on brazing and welding of experimental metal bonded diamond segments to the body of the cutting blade. "Toolgal" also made contacts with industries in Poland working in the field , proposing consultations and technical help. Prospects on future cooperation with the "CDT", Zabrze, Poland company looks quite positive.

Methods and Results

1. Experimental

1.1. Processing of Protective Coatings

1.1.1. Processing of thin protective coatings

In the present research PIRAC, Powder Immersion Reaction Assisted Coating, developed at the Technion by PI and his group was [11-13] was employed to obtain thin 1-2 mkm protective coating – diffusion barriers on diamond particles. The scheme of PIRAC is similar to pack cementation, but the process is based on surface diffusion of metal atoms with high affinity to carbon, such as Cr, Ti and Nb and this is followed by nucleation and growth of carbide layer on the surface of diamond particles. At certain conditions carbonitride coatings can be formed.

High strength artificial industrial diamonds SDA-100D from General Electric Co. were used in the experiments. Diamond particles of 300-600 mkm size were immersed into corresponding metal powders of relatively coarse grit size (5-200 mkm) and placed into sealed stainless steel container with high concentration of Cr. Cr reacts with oxygen forming a stable Cr_2O_3 oxide. This reaction prevents oxygen from penetrating through the container walls, so that a very low O_2 pressure not exceeding 10^{-5} Pa (10^{-7} Torr) is maintained inside the container. Oxygen inside of the container is consumed as a result of reaction with the container. Low pressure of nitrogen (10^{-3} –10^{-4} Torr) may be a result of formation of less stable Cr nitrides which decompose at low pressure at higher temperatures. This may result in formation of nitrides or carbonitrides. To prevent involvement of nitrogen in PIRAC reactions Ti powder can be used as getter. Relatively coarse metal powders (Cr,

Ti, V, Ta and Nb) were used for PIRAC coatings to prevent sintering of metal powders during PIRAC processing and allows convenient sieving of the coated particles from the metal powder bed. The experiments of diamond coating were performed in 900 – 1100^{0}C temperature range. In part of the treatments crystalline Halogen (iodide) was admixed to metal powders in order to accelerate the transfer of metal atoms onto surface of diamond particles. After the PIRAC treatment the phase composition of the reacted layers was identified employing x-ray diffraction (XRD). The microstructure of the coatings obtained was characterized in scanning electron microscope (SEM) with energy dispersive analysis (EDS). During coating of diamond particles with formation of carbides carbon is supplied from diamond and as a result part of the diamond (usually not more than 2%) is consumed. Presence of monoatomic nitrogen can reduce consumption of carbon and in the same time result in formation of carbonitrides. It should be mentioned that 1)Ti, V, Ta and Nb nitrides are thermodynamically more stable than corresponding carbides and b) solubility of nitrogen in Co is practically zero at processing temperatures (for metal-bonded diamond composites) – so carbonitride coated diamond particles should be very stable in Co based matrices.

1.1.2. Processing of electrolytic thick coatings

Since PIRAC carbide or carbonitride coatings are electrically conductive it is possible to use a relatively simple technique of electrolytic deposition to produce relatively thick tens and hundreds of microns metal coatings. Such coatings can improve drastically the adhesion of diamond particles to the metal matrix.

Experiments on electrolytic coating of diamond particles by Co and Co-W alloy, that are often used also as metal matrices in fabrication of metal bonded diamond tools were carried out using conventional compositions for electrolytic coatings of Co and Co-W alloy, namely a)$CoCl_2$x6H2O – 300 g/l and H_3BO_3 – 300 g/l for Co and b) $CoCl_2$x6h2O – 28g/l, Na_2WO_4 – 70 g/l, $C_4H_4KNaO_6$ – 100 g/l and NH_4Cl – 50 g/l for Co-W alloy. Electrolytic coating was performed at various current densities including very high current densities, up to 250 A/dm^2, as compared with those usually used in electrolytic deposition (5-10 A/dm^2). Very high current densities were employed to increase the deposition rate and to obtain very fine microstructure of deposited layers. PIRAC coated diamond particles were placed on an electrode disc made from Cu and were blended ultrasonically during electrolytic coating (this prevents sticking of coated particles to the electrode and to each other). The thickness of the layer was estimated from the weight gain as well as from measurements of the thickness in the cross section of the coating in SEM or optical microscope. Diamond particles were broken on purpose to obtain the cross section view.

1.1.3. Thick soft cushion coatings via embedding diamond particles into metal matrix

Experiments were also carried out on coating of diamond particles by a thick protective layer acting as a soft cushion and protecting diamonds from contact that may result in cracks during processing of dense metal bonded diamond composite under pressure. This was achieved via embedding diamond particles into metal matrix: metal was filled into holes of 3 mm diameter, diamond particles were placed in the middle and were covered by a layer of a metal matrix. Such an assembly

containing hundreds of particles was annealed in hydrogen flow in temperature range of 500-900^{0}C, resulting in partial sintering/densification. Co and Fe powders were used as matrices in this part of research.

1.1.3. Investigation of thermal stability of coated diamonds

PIRAC coated diamond particles as well as uncoated were placed into Co or Fe based matrices which were consolidated to full density by cold sintering [5] at pressure 2.5 GPa after the compact of metal bonded diamond composite was treated in hydrogen flow to remove the oxide layers from the surface of the metal powder particles. Dense metal-diamond composites were treated at temperatures 900 and 1000^{0}C, typical for high temperature range of processing such composites. After such heat treatments specimens were tested in bending and the surface of the diamond particles on the fracture face was investigated employing SEM with chemical analysis, EDS.

1.2. Development of Rapid Processing Routes of Metal-Bonded Diamond Composites

As it was already mentioned hot pressing is used in most cases for fabrication of dense metal-bonded diamond composites – full density is a necessary condition for production of high performance structural materials and good bonding integrity of diamonds in the metal matrix. Rapid heating under pressure employing resistive heating (large currents) or induction heating of non-dense compacts is often used in production of metal-matrix composites including metal-bonded diamond composites. Formation of a liquid phase during rapid heating may promote densification to full density and improve adhesion between powder particles. Since during hot pressing processing employing resistive or induction heating non-dense compacts of metal-bonded diamond composites are heated under pressure the metal matrix is usually densified with closure of open pores prior melting of low melting phase the formed liquid "microlake" is entrapped in solid matrix. As a result the positive effect of the appearance of the liquid phase is diminished and the size of the liquid phase is defined by the size of the initial particles of such low melting phase. Appearance of the liquid phase accelerates diffusion and may result in undesirable reactions of diamond particles or protective coatings with the liquid phase. Therefore it is important to have the liquid phase for a time period as short as it is necessary for successful consolidation to full density.

During present research SDI or Short Distance Infiltration technique was developed by and was used for fabrication of metal-bonded diamond composites. Schematic of SDI is shown in Fig. 1. The non-dense compact is heated rapidly (to avoid solid state reactions) under low pressure up to temperature above melting temperature, T_m, of the low melting phase. Than higher pressure is applied resulting in extrusion of the formed liquid into pores. Compared to traditional melt infiltration, SDI has the advantage of the considerably shorter infiltration distances (microns vs. millimeters/centimeters). SDI leads to full densification. Reaction of the liquid with solid phase particles may result in formation of intermetallic phases or new thermodynamically stable ceramic phases if liquid phase reacts with ceramic particles introduced into metal matrix.

Ag-Cu eutectic (T_m = 780°C), Al (T_m = 660 °C), Cu-23Mn-17Sn (T_m = 790 °C) – this alloy was designed and fabricated on special order for present research, and NiB (T_m = 1050 °C). Relatively low processing pressures in the range of 50-200 MPa were applied with temperatures below and above T_m of the low melting phase. Pressure cells made from Ni based superalloys were fabricated and used for rapid densification at elevated temperatures. Hard particles such as W, WC or Cr_3C_2 were introduced in part of the matrices to affect the microhardness of the specimens after processing.

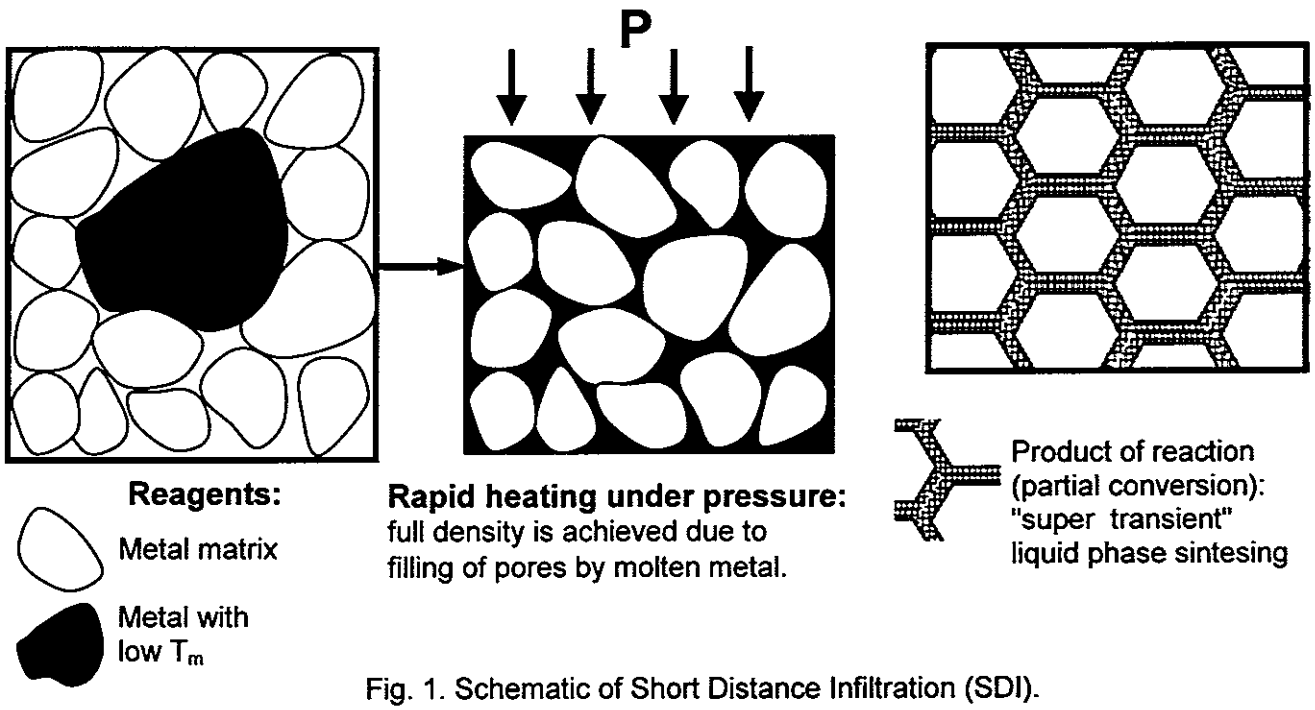


Fig. 1. Schematic of Short Distance Infiltration (SDI).

1.3. Characterization of Microstructure

Coatings obtained on diamond particles via PIRAC and electrolytic deposition were characterized by X-ray diffraction, XRD, (Philips) scanning electron microscopy, SEM, (JEOL) with chemical analysis employing energy dispersive analysis, EDS, (Link), Auger electron spectroscopy (AES) and optical microscopy. SEM/EDS and optical microscopy was used to study microstructure of consolidated specimens, fracture surfaces and metal matrix-diamond interfaces.

1.4. Mechanical Testing

Mechanical testing : three point bending tests/transverse rupture strength, σ_{TRS}, yield stress in compression and compression strength of uncoated and coated diamonds was performed employing Instron testing machine (Model 1195) with the cross head speed in the range of 0.05- 0.2 mm/min. Microhardness of the consolidated metal matrices was measured at loads 50-200 g (Buehler). Wear resistant simulation tests were performed when consolidated specimen/segment containing coated and uncoated diamond particles were tested against grinding wheel.

2. Results and Discussion

2.1. Protective Coatings

2.1.1. PIRAC coatings

Example of PIRAC coated diamond particles are shown in Fig. 2. Examples of XRD patterns of PIRAC coated diamonds are presented in Figs. 3-5. It can be seen that PIRAC coating in presence of halogen vapor (iodine) results in enhancement of delivery of metal atoms to the surface of diamond particles and thicker coatings of carbides (higher peaks on XRD spectra). By PIRAC treatment in Nb powder without halogen it was not possible to obtain protective coatings because of counterdiffusion of carbon to the surface of Nb powder particles, resulting in formation of Nb carbides acting as diffusion barriers. Comparing XRD patterns obtained for specimens treated at 1000 and 1100^{0}C it can be seen that thicker coating are obtained at 1100^{0}C after shorter exposure. In the same time we should keep in mind that exposure of diamonds at 1100^{0}C may result in formation of microcracks and deterioration of diamonds. Mechanical testing (strength in compression) after mention PIRAC treatments of SDA-100D diamonds including those performed at 1100^{0}C for 1h didn't any decrease of strength as compared to as received diamond particles. Tests were performed on large number of particles (100).

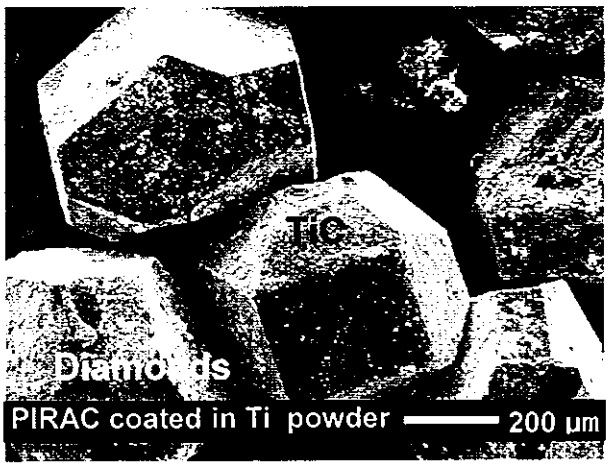


Fig. 2. Diamonds PIRAC coated in Ti powder, 1000°C, 1h.

All PIRAC coatings in Cr, V, Ti and Nb powders of thickness 1-3mkm can be obtained after reasonable exposures of 1-3 h, making the process coast effective. The thickness growth of of PIRAC carbide and carbonitride coating follows the parabolic law, indicating that the process is governed by diffusion of elements through the formed coating layer.

It should be mentioned that all carbide and carbonitride coating obtained on the surface PIRAC coated diamond particles are electrically conductive and thus PIRAC coated diamond particles can be used for electrolytic coating of thick – tens of microns - protective layers.

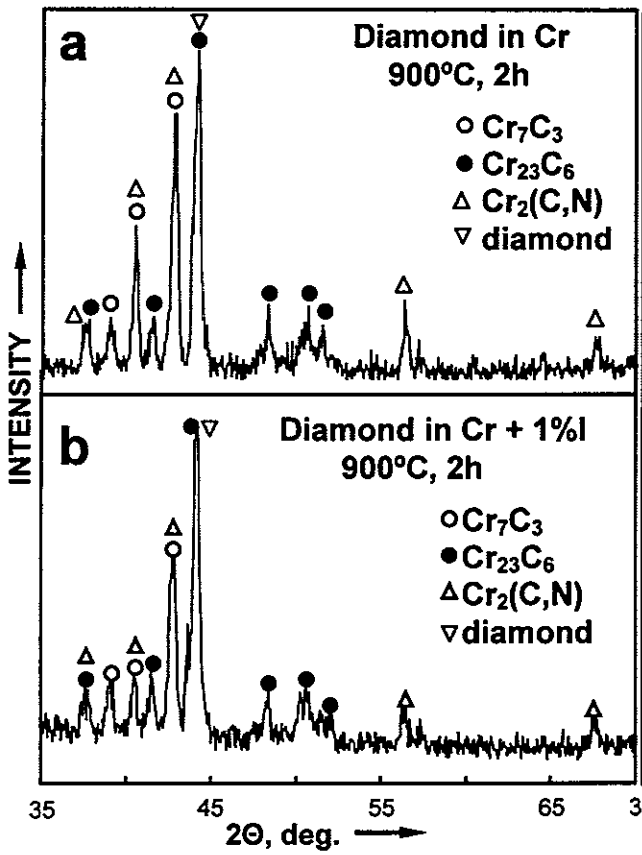


Fig.3. XRD paterns of PIRAC coated diamonds in Cr powder; a)Cr,900°C,2h; b) Cr + 1%I, 900°C,2h

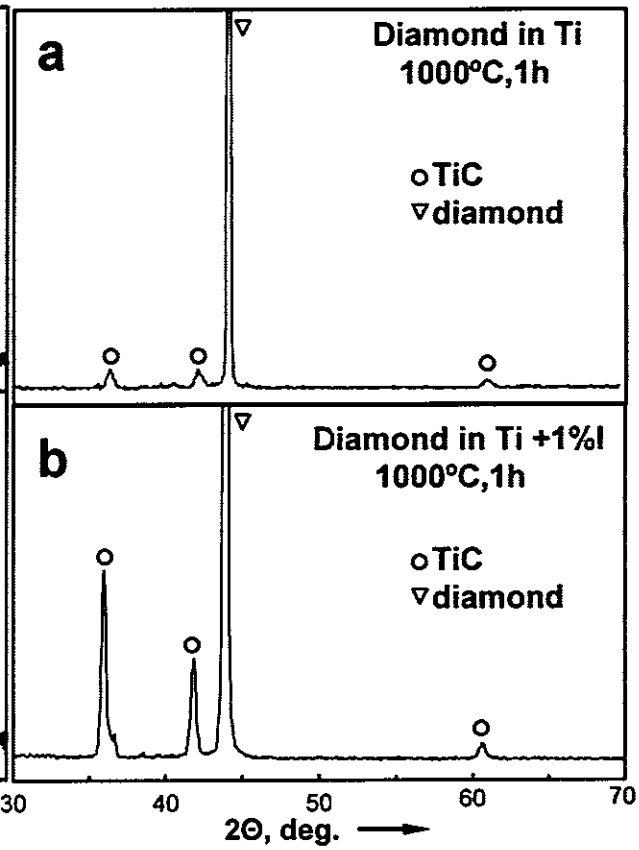


Fig.4. XRD paterns of PIRAC coated diamonds in Ti powder; a)Ti,900°C,2h; b) Ti + 1%I, 900°C,2h

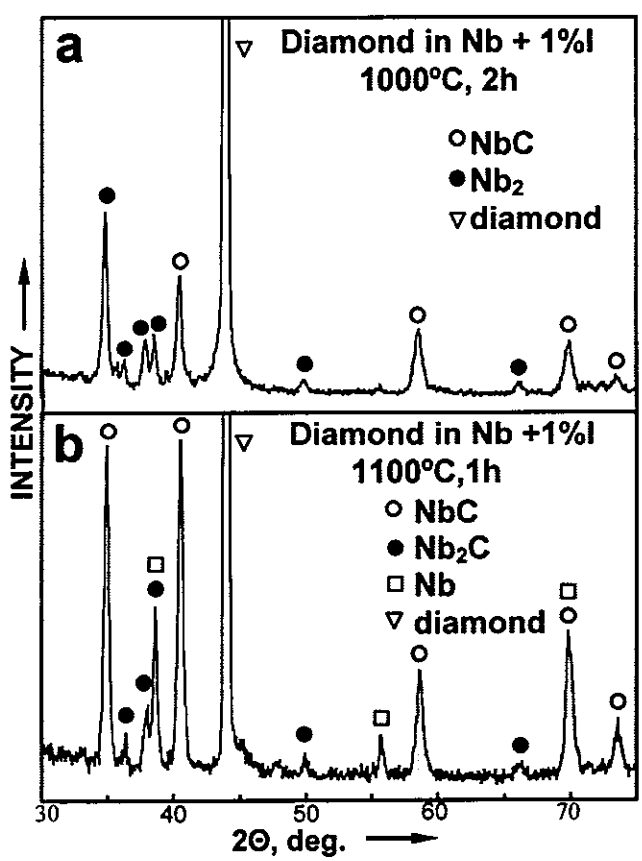
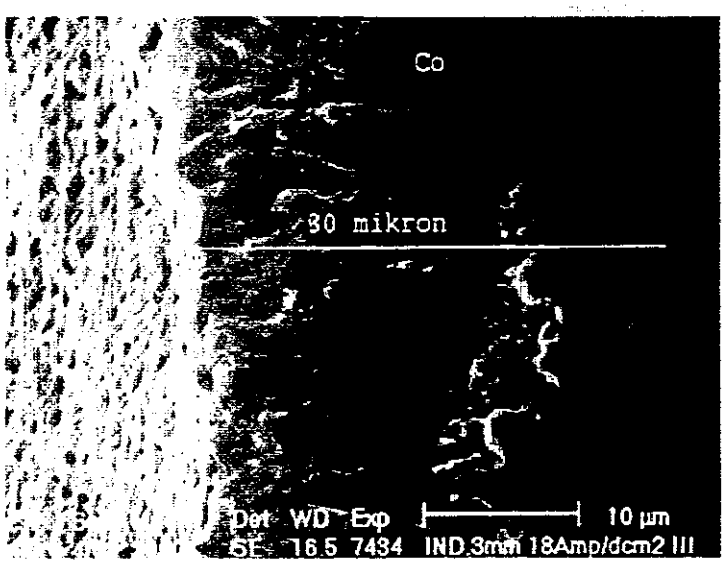


Fig.5. XRD patterns of PIRAC coated in Nb powder diamonds: a) Nb + 1%I, 1000°C, 2h; b) Nb +1%I, b) Nb + 1%I, 1100^0 1h.

2.1.2. Electrolytic coatings

Examples of electrolytic Co and Co-W alloy coatings on diamond particles are shown in Fig. 6. Morphology of the coatings depend on current density and on time of coating. Needle shape morphology is typical for Co coatings obtained at high current densities and long deposition times. Spherical type of grains with very fine microstructure is observed for short deposition times and lower current densities for Co coatings and for Co-W coatings. Thickness of electrolytically deposited Co layers on PIRAC coated diamonds (Cr carbonitride) as function of current density at different deposition time is shown in Fig. 7. It can be seen that thick tens of microns layers can be obtained at high current densities in relatively short times. This applies also to electrolytic coating of Co-W alloy, as it can be seen from Fig. 8, where thickness of electrolytically deposited layers is shown as function of deposition time at various current densities. Possibility to obtain thick and dense electrolytic coatings of Co and Co-W alloy in relatively short time indicates that the process can be cost effective.

a



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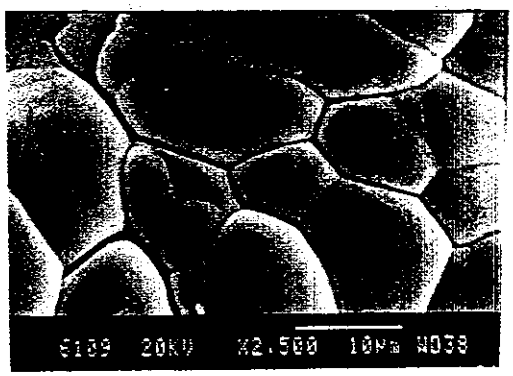

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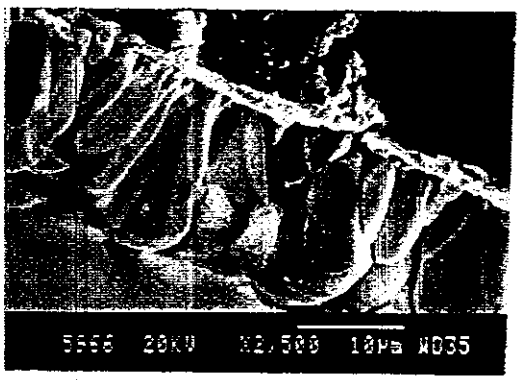


d

Fig. 6. Examples of electrolytic coatings on PIRAC coated (Cr carbonitride) particles: a) Co, 80 A/dm2, 8 min, b) Co, 18 A/dm2, 25 min – cross section, c), d) Co-W, 100 a/dm2, 5 min, d) – cross section.

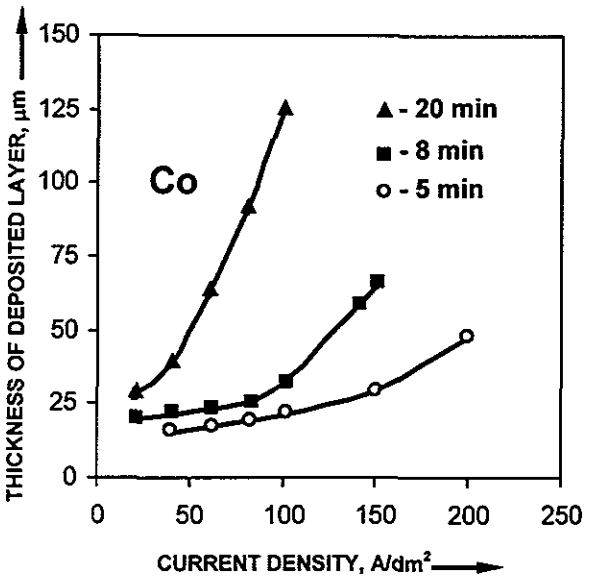


Fig. 7. Thickness of electrolytically deposited *Co layer as function of current density* at various deposition times

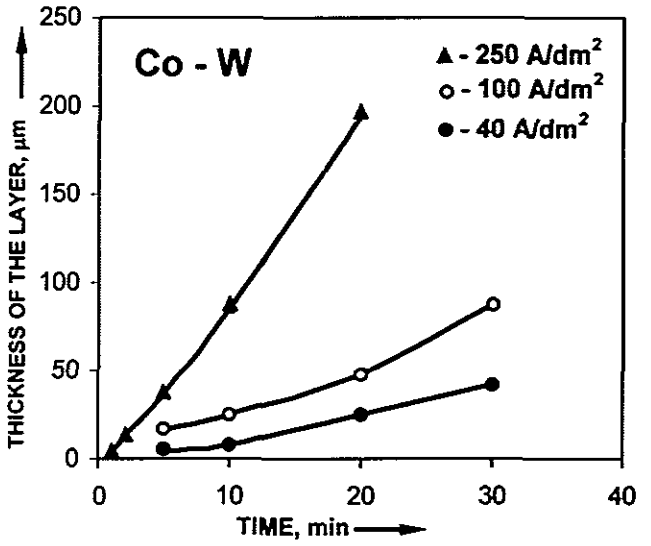
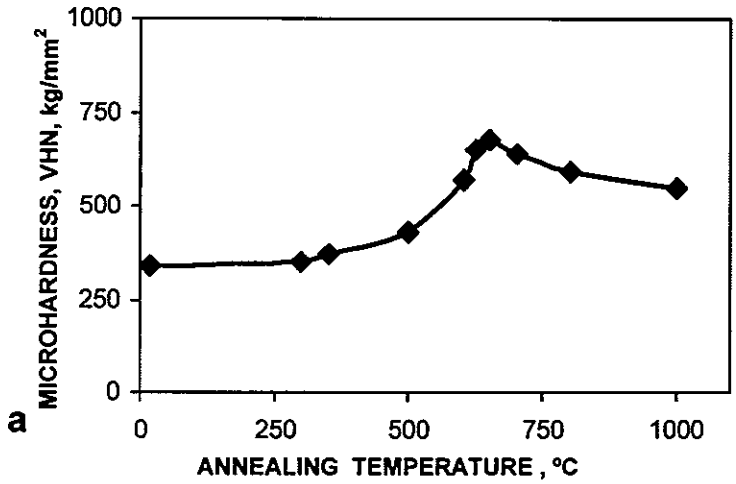


Fig. 8. Thickness of electrolitycally deposited *Co-W alloy as function of deposition times* at various current densities

XRD analysis of Co and Co-W alloys deposited at high current densities indicates presence of amorphous phase or phase with extremely fine grain size – XRD peaks are very broad. This may be a result of very fast deposition at room temperature when there is no time for ordering of the microstructure (similar to microstructures obtained during sputtering or rapid solidification). EDS analysis in SEM of electrolytically deposited Co-W allows indicates compositions close to Co-38wt.%W. In principle changing the composition of the electrolyte composition of the deposited layer can be changed.

Co-W alloys are known as precipitation hardening alloys with Co_3W being the phase causing hardening. Annealing at temperatures above 450^{0}C for Co and above 550^{0}C for Co-38W alloy results in crystallization and in Co-38W alloy peak corresponding to Co_3W appears. Such a precipitation results in aging with increase of microhardness of deposited layer. This can be seen from Fig. 9a, where microhardness as a function of annealing/agiing temperature is shown (1 h exposure at temperature). The microstructure on aged Co-38W deposited layer is shown in Fig.9b. It can be seen that annealing at temperatures higher than 700^{0}C result most probably in overaging and decrease of microhardness. But the microhardness remains still relatively high even after anneal at 1000^{0}C (processing temperatures of metal-bonded diamond composites usually don't exceed 1000^{0}C). Possibility to change the microstructure and microhardness of electrolytically deposited Co-W alloys can be used to improve the bonding integrity of diamond particles in metal matrix in service conditions as well to adjust the wear resistance of the composite to specific material .

Electrolytically deposited pure Co shows high microhardness VHN = 420 kg/mm as compared to VHN < 300 kg/mm^2 for commercially pure Co, obtained by hot pressing of Co powders. Annealing of electrolytically deposited Co layers at temperatures above 500^{0}C result in decrease of microhardness.



a b

Fid.9. Electrodeposited Co-38W alloy (current density 100 A/dm2, time of deposition 10 min); a) microhardness as function of annealing temperature (1 h exposure), b) SEM micrograph of the surface after annealing at 650^{0}C for 1 h.

2.2. Development of Matrices and Short Distance Infiltration, SDI, - Rapid Processing Route of Metal-Bonded Diamond Composites

It should be mentioned that the powder blends used for processing of metal bonded diamond composites were prepared using prealloyed powders of low melting phase (or Al powder) and elemental micron size Co, Fe powders as well as additions of micron size of W, WC, and Cr_3C_2. Mixture of powders were blended using in most cases high energy attrition milling (Union Process) with relatively low media to powder ratio (2.5:1) to avoid mechanical alloying during blending. Diamond particles were placed into matrix and blended manually or using "Turbula" to avoid fracture of particles. After application of higher pressure during SDI resulting in consolidation, the pressure was maintained at least for one minute. Effect of exposure under pressure on microstructure and mechanical properties was investigated too and it was shown that longer exposures at higher temperatures may result in coarsening of microstructure and deterioration of mechanical properties. Rapid processing resulting in dense material allows processing in open air making them process cost saving and tolerant to industrial conditions.

2.2.1. Matrices with Ag-Cu eutectic as low melting phase

72Ag-28Cu eutectic has relatively low melting temperature, T_m = 780^{0}C. Ag is not dissolved in Co and Fe and Cu is only slightly dissolved in solid Co or Fe. Thus matrices based on, Co, Fe or their alloys are a good model for processing of metal-bonded diamond composites *via* SDI route. A number of compositions based on Co, Fe and their alloys were investigated. As it was mentioned earlier in SDI route non-dense compacts are rapidly heated above melting temperature of the low melting phase under relatively low pressure, 2-5 MPA (the pressure on this stage is applied only to assure rapid heating from the pressure cell walls) and then higher pressure is applied (P=40-200 MPa, depending on composition and processing temperature) resulting in extrusion of the liquid

phase into the pores. For comparison experiments were performed when the higher pressure was applied at T below T_m. As it can be seen from SEM micrographs in Fig. 10 for composition 45Co-45Fe-10Ag/Cu eutectic hot pressed at T = 760°C below T_m relatively large regions of low melting phase are retained (Fig. 10a), corresponding to the initial size of Ag-Cu powder, while for specimens processed at temperatures above T_m very fine regions of Ag-Cu phase are observed (Figs. 10b and 10c) with very homogeneous distribution of this phase. In specimens prepared at 780°C, melting temperature, both relatively coarse as well as fine regions of Ag-Cu eutectic are observed (Fig. 10b).

Mechanical properties of 45Co-45Fe-10Ag/Cu specimens processed *via* SDI are also higher VHN = 320 ± 10 kg/mm^2 as compared to 280 ± 15 kg/mm^2 for specimens hot pressed at 760°C and σ_{TRS} = 1250 ± 60 MPa as compared to σ_{TRS} = 1020 ± 70 MPa for specimens hot pressed at 760°C. Similar results were obtained for Co matrix with 10wt.% of Ag-Cu eutectic as well as for compositions with as low as 5wt.%of Ag-Cu eutectic. This aspect is important since Ag-Cu eutectic, containing 72% of Ag is expensive.

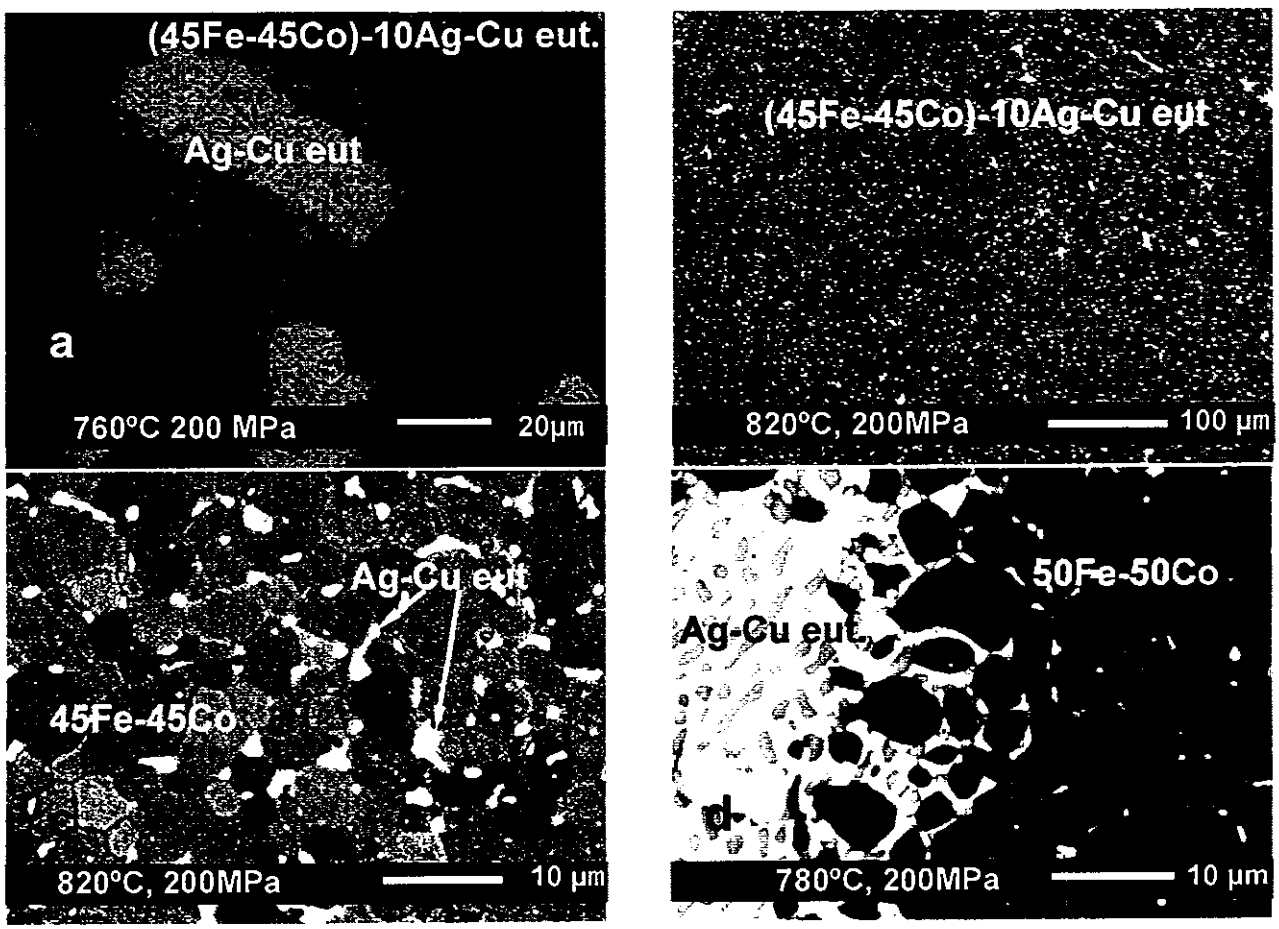


Fig.10. SEM micrographs of polished specimens prepared *via* hot pressing of 45Co-45Fe-10Ag/Cu eutectic: a) at 760°C, b)and c) at 820°C and d) at 780°C .

2.2.2. Matrices with Cu-23Mn-17Sn as low melting phase

The alloy Cu-23Mn-17Sn was fabricated by rapid solidification on a special order. The melting temperature of the alloy is about 790°C only slightly higher than that of Ag-Cu eutectic but the price

is considerably lower (about 25% of the price of Ag-Cu eutectic). In addition Mn is forming with Co and Fe unlimited solid solutions and Sn may form intermetallics with Co, Fe as well as with Cu and Mn. A wide number of compositions were prepared, based on Co, Fe as well as Co-Fe and Fe-Co-Ni alloys (elemental Co, Fe and Ni powders were used) without and with addition of hard particles. Composition based only on Cu-23Mn-17Sn phase with 70wt.% of WC was also prepared employing SDI. In all cases when the higher pressure was applied at temperatures above 800^{0}C, T_m of this Cu-23Mn-17Sn alloy dense a specimens with very fine homogeneous structures were obtained . Very good mechanical properties with an excellent bonding integrity of coated diamonds to the metal matrix were obtained for composition Fe-20Co-10Ni-10Cu/Mn/Sn alloy. Examples of microstructures for such composition after various processing temperatures are shown on SEM micrographs in Fig. 11 (fracture surfaces). It can be seen that the microstructure remains very fine even after processing at 900^{0}C. The same applies to the same composition with addition of 10 wt.% of WC (Fig.12).

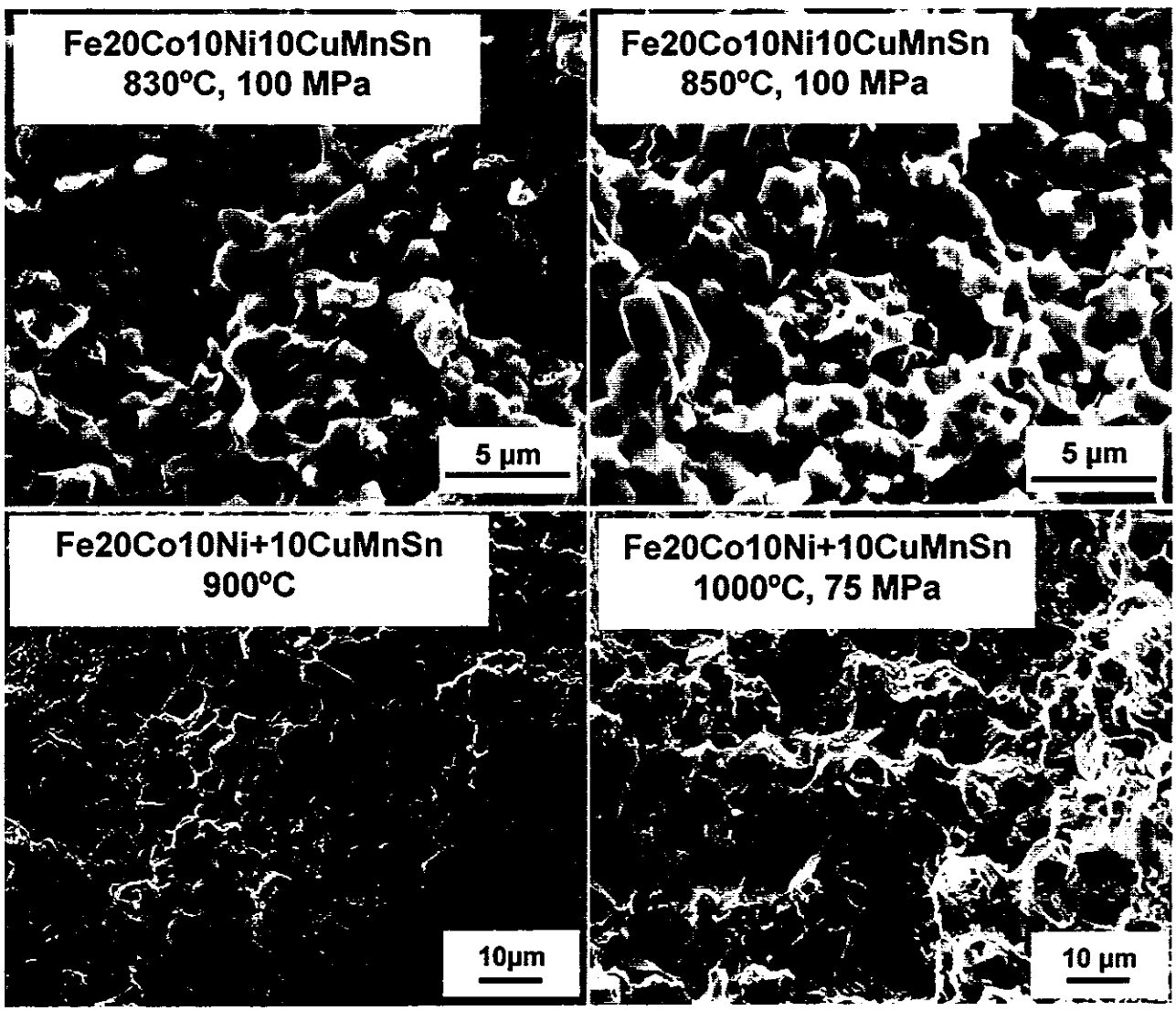


Fig. 11. SEM micrographs (fracture surfaces) of specimens processed *via* SDI for Fe-20Co-10Ni alloy with Cu-23Mn-13Sn as a liquid phase with low melting temperature (T_m = 800^{0}C).

Mechanical properties of specimens prepared from Fe-20Co-10Ni-10Cu/Mn/Sn alloy without and with additions of hard particles *via* SDI are presented in Tables 1-3. It can be seen that very high transverse rupture strength σ_{TRS} in combination with high microhardness can be obtained for Fe-20Co-10Ni-10Cu/Mn/Sn composition employing SDI. The properties obtained after 5 exposure at temperature under pressure are practically the same as after 1 min exposure. Longer exposures of 25 min not only makes the process slower but also results in some deterioration of mechanical properties – this may be a result of partial coarsening of the microstructure. Addition of hard particles such as WC and Cr_3C_2 results in some increase of microhardness. The high values obtained for σ_{TRS} are comparable or even higher than for matrices based on pure Co, but the microhardness is considerably higher and can be changed in certain range (the microhardness of matrices based on pure co are below 300 kg/mm^2). It should be mentioned that the price of Fe-20Co-10Ni composition as about 30% of the pure Co, making this composition (or similar – no systematic research on optimization of the composition was performed) attractive for practical applications.

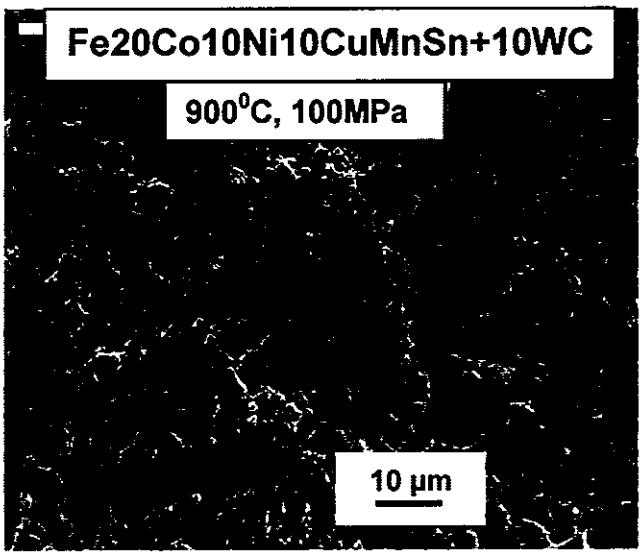


Fig.12. SEM micrograph (fracture surface) of a specimens processed *via* SDI from Fe-20Co-10Ni +10 WC alloy with Cu-23Mn-13Sn as a liquid phase with low melting temperature (T_m = 800^{0}C)at 900^{0}C.

EDS analysis shows that most of the Mn is dissolved in FeCoNi alloy, while very fine regions Cu and Sn reach are homogeneously distributed in the matrix.

In Fig. 13. SEM micrograph shows polished microstructure of a composition with Co-23Mn-17Sn as a low melting phase containing 70vol.% of fine WC particles processed *via* SDI. It can be seen that full density is achieved resulting in high mechanical properties: σ_{TRS} = 1460 MPa and microhardness of about 800 kg/mm^2 – this are very high numbers considering low processing temperature (cemented carbides are produced via liquid phase sintering at temperatures above 1450^{0}C.

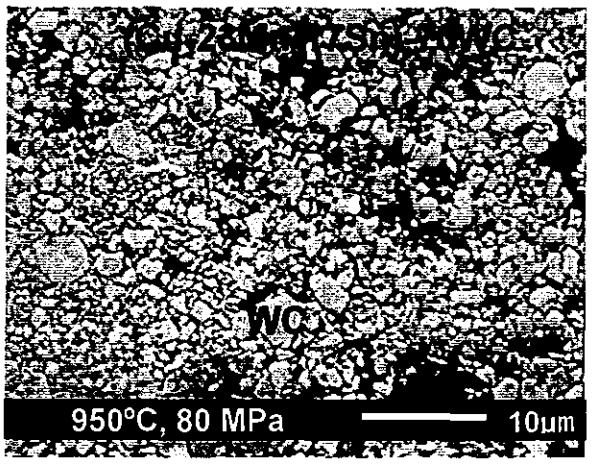


Fig.13. SEM micrograph of polished specimen 70vol.% WC – Cu/Mn/Sn alloy as a low melting phase processed via SDI at 950°C at pressure 100 MPa.

2.2.3. Matrices with Al as a low melting temperature phase

Aluminum powder was also used as a low melting phase for processing of metal bonded diamond composites *via* SDI. Al forms thermodynamically very stable intermetallics with Co,Fe and Ni and reactions in the solid state start already at 500°C, below T_m = 660°C. Reactions with formation of such intermetallics are very exothermic and can lead to thermal explosion mode of SHS [14]. Taking this into account heating of compositions containing Al and Co, Fe or Ni above T_m of Al should be extremely fast to prevent solid state reactions or thermal explosion mode of SHS prior to application of higher pressure and extrusion of liquid Al into pores. We were able to apply SDI processing route to Co and Co-Fe matrices with Al as a low melting phase in laboratory tests, but introduction of such processing as an industrial processing route seems very questionable. But Al can be used as a low melting for SDI processing of matrices that don't contain large fraction of reactive components, such as matrices based on Cu or containing large volume fraction of non-reactive phase, such as for example hard carbides or nitrides. Example of such matrix material with a composition: WC-17Co (coating) – 15 Al, processed *via* SDI is shown in Fig. 14.

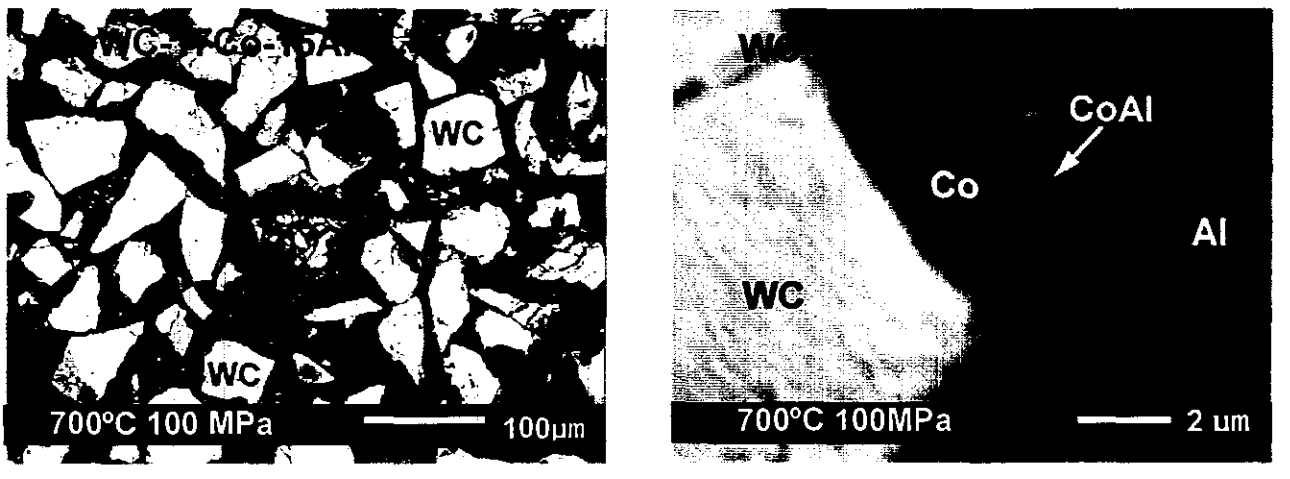


Fig. 14. SEM micrographs of WC-17Co(coating) with 15% of Al as a low melting phase processed *via* SDI at 700°C and pressure 100 MPa.

Table 1. **Fe-20Co-10Ni + 10CuMnSn, Hot press**

Number	T,°C	P,MPa	t(T), min	VHN, kg/mm^2	σ_{TRS}, MPa
1	800	100	5	390	1910
2	800	100	25	380	1560
3	825	100	5	380	1590
4	825	100	25	400	1350
5	850	100	5	425	1590
6	850	100	25	405	1280
7	900	75	5	415	1430
8	900	75	25	345	1350

Table 2. **Fe-20Co-10Ni+10CuMnSn + WC**

Number	%WC	T°, C	P, MPa	t(T), min	VHN,kg/mm^2	σ_{TRS} MPa
1	5	900	100	5	405	1360
2	10	800	100	5	345	1200
3	10	850	100	5	410	1100
4	10	900	100	5	460	1240
5	15	900	100	5	340	1340

Table 3. **Fe-20Co-10Ni+10CuMnSn + Cr_3C_2**

Number	%Cr_3C_2	T°, C	P, MPa	t(T), min	VHN,kg/mm^2	σ_{TRS} MPa
1	5	800	100	5	320	1040
2	5	800	200	5	350	1460
3	5	850	100	5	340	1050
4	5	900	100	5	470	1000
5	7	800	100	5	300	1400
6	7	900	100	5	370	1320
7	10	800	100	5	325	1330
8	10	900	100	5	360	1240

2.2.4. NiB and Ti-Ni eutectic as low melting temperature phases

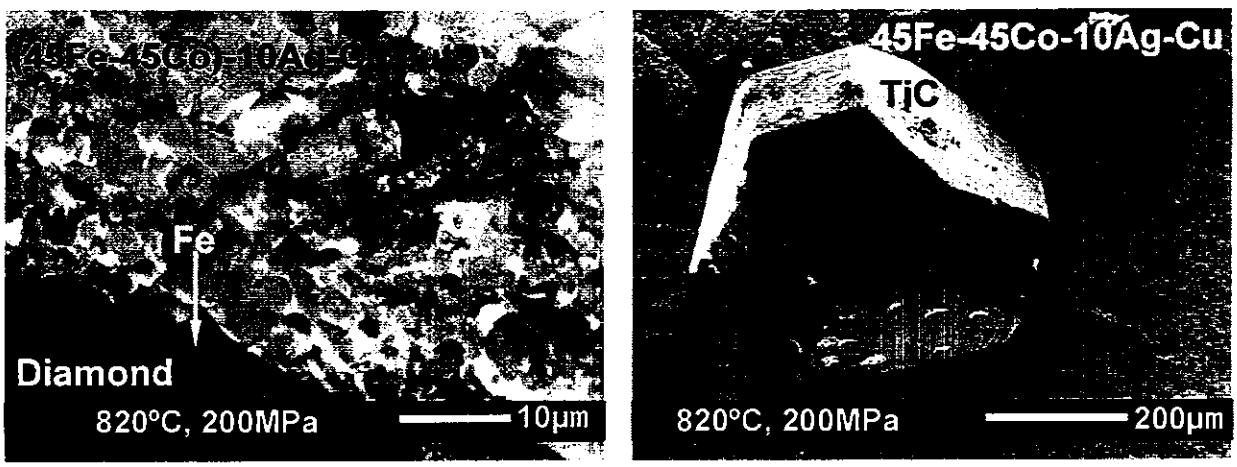
NiB (Tm = 1050^{0}C) and Ti-Ni eutectic (Tm = 950^{0}C) were also checked as possible low melting phases for SDI processing of metal bonded diamond composites.

Results obtained for systems Fe with additions of NiB (4 and 8wt.%) show that the temperature needed for successful processing vai SDI is above 1100^{0}C, most probably because of high viscosity of liquid NiB just above melting temperature [15]. This makes the compositions containing NiB as a possible low melting temperature phase not suitable as matrices for metal-bonded diamond composites. Ti in particles of Ti-Ni eutectic are picking up oxygen from the metal powder matrices (Co, Fe, Ni) during conventional treatment of compacts in hydrogen flow, the procedure that is used to reduce the surface oxides of the metal powder matrix. As a result Ti partially transforms to Ti oxide, changing the phase composition. Use of Ti-Ni eutectic with most carbide and nitride matrices results in highly exothermic reactions leading during rapid heating to thermal explosion mode of SHS [12]. Temperatures that can be developed during thermal explosion are dangerous for diamonds.

2.3. Investigation of Thermal Stability of PIRAC Coated Diamonds

Dense specimens with diamond particles coated *via* PIRAC in Cr, V , Ti and Nb powders as well as with uncoated diamonds in Co, Fe, Co-Fe and Cu-Mn-Sn based matrices were prepared by cold sintering and via SDI – Short Distance Infiltration. Prior to consolidation non-dense compacts were treted in hydrogen flow to remove oxide layers from the surface of metal powders. Cold sintered specimens were heat treated at various exposures at 900 and 1000^{0}C. Part of the specimens fabricated *via* SDI were also annealed at 900 and 1000^{0}C. After processing and heat treatments specimens were tested in bending (transverse fracture strength) and surface of diamond particles and diamond-matrix interfaces were investigated employing SEM/EDS.

In Fig.15 SEM micrographs of fracture surfaces of specimens made *via* SDI for 45Co-45Fe-10Ag/Cu eutectics are shown. EDS analysis of the interface uncoated diamond-matrix Fig. 15a



a **b**

Fig. 15. SEM micrographs of fracture surfaces of 45Co-45Fe-10Ag/cu eutectics specimens prepared *via* SDI at 8200C and pressure of 200 MPa: a)uncoated diamond, b) PIRAC coated in Ti powder.

indicates presence of Fe-C rich layer, close in composition to Fe carbide Fe_3C with signs of local chemical etching/ pitting on the surface of diamond particle, as a result of reaction of diamond with Fe from the matrix. EDS analysis of the interface matrix-PIRAC coated diamond in Ti powder in Fig. 15b indicates presence of Ti on the surface and EDS analysis of the interface on the broken diamond indicate presence of TiC. The surface of coated diamond particles is smooth.

Additional example of interface broken piracy COATED IN Ti powder diamond-70WC-(Cu-23Mn-17Sn) matrix of a specimen fabricated *via* SDI at 10000c, P = 50 MPa is shown in Fig. 16. It can be seen that TiC coating is still present on Metal matrix-diamond interface and there is a good bonding integrity between coated diamond particle surface and the matrix. It should be mentioned that for uncoated diamonds in the metal matrices in most cases fracture path proceeds on the interface matrix-diamond, although most of the diamond particles are damaged by pitting – reaction with the metal matrix , while for most of the PIRAC coated diamonds fracture path proceeds through undamaged strong diamond particles. This indicates strong bonding between PIRAC coated diamonds and metal matrix.

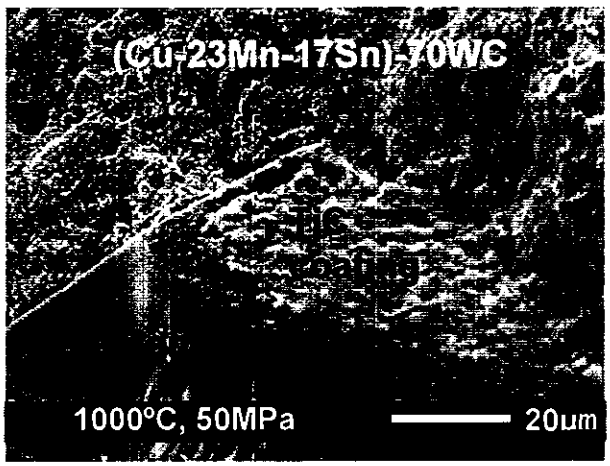


Fig. 16. SEM micrograph of the fracture surface of 70WC-(Cu-23Mn-17Sn) matrix with PIRAC coated in Ti powder diamonds fabricated via SDI at 10000C, P = 50 MPa.

In Fig. 17. SEM micrographs of fracture surfaces of Fe-20Co-10Ni -10Cu/Mn/Sn matrix without (Fig. 17a) and with 10% of WC (Fig. 17b) with PIRAC coated in Cr powder diamonds are presented fabricated *via* SDI at 830^{0}C (Fig. 17a) and at 850^{0}C (Fig. 17b) and P = 100 MPa. It can be seen that in both cases surface of diamond particles is very smooth and Cr carbide layer acting as diffusion barrier is present on the interface metal alloy matrix-diamond. There is a strong bonding between Cr carbide layer and the matrix.

Thermal treatments of cold sintered or SDI processed specimens with PIRAC coated diamond particles in Cr, V, Ti an d Nb powders for all matrices studied show that for all PIRAC coatings and all matrices studied show that exposures up to 3h at 1000^{0}C doesn't result in any deterioration of the coatings or reaction of coated diamonds with the matrices. In the same time uncoated diamonds react with Fe containing matrices with formation of Fe carbide already at 850^{0}C with a very

pronounced reaction at 0.5 h exposure at 1000°C. The same applies to matrices containing Mn. In matrices based on Co reaction starts at 900°C with dissolution of carbon in Co.

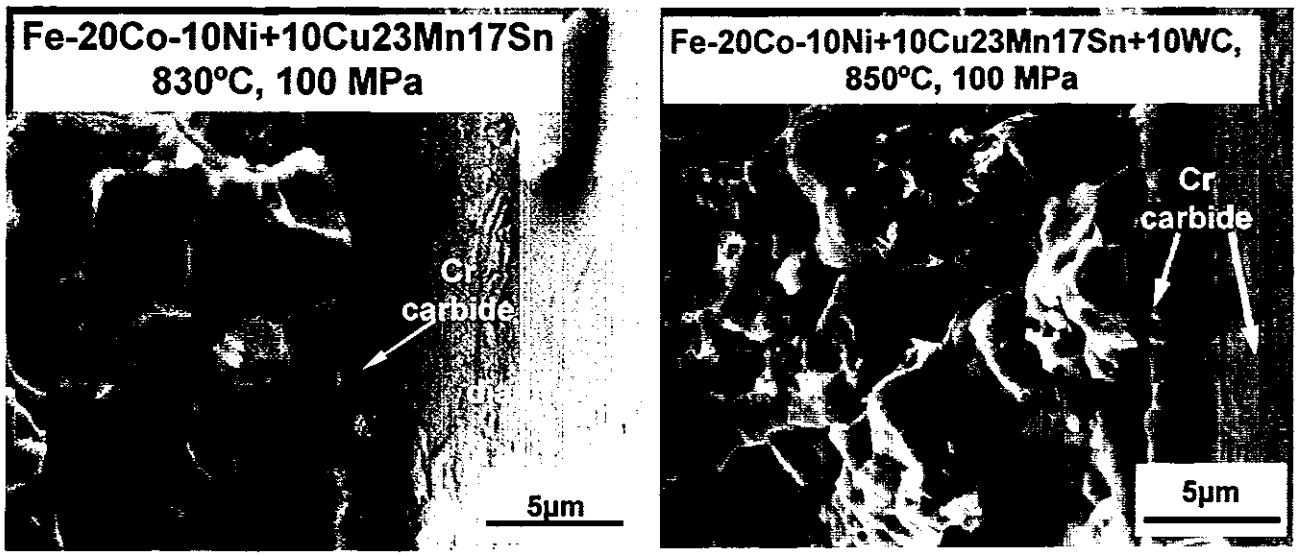


Fig. 17. SEM micrographs of fracture surfaces of Fe-20Co-10Ni -10Cu/Mn/Sn matrix a) without and b) with 10% of WC with PIRAC coated in Cr powder diamonds.

This coatings obtained by PIRAC may act as effective diffusion barriers preventing reactions of diamond particles with metal matices at high processing temperatures. From all coatings Cr and Ti carbide and carbonitride coatings can be processed via PIRAC at the lowest temperatures and thus if there are not special requerements from point of veiw of thermal stability in specific matrix such coatings being cost effective can be recommended for most of practical applications.

3. Conclusions

1. Continuous several microns coating of Cr, Ti, V, Ta and Nb carbides and carbonitrides were obtained on diamond particles via PIRAC – Powder Immersion Reaction Assisted Coating or via modified PIRAC when in addition to metal powder with high affinity to carbon halogen (Iodine) catalyst is added. The PIRAC coating process didn't results in deterioration of mechanical strength of diamond particles.
2. Thick up to 150 mkm layers of Co and Co-W alloys were electrolytically deposited onto PIRAC coated diamond particles in relatively short time (< 1 h) at high current densities. Ultrasonic mixing during such processing prevents sticking of diamond particles to the electrode and to each other. Coatings formed are amorphous or nanocrystalline and for Co-W alloy coatings high microhardness can be obtained by proper annealing/aging treatment.
3. Thick up to several millimeter Co and Fe metallic layers were obtained on PIRAC coated or/and elecrolytically coated diamond particles by placing them into metal matrix and subsequent sintering at different temperatures.
4. Rapid processing of dense metal bonded diamond composites was developed based on rapid heating at low pressure of non-dense compact containing low melting phase above melting

termperature of this phase with application of higher pressure. This results in extrusion of liquid phase into pores, densification of material to full density and in some cases in partial reaction between liquid phase and the solid matrix. The process was called Short Distance Infiltration ,or SDI.

5. A number of Co, Fe, Co-Fe based matrices with a number of phases with low melting temperature were developed for the SDI processing and successfully used for fabrication of metal bonded diamond composites. Best mechanical properties were obtained for a matrix Fe-20Co-10Ni – (Cu-23Mn-17Sn).
6. Thermal stability of PIRAC coated diamonds in Co and Fe based matrices was investigated at 900 and 1000^{0}C and in was shown that PIRAC coatings may act as effective diffusion barriers preventing reactions of diamond particles with metal matices at high processing temperatures.
7. The processes developed during present research: PIRAC, electrolytic coatings of PIRAC coated diamonds and Rapid processing of dense metal bonded diamond composites *via* SDI – Short Distance Infiltration – are cost effective processes and can be effectively used by industries in both countries.

Impact Relevance and Technology Transfer

Knowledge accumulated at the Technion prior to starting date of the project as well as knowledge accumulated during present mutual research in the field of processing of high performance materials including advanced metal-bonded diamond composites for stone cutting, drilling and grinding was transferred to the Cooperating Investigator, Dr. Joanna Karwan – Baczewska, University of Mining and Metallurgy, Cracow. During her visits to Technion, Dr. J. Karwan–Baczewska was trained in working with advanced and unique processing equipment developed and existing at the Technion, such as High Pressure Consolidation/Cold Sintering, Hot Pressing Techniques with rapid heating as well as was trained in modern techniques of microstructure investigation SEM with chemical analysis - EDS of composite materials and coatings. High pressure cells were designed and fabricated at the Technion and sent to UMM in the beginning of 1997 and were used in the course of the project are are still used for processing of dense compacts of metal matrix composites at ambient temperature. In the end of 1998 pressure cells for hor pressing made from special superalloys were fabricated at the Technion as well as a furnace for hot pressing with rods and punches made from superalloys were sent to UMM, Cracow and were used in the course of the mutual research and are still in use. In addition to the this equipment pieces drawings of the pressure cells with materials and heat treatment specifications were sent to UMM and can be fabricated if needed locally.

In the course of the mutual research Dr. Karwan-Baczewska participated in a number of international conferences, presenting the results obtained and discussing with scientists from U.S., Europe and Japan the results as well as advanced topics of materials processing. A number of students were involved in UMM in the project and thus wer able to learn novel methods of materials

processing and characterization. Dr. Karwan-Baczewska presented two seminatr talks during her visits to Technion and had fruitful discussions with staff members and graduate students of the Faculty of Materials Engineering. During his visits to UMM, Prof. E.Y. Gutmanas presented a seminar talk and gave explanations to the technical staff on use of transferred equipment.

There were working contacts between Israel industry – "Toolgal Ind. Diamonds Ltd.", Degania A and Industries in this field in Poland: "Trzhebinia" and "CTD" – Zabrze. During last two years one of the technologies of fabrication of metal bonded diamond tools was transferred to "CTD' as well as laser beam welding apparatus for welding metal matrix segments with diamonds to the body of a cutting blade. Contacts are developing and more input from Toolgal Ind. Diamonds Ltd. into industry in Poland is expected in the near future.

Project Activities/Outputs

List of attended International Conferences and Meetings in the field of the project:

1. Annual TMS Meeting, Orlando, U.S., February 7 – 14, 1997.
2. 3rd International Conference „Non - Ferrous Metals' 97", Craców, September 11-12, (1997), Poland.
3. World Ceramics Congress & Forum on New Materials (CIMTEC'98), Florence, Italy, 14th-19tJune 1998.
4. 1998 Powder Metallurgy World Congress & Exhibition, Granada, Spain, October 18-22, (1998).
5. IV-th International Conference Non-Ferrous Metals'99, Kraków, June, 24-25 1999.
6. Eight International Conference On Composites Engineering (ICCE/8), August 5-11, 2001, Tenerife, Canary Islands, Spain.

List of training (Dr. Joanna Karwan-Baczewska at the Technion)

1. October 1996 – high pressure consolidation, PIRAC coating .
2. June-July 1998 – SEM/EDS of composite materials
3. September 1999 – hot pressing, Rapid heating – short distance Infiltration (SDI)
4. July 2000 – High Resolution SEM

Publications

1. J. Karwan-Baczewska, I. Gotman, E.Y. Gutmanas, *„Processing of Metal-Bonded Coated Diamond Composites"*, Proceedings of 3 rd International Conference „Non - Ferrous Metals' 97", Kraków, September 11-12, (1997), Poland, 350-353.

2. J. Karwan-Baczewska, I. Gotman, E.Y. Gutmanas, *„Processing and Properties of Metal - Bonded Coated Diamond Composites"*, Proceedings of the 1998 Powder Metallurgy World Congress & Exhibition, Granada, Spain, October 18-22, (1998), vol. 4, 217-222.

3. J. Karwan-Baczewska, I. Gotman, E.Y. Gutmanas, *"Dense Iron Based Alloys via Supertransient Liquid Phase Sintering"*, IV-th International Conference Non-Ferrous Metals'99, Kraków, 24-25 czerwca 1999.

5. E.Y. Gutmanas and I. Gotman, "Surface Modification of Graphite and Diamond via Reaction Metal Powders", in *9th CIMTEC – World Forum on New Materials: Surface Engineering*, ed. P.Vincenzini, Techna Srl.(1999) p.p.375-382.

6. G. Boczkal, J. Karwan-Baczewska, *„Technologie wytwarzania kompozytów metalowo-diamentowych" (Technology of Manufacturing of Metal- Bonded Coated Diamond Composites"),* Rudy i Metale Nieżelazne - Metalurgia Proszków , R.46, Nr 3, (2001), 125-131.

Project productivity

The project did accomplish all of the proposed research goals. The knowledge and experience accumulated in the course of the project are used for development of advanced methods of materials processing in Poland. More involvement of local industry in Poland was expected in the early stages of the research. We hope that activities of the industry in Poland during last year and currently and cooperation with Toolgal Industrial Diamonds Ltd., Degania A, Israel will result in practical implementation of the result of the reported research and use of the knowledge and experience accumulated at the UMM, Cracow.

Future work

The project resulted in close cooperation between two Institutions: Technion, Haifa and UMM, Cracow. This cooperation and knowledge and experience accumulated at UMM provides opportunities for future mutual research with possible industrial applications.

One of the possibilities is to use rapid heating and developed Short Distance Infiltration method with compositions, in which components can react with exothermic heat release – thermal explosion mode of Self-Propagating High –Temperature Synthesis (SHS), but in a controlled way. Such approach cab be also used for production of metal and ceramic-bonded diamond composites and especially advanced grinding wheels, which can be used in metal working industry, aircraft industry and electronics. Discussions on such mutual project are on the way. The research group at the Technion is one of the leading in the field in the world in fabrication of dense in situ composites via pressure assisted thermal explosion mode of SHS – the VI International Symposium on SHS, SHS-2001 *organized be the research group at the Technion (Dr. I. Gotman and Prof. E.Y.Gutmanas)* was held at theTechnion. At UMM, Cracow at the same Faculty where Dr.J.Karwan-Baczewska is working there is a very strong research group working in the field of SHS (Prof. R.Pampuch and Prof. J.Lis). For support EU as well as Goverments of both countries will be approached.

Another possible mutual project is in the field of Cu based nanocomposites, which posses combination of high strength and high electric and thermal conductivity and can be used in electronic industry. It should be mentioned that Poland has Cu mines and is one of the leading producers of Cu in Europe.

Literature cited:

1. EURO PM 2002, European Conference on "Hard Materials and Diamond Tooling", Lausnne, Switzerland, October 2002, Proceedings, EMPA 2002.
2. K. Hanada, M. Mayuzumi, N. Makayama and T. Sato, J. Mater. Proc.Techn. **119**(2001)216-221.
3. Z.Z.Fang, A. Griffo, B.White, G.Lockwood, D. Belnap g. Hilmas and J.Bitler, Int.J.Refr.Met.HardMater. **19**(2001)453-459.
4. V.M.Prokhorov, V.D. Blank and G.A. Dubinsky, Synt.Metals **121**(2001)1335-1336.
5. E.Y. Gutmanas, "Cold Sintering - High pressure Consolidation", ASM Handbook, "Powder Metal Technologies and Applications", ASM International, Materials Park, OH, (1998) p.p.574-582.
6. E.A. Levashov, I.P. Borovinskaya, A.S. Rogachov, M.Koizumi, M.Ohyanagi and S. Hosomi, Int.J.SHS **2**(1993)189.
7. M. Ohyanagy, T. Tsijukami, S. Suganura, M. Koizumi, E.A.Levashov and I.P. Borovinskaja, Mater.Sci.Forum **308-311**(1999)145.
8. Gotman, N. Travitzky and E.Y. Gutmanas, "Dense *in-situ* TiB_2/TiN and TiB_2/TiC CMCs: Reactive Synthesis and Properties", *Mater. Sci. Eng.* **A244**, 127-137 (1998).
9. E.Y. Gutmanas and I. Gotman (**invited**), "Dense High-Temperature Ceramics by Thermal Explosion under Pressure", *J. Eur. Ceram. Soc.* **19**, 2381-2393 (1999).
10. D. Horvitz, I. Gotman, E.Y. Gutmanas and N. Claussen, "*In situ* Processing of Dense Al_2O_3-Ti Aluminide Interpenetrating Phase Composites", *J. Eur. Ceram. Soc.* **22**, 947-954 (2002).
11. I. Gotman and E.Y. Gutmanas, "Microstructure and Thermal Stability of Coated SiC and Si_3N_4", *Acta Metall. Mater.* **40S**, 121-131 (1992).
12. E.Y. Gutmanas, I. Gotman and W. Kaysser, "Coating of Non-Oxide Ceramics by Interaction with Metal Powders", *Mater. Sci. Eng.* **A157**, 233-241 (1992).
13. I. Gotman, E.Y. Gutmanas and P. Mogilevsky, "Interaction between SiC and Ti Powder", *J.Mater. Res.* **8**, 2725-2733 (1993).
14. A.G. Merzhanov, Dokl. Akad. Nauk USSR **233** (1977) 430.
15. G. Boczkal, J. Karwan-Baczewska, *„Technologie wytwarzania kompozytów metalowo-diamentowych" (Technology of Manufacturing of Metal- Bonded Coated Diamond Composites"),* Rudy i Metale Nieżelazne - Metalurgia Proszków , R.46, Nr 3, (2001), 125-131.