Development of New High Performance Nanocrystalline Hard Metals

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ABSTRACT

It is known that performance of nanocrystalline hard metals suppresses that of ordinary materials. Lots of techniques for manufacturing nanopowders were developed and successfully used but preparation of nanocrystalline bulk pieces still faced certain problems. The resulted materials sintered by conventional technologies were nanocrystalline pieces. However physicomechanical testing of the pieces showed that their performance was not improved to an expected level, a possible reason considered to be an excessive free carbon: remaining in the material during the synthesis and playing an important role in preserving nanocrystallinity, at the same time it makes obstacles to obtaining hard metal pieces with high performance. Problems of elimination of excessive free carbon during the process of manufacturing of new high performance nanocrystalline hard metal pieces were solved by using a method and a device developed in the RCSR on the basis of Spark Plasma Synthesis (SPS) method.

Keywords: nanotechnology, SPS, hard metals

Carbides of transition hard metals, in particular, titanium carbide, are materials with unique properties they are good subjects for numerous investigations [1, 2]. A fact of broadening of the production of titanium carbide and its wide application in various areas, has transferred it to the ranks of the materials widely used in the industry and not only in the area of solid state physics as it was used earlier as a convenient and model material for research studies [2]. High demands are made of the materials with titanium carbide content used in rocket production, aircraft, nuclear power and microelectronics industry. A probability of using titanium carbide to that or other production is defined by a complex variety of properties [3], one of them and the most important, being structural condition of the material. Most promising is using of titanium carbide in microcircuitry in the electronic industry [4]. Main disadvantage of using hard metals based on titanium carbide if compared with those based on tungsten carbide is lack of elasticity of the material though we think that this kind of disadvantage can be removed in case if the alloys are fabricated on nanocrystalline level. Physical-mechanical properties of nanocrystalline materials significantly differ from those with crystalline structure. Nanocrystalline carbides are characterized with excellent catalytic properties [5].

Fabrication of hard metals by powder metallurgy technique embraces the following steps: production of the powders of hard metal components, preparation of the charge of hard metals, forming, sintering and control. We have developed a nanotechnology for manufacturing of powders of hard metals. After compaction and sintering of the obtained nanopowders with standard technology the structure of alloys remains nanocrystalline. Investigation of physicomechanical properties showed that their characteristics are a little better than those of the obtained by standard technology. However the hard metals with nanocrystalline structure were to have much higher performance. A reason preventing to achieve much better results appeared to be an excessive free carbon which remains there during the synthesis of nanopowders. Namely the excessive free carbon was a reason for the preserved nanostructural state at synthesising the samples by an ordinary technology: due to being plated on carbide particles an excessive free carbon makes obstacles to their growth. The same excessive free carbon was an obstacle on the way of obtaining hard metal samples with high performance since the structure was nanocrystalline. All details of the technological cycle of fabricating nanopowders will be studied within the scope of the project. Mechanism of formation of carbon will be established during the process of synthesizing and an excessive carbon will be eliminated. Reduction of the amount of free carbon in hard metal nanopowders will make possible to prepare pieces with high physicomechanical and operation properties by using SPS device.

New technology is based on realization of the methods elaborated by group of Georgian Technical University. The new technology provides formation of nanocrystalline material. This method is based on thermo-chemical synthesis. Carbides - hard components of hard metals –are obtained by a high-temperature synthesis, and therefore they are coarse-grained. Despite the fact that they are disintegrated to ~ 0.1μm upon grinding, during the process of sintering they grow up to 1-10μm. Bonding components of hard alloys are not disintegrating. Upon grinding they undergo plastic deformation and after heating their size increases up to ten and even hundreds of microns. Issued from the above mentioned it is clear that for the obtaining of dispersed system it is necessary to conduct a low temperature synthesis. Such a synthesis may be provided by obtaining of chemical compounds (chemical synthesis) and their subsequent pyrolysis (thermal synthesis). The subsequent operations are similar to the technologies common for making hard alloys, but with one difference - in such case the plasticization of powder is not necessary. Nanocrystallinity of bonding material of hard alloys promotes to good ability of compressing the powders. It should be noted that upon heating, grains of the components of hard alloys are not coarsening when the process is thermo-chemical synthesis and a final product remains nanocrystalline.

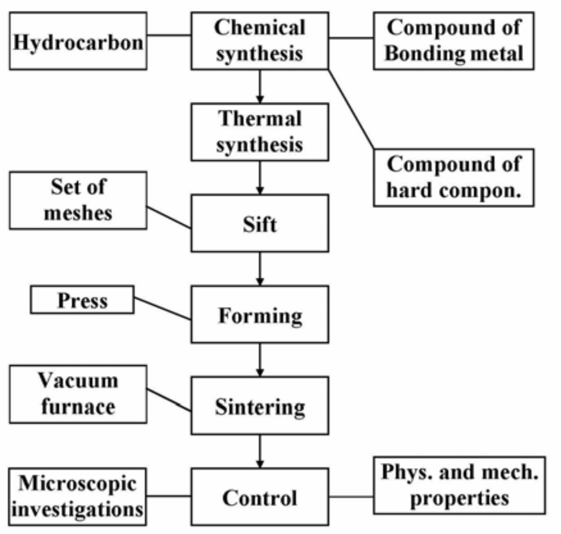

Fig.1 Schematic drawing of a technological cycle for the production of nanocrystalline hard metals

The thermo-chemical method (Fig.1.) is based on formation of nanocrystalline hard metal charge because of high temperature (~900oC) chemical interaction of titanium hydride and bonding metal salts with hydrocarbon compounds and the resulting product is a hard alloy charge where all components are in nanocrystalline (of an order of 200-300 nm) state. Sintering of such material will possibly lead to coarsening of grains and certainly the material will not remain nanocrystalline. But if nanocrystalline carbide particles will be coated with nano particles of bonding material or demarcated by them, then they will not grow upon sintering and hard metal will preserve nanocrystallinity.

A number of new techniques for powder consolidation aimed at fully dense bulk nanocrystalline materials have been proposed in recent years [6-11]. Preparation of bulk pieces requires compaction and sintering of the obtained nanocrystalline powders. This process is connected with lots of problems, namely, it is very difficult to preserve nanocrystalline structure of powders in the bulk. Standard methods for manufacturing of bulk material are: cold compaction with further sintering, hot pressing, sintering under high pressure, electric discharge synthesis, shock-wave sintering and gasostate sintering. Basing on these methods by different companies there were designed and built various installations: for hot pressing, max temperature 2400o C, max pressure 40MPa (1000A, Thermal Technology INC., USA); High temperature graphite furnace, max temperature 2400o C, equipped with quenching facilities (1000-4560-FP20, Thermal Technology INC., USA); Spark Plasma Sintering unit (SPS), max temperature 2000o C, max. load 20000 kN (Dr Sinter 2050, Sumitomo Coal Mining Co., Ltd, Japan); Microwave sintering unit, 6 kW operating at 2.45 GHz (S6G Cober Electronics Inc., USA) and etc Using of these methods and of an appropriate installation is not effective because of intensive growth of grains which stimulates formation of an ordinary structure instead of the desired nanostructure.

One way to prevent the processes of grain growth is adding of inhibitors to the powders. However this route is not the best one because composition of the material will possibly be changed due to contaminations brought in the powders: nanocrystallinity may improve properties of the material, however adding of inhibitors may reduce these properties. But very often such additions have negative effect on the alloys. It seems that an excessive free carbon appearing in our experiments at thermochemical synthesis works as a natural inhibitor. Pressing of hard metal in the presence of excessive free carbon is difficult. Only some parts of hard alloy can be consolidated and the structure becomes porous. Nanocrystalline structure in agglomerates is preserved. In such cases, due to porosity, strength characteristics of the structure of the alloys are not as high as required of nanocrystalline structure. Therefore improving of characteristics induced by preservation of nanocrystallinity is not as efficient as expected. Another way to prevent the processes of grain growth is: guiding of sintering processes in the time limited to a certain extent. This route is realizable in the installation based on using SPS method which is considerably new and it can be used to conduct in situ preparation and synthesis of composites with superfine microstructures. In spite of the fact that there are already designed and constructed the SPS method-based industrial installations, physical essence of the provided processes are not yet clarified to final extent.

As notified earlier nanocrystalline hard metals can be fabricated by an ordinary sintering technology. Presence of excessive free carbon impedes processes of grain growth but does not promote significant increase of physicomechanical performance of the alloys. We have developed a new device for sintering of nanocrystalline hard metals. Principle of working of the device was based on plasma-sparkling sintering method. Fig.2 shows press-form for forming and sintering cylindrical hard metal samples. Powder is isolated from matrix and high-ampere pulse current passes through puncheon to powder.

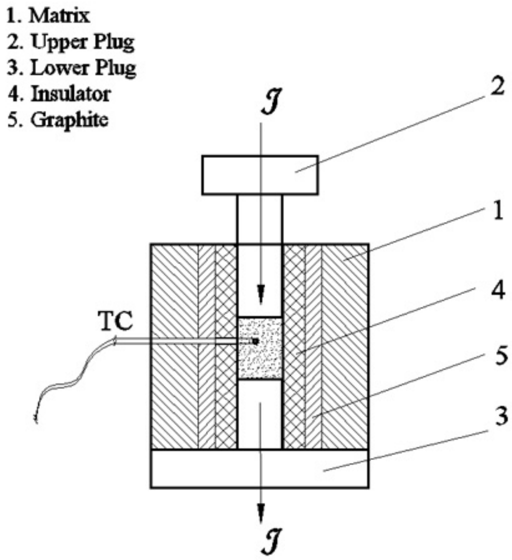

Fig.2. Press-form for the synthesis of nanocrystalline hard metal.

Principle of working of the SPS-based device is the following: Passing of a pulsed DC of low voltage and high magnitude through a powder material creates high temperature mainly in the area of particle contact. High temperatures created in microseconds are not sufficient for spreading through the whole mass of a powder and hence, temperature of powder mass remains rather low and the processes of grain growth do not proceed. However the temperatures created between the surfaces of powder particles are quite sufficient for providing the processes of synthesizing and therefore the obtained material remains nanocrystalline. Devices of the SPS type available worldwide are intended for using only of conductive powders, or the materials capable to gain conductivity after heating. Otherwise there can not be created any spark between powder particles and subsequently, plasma can not be created. Therefore using of such devices for dielectric materials is not appropriate. Another problem while applying such devices is using of nanocrystalline powders with high rate of aggregation.

For measuring the temperature chromel-alumel thermocouple is introduced in the powder. Passing of pulse current through the powder provides the process of sintering due to creating a sparkle and the followed up plasma (Fig.3) between contact points of hard metal particles. Heat is released only in the contact points between grains. Duration of pulsing can be varied from one to several tens of milliseconds. During such a little period of time only a surface is heated and the heat can not be spread through the grains. Therefore the temperature of a sample is much less than that at the contact points of grains. High interfacial contact temperature promotes sintering of the sample and due to low integral temperature - prevents the process of grain growing thus providing for maintenance of nanocrystalline structure.

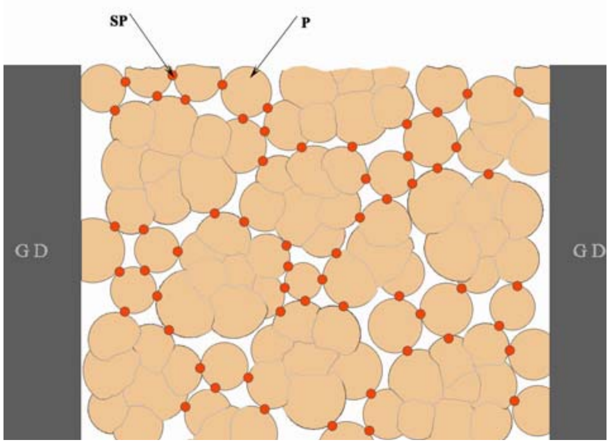

Fig.3. Scheme of hard metal structure-formation at sintering by using ark-plasma method.

The developed device also solves a problem of excessive free carbon creating at the fabrication of nanocrystalline hard metals based on titanium carbide. The solution is analogous: in this case it is also necessary to bring an excessive amount of free carbon into the charge for fabricating nanopowders with normal structure. This excessive free carbon furtherly makes obstacles to the alloys to be normally sintered. If carbon introduced into the charge is of fewer amounts, then there is detected presence of new structure compounds besides the main phase in nanopowders. Fig.4 shows X-ray diffraction pattern of the nanopowder with an excessive amount of the introduced free carbon: there are observed molybdenum, tungsten and their carbides (W_2C and Mo_2C) (Fig. 4a). It is easy to overcome this disadvantage if the powders are sintered on the developed device (Fig. 4b)

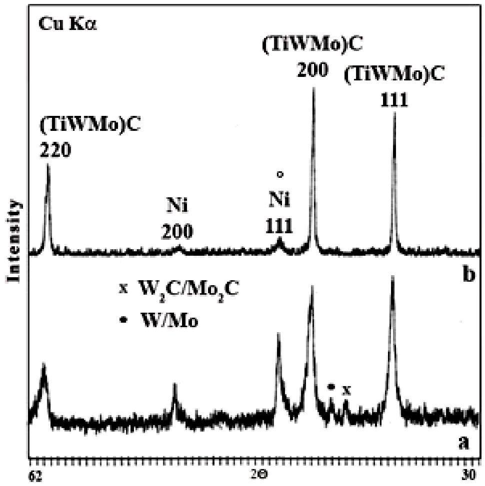

Fig.4. X-ray diffraction patterns of hard metal TiC-Ni-Mo-W: a- nanopowder with molybdenum, tungsten and their carbides, b- sintered alloys with normal structure.

From the nanopowders with rather defective structure (Fig.5a) can be easily fabricated alloys with normal structure (Fig. 5b) if the SPS method and the developed device are applied.

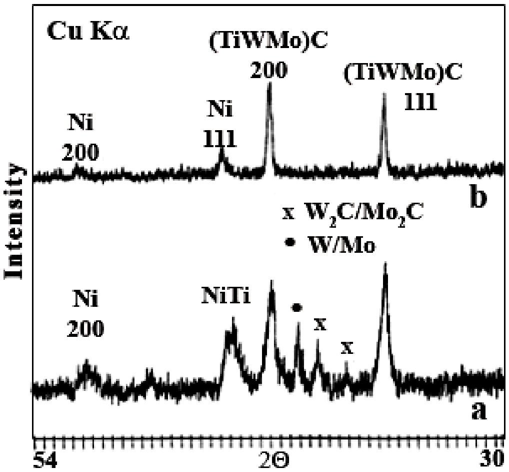

Fig.5. X-ray diffraction patterns of hard metal TiC-Ni-Mo-W: a- nanopowder with W/Mo, W_2C/Mo_2C, NiTi, b- sintered alloys with normal structure

Unique experiments were conducted on fabrication of nanocrystalline hard metal with the help of the developed device immediately from the alloy components omitting the procedure of preparing initial nanopowders. Fully sintered nanocrystalline hard metal of the (TiW,Mo)C-Ni system was obtained from the charge comprised of titanium hydride, nickel chloride, molybdenum- and tungsten oxides and soot (Fig. 6).

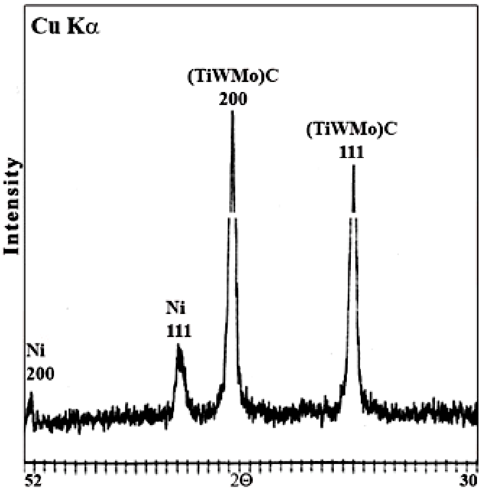

Fig.6. X-ray diffraction patterns of fully sintered nanocrystalline hard metal of the (TiW,Mo)C-Ni system obtained from the charge comprised of TiH_2, $NiCl_2$, MoO_3, WO_3 and soot.

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