Bulgarian Academy of Sciences

Institute of Information and Communication Technologies

Department: Embedded Intelligent Technologies

DISSERTATION

HIGH TEMPERATURE PROCESSING OF MATERIALS AND ALLOYS CONTAINING NANO ELEMENTS

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A B S T R A C T

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Goal and tasks of the dissertation:

The aim of dissertation thesis is to study high temperature processes for materials and alloys and to offer innovative technologies for obtaining new materials and alloys using nanoelements.

To accomplish this goal, the following tasks will be solved:

1. An overview, analysis and systematization of types of high-temperature technoologies and means for their realization will be made.

2. An overview, analysis and systematization of types of materials in the micro- and nano-field will be made.

3. Existing high-temperature processes for the synthesis and sintering of metals will be studied.

4. A structure, organization and composition of a high-temperature technological line based on a Taman furnace will be proposed.

5. Innovative technologies with the use of an updated high temperature furnace will be proposed.

6. Experiments will be made to improve the operation of the Taman furnace.

7. Real experiments will be conducted and results will be presented for diamond tools. The results will be analyzed.

8. Real experiments will be carried out and results will be presented for sintering of silicon carbide. The results will be analyzed.

9. Real experiments will be carried out and results will be presented for sintering of boron carbide. The results will be analyzed.

10. Real experiments will be conducted and results for high temperature sintering and pressing of solid materials will be presented. The results will be analyzed.

1. INTRODUCTION

The high efficiency of powder metallurgy (PM) lies in the production of materials or products that are technologically impossible or uneconomic to be produced by other methods. A distinctive feature of PM is that the items are prepared in substantially non-waste technologies. Regardless the higher cost of the powders in comparison with the ones of die casted metals, the material costs per unit of products obtained by the methods of PM are always lower than for products obtained by cutting, stamping, milling and others. For example, the coefficient by PM methods of the used material is in the range 95-97%, while by cutting this value is only in the range of 50-60%. Another advantage of PM method is the relatively low number of operations - generally no more than 3-5, allowing the manufacture of products to be concentrated in one enterprise, which is associated with an increase in labor productivity, reducing energy losses, reducing the number of workers and as a result - with the decrease in the price of the final product. The used processes are usually easily amenable to automation, furthermore by using press machines the quantity of dust needed to obtain a material with a certain density is dosed accurately, avoiding material losses inevitable in producing of die cast parts. The method of PM is unique in the production of metal or ceramic-based composites, copper-graphite conductive parts, WC-Co for machine tools, W-Cu alloys and many others. The proposed methods for developing include composite materials based on titanium carbide TiC - steel (ferotik) and on the basis of boron carbide (B4C).

2. HIGH TEMPERATURE PROCESSES

In modern technological processes with high temperatures, the so called Tammann furnaces - Fig. 1, named after their inventor, are the most commonly used equipment. Unlike furnace aggregates, employing tungsten heaters, induction heating, and even low-temperature plasma, the Tammann furnaces have proved themselfs to be indispensable. Their versatility is due to their relatively simple structure. The use of graphite as a heating element and boats for transport of materials (Fig. 2) allows its quick replacement after an accident. Its high chemical resistance in the working process (in an environment of protective gases such as nitrogen, hydrogen, methane, argon) makes it indispensable in a variety of processes. Tungsten, which is also used in high temperature equipment, is susceptible to chemical interaction with materials in sintering furnaces. Induction heating, which is alsoused as graphite heater has a complex construction, maintenance and repair of induction heating furnaces is relatively time-consuming and expensive operation. The plasma heating facilities are of limited use in specialized operations.

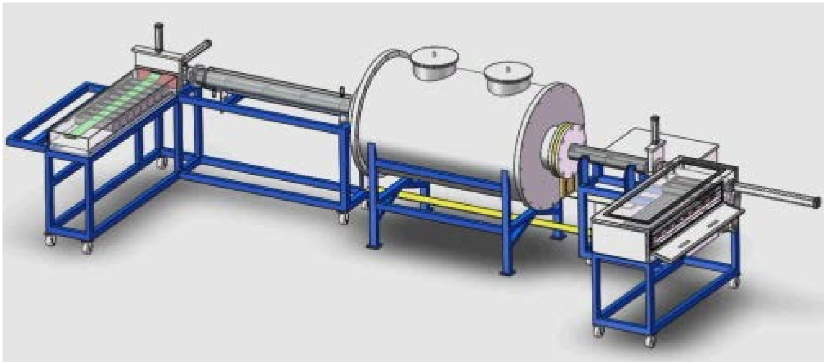


Fig.1.General scheme of Tammann furnace

Fig.2. Boat

A significant advantage of Tammann furnaces compared to other high-temperature plants is their high performance and ease of servicing.

Tammann furnaces are used in modern processes for the production of materials in the form of powders, and the sintering of composite, high-temperature ceramics "methallylene". Powders, produced in Tammann furnaces are carbides, tungsten, the complex titanium-tungsten carbide, chromium, tantalum and niobium, molybdenum. Produced are borides, nitrides and silicides of transition metals. These compounds have thermal and electrical conductivity equal to or higher than the metals from which they are produced and due to this specificity, resulting from their crystalline structure (phases of deployment), they are known under the name "methallylene". In Tammann furnaces are produced aluminide (aluminum di- and dodecaboride) used as modifiers in foundries.

In Tammann furnaces is carried out the sintering of composites such as tungsten karbid-cobalt or titanium-tungsten carbide-cobalt, chromium carbide-nickel, etc., as well as pseudo alloys: tungsten-copper, silver-tungsten, nickel-volfarm. These composites are hard alloys for metal processing (cutting, drilling, finishing processing, impact-compaction and deformation tools) for mining; for deep drilling, such as wear parts (nozzles, etc.); for accurate measuring instruments; electric-bodies for high voltage equipment.In Tammann furnaces is carried out sintering of items of hard and wear resistant methallylene (titanium carbide, titanium diboride) of boron carbide, silicon carbide, silicon nitride. These products are used in high-temperature equipment such as refractories, thermocouples in precision metallurgy such as rocket nozzles and air as wear-resistant products.

Tammann furnaces has gained a wide application in the manufacturing of carbon and graphite fibers and articles thereof. Recently they are also used for the preparation of nanopowders out of refractory compounds (carbides, borides).

3. HIGH TEMPERATURE TECHNOLOGIES

The high temperature technologies have applied research results in the following areas:

1. Cheaper obtaining of micro and nano powders for various areas, including the use as modifiers in casting non-ferrous metals and composites, modified as alloys based on copper, iron, steel.

2. Impregnation of articles of tungsten, molybdenum (hard caking heavy elements), as well as carbides, borides or nitrides of the transition metals of the IV, V and VI subgroups of the periodic system of elements.

3. Obtaining of special materials based on graphite.

4.Obtaining of materials for hard, wear-resistant coatings of nano-elements for high-temperature processes.

Some of the approved technologies of the Tammann furnace are as follows:

Carbo thermal obtaining of Si-Mn-V ferro alloy – Fig. 3

Fig. 3. The furnace and the hot material

It is known that manganese and, in particular, vanadium in small quantities increase significantly the quality of the steels. Complex alloys are increasingly widely used in the field of metallurgy for deacidification, alloying, modifying and desulfurization. It is significantly more effective that the elements are obtained in the composition of a ferro complex, rather than as individual items. In this aspect of interest is the study of the possibility of co-reduction of the agglomerate obtained from mixtures of the concentrate of a carbonate manganese ore and deactivated vanadium catalyst.

Our country has its own vanadium deposits. Important as the raw source of vanadium have some waste products. These include exhaust vanadium-oxide catalysts for the oxidation of sulfur dioxide in the production of sulfuric acid. The vanadium catalyst in the process of work is deactivated, and subsequently disposed. Thus in the country have been

accumulated significant amounts of exhausted vanadium catalyst. At the same time it contains a significant amount of scarce vanadium.
On the other hand, Bulgaria has deposits of manganese ores. Deposit near Obrochishte (Varna region) includes large stocks of relatively poor carbonate manganese ore. The opportunities for pyrometallurgical carbo-thermal processing of manganese ore there is a subject of research interest.
One way to use of poor-ore materials and at the same time the waste materials is their thermal processing in Tammann furnace.

Electro-alumo thermal obtaining of Si-Mn-V – Fig. 4

Fig. 4. The alloy and the Si-Mn-V stouns

For the realization of the task is undertaken a balance alumo – thermal calculation of the expected amount of alloy, slag and gas phase. For the calculation are used the same ratios of conversion of the elements in the alloy, the slag and the gas phase, as in the above (carbo-thermical) process.
After these steps there is an available batch for the preparation of multi-component alloy in the Tammann furnace. The batch is composed of agglomerate and a stoichiometric amount of reducing agent - aluminum. Aluminum is in the form of shavings. The used agglomerate is similar to the preceding one with a 70% content of manganese concentrate and a 30% content of vanadium catalyst. The agglomerate and the calculated reducing agent are mixed and disintegrated to a particle size below 1 mm, then charged graphite crucible. For the process is used a Tamman furnace. A better separation of metal and slag when pouring is reached.

Electro-silico-alumo thermal obtaining of Mn-V

For the realization of the task is undertaken a balance silico-alumo thermal calculation of the expected amount of alloy, slag and gas phase. For the calculation are used the same ratios of conversion of the elements in the alloy, the slag and the gas phase, as in the above

process.
After these steps there is an available batch for the preparation of multi-component alloy in the Tammann furnace. The batch is composed of agglomerate manganese concentrate and vanadium catalyst) and a stoichiometric amount of reducing agent - FeSi and aluminum. Aluminum is in the form of shavings. FeSi is standard, crushed into small pieces. The agglomerate and the calculated reducing agent are mixed and disintegrated to a particle size below 1 mm, then charged into a graphite crucible.A better separation of metal and slag when pouring is reached.

Similar heat treatment may be performed in an electric furnace.

Preparation of Si-Mn-V alloy by heat treatment carbo

A preliminary carbo thermal calculation is undertaken, similar to that in Tammann furnace and of the estimated amount of alloy, slag and gas phase.
For the electro-carbo termal processing and in order to compare the subsequent results are used two types of agglomerate:
- an agglomerate obtained only from gravity manganese concentrate;
- an agglomerate obtained only from gravitational manganese concentrate and the recovery of vanadium catalyst in a ratio of 70 to 30 weight percent.

The first option includes a batch consisting of an agglomerate of manganese concentrate, semi-coke, lime and flux. Before feeding into the furnace the charge should be well homogenized. The filling is carried out in the following way: the floor of the bath is first coated with a thin layer of the batch mixture, the electrode is lowered down to the ignition of the arc and is maintained at the specified load current. Then portionwise is fed the batch until its complete exhaustion. During the course of the process is maintained a constant level of charge in the tub and a constant value of the current load. It is necessary to maintain such an electric mode, which creates conditions for the optimum speed of movement of the batch from top to bottom (batch processing). This optimal speed of processing is determined by the maximum degree of reduction of the oxides and batch formation processes. After accumulation of a certain quantity of alloy and slag at the bottom of the bath of the furnace, it is released into the iron cast mold, which is plastered with lime milk and graphite. The process is continuous and ends after the processing of the specified amount of the batch mixture.

In the second embodiment, the furnace is fed agglomerate of manganese concentrate vanadium catalyst and coke. There is no addition of metallurgical lime and fluxes in this process. The process is conducted similarly to the first.

The third option is conducted through the fluxing of the agglomerate of manganese concentrate and vanadium catalyst with metallurgical lime and fluorspar. The process flow is identical to the process with the first two prozesses.

Preparation of si-mn-v ferro-alloy by electro-alumo thermal processing

Another option is an electro-alumo thermal reduction of the agglomerate of manganese concentrate and vanadium catalyst with a flux in an electric single-phase electric furnace. The chemical composition of the agglomerate is the same. The furnace is similar as in the carbo thermal process.

4. INNOVATIVE TECHNOLOGIES WITH TAMMAN FURNACE

Boron carbide - properties and application

The boron carbide occupies in the hierarchy of material hardness the third place after artificial diamonds and cubic boron nitride modification. In contrast to these two materials, the synthesis of B4C proceeds relatively easily. It is interesting to mention that the synthesis of (BN)c out of (BN)h is carried out at more difficult conditions (temperature, pressure) than the synthesis of diamond from the carbon material. Boron carbide belongs to ultrahard (~ 40 GPa) and also to the refractory (2450 oC) materials. It has high chemical and good resistance to high temperature oxidation. The presence in the composition of the compound of the isotope 10C (barn) determines the highest absorptivity (600 barn) of B4C with respect to the neutrons of thermal energy spectrum:

10B + 1on → 42He + 73Li + 2.78 MeV

The products of the reaction are not radioactive and the radiation is "soft" and can be ignored. Tablets of hot pressed B4C are used in the preparation of the regulatory nuclear reaction systems of different construction (PWR, BWR) of nuclear power plants. The combination of low density (2.52 g.cm-2), extreme hardness and high value of the modules of elasticity (E ~ 400 GPa, B ~ 200 GPa, G ~ 200 GPa) determines the application of B4C in military engineering for the production of body armor, armor for tanks and helicopters. Manifactured from boron carbide are also gauges, templates, sharpening tools, safety thermocouples, mortars and others; as well as high quality sand blasting and shot blasting nozzles in metallurgy, machinery, ships, architecture, dentistry. Some typical application areas are presented in Figure 3. A comparison of the wear resistance of nozzles of different superhard materials (corundum, self-bonding SiC, hard alloy WC-Co, SiC) to corundum (Al2O3) shows the superiority of the production of boron carbide (Fig.5). Nanoscale powders are used in Boron Neutron Capture Therapy (BNC) of tumor diseases. The high thermal and chemical stability determine the application of B4C in the architecture of the fuel cell acting as a catalyst carrier.

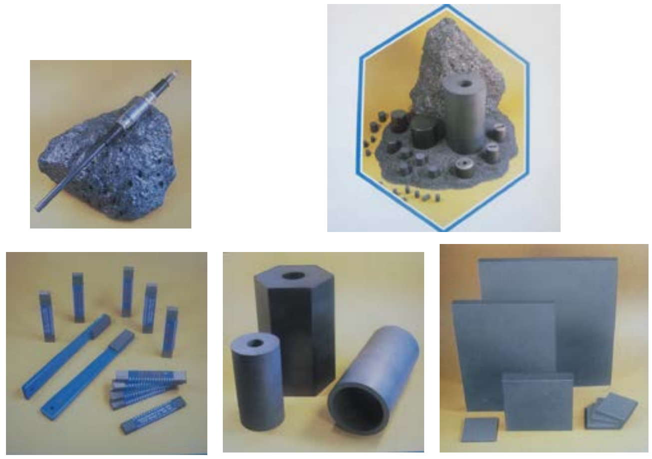


Figure 5. Boron carbide: Applications

Technological features of the process of activated sintering the high temperature wear-resistant material out of boron carbide are innovative.

Process technology:

1. Homogenised mixture of nano-powders of the boron carbide with tungsten carbide in the presence of a liquid phase in a ball mill,
2. Vacuum drying the homogenized mixture with a vacuum dryer,
3. Lamination / mixing nano-powder with a plasticizer. A pre-heating mixing Z blender is used.
4. Isostatic pressing of shapes with an isostatic press.
5. Deplasticizing of the pressed handlings in a cold furnace in an atmosphere of hydrogen or inert gas (nitrogen, argon)
6. High temperature sintering in a hydrogen atmosphere at a temperature 22400 C - 22600 C in a Tamman furnace.

5. NON-DESTRUCTIVE TESTING

For the study of the source materials (powders) as well as for the study of 3D internal structure of the output - materials and alloys, are used the devices:

1. Laser particle size analyzer ANALYSETTE 22 Nano Tec plus, consisting of a module for measuring, dispensing modules for "wet" measurement in the range of 0.01-2000 microns and for "dry" measurement in the range of 0.1-2000 microns, 3 semiconductor lasers with a life of 10,000 hours, with a protection class of EN 60825, and a management software - Fig. 6.

Here we can use it for the accurate measuring and dispensing of the concentration, size and size distribution of micro and nano particles in a mixture of materials or alloys designed for high-temperature processing.

Fig. 6. A laser nano particle sizer

Industrial computerized tomography STDS-600-200 / XTH 225 for non-invasive scaning of the internal structure of a 3D objects, up to 225 kV 225 W X-radiator, with a built-in anti-radiation protection for personnel, with spot (section) of the X-ray of less than 3 μm, a manipulator with 5 axes for adjustment to the position of the object, with a weight and dimensions of the object up to 15 kg / 200h300h600 mm, and a specialized software - Fig. 7.

Here we can examine the internal 3D structure obtained by heat treatment of metals and alloys containing micro- and nano-elements.

Fig. 7. Industrial 3D Tomograph

Tested were the source materials (powders) for high temperature production of high-melting compounds (nitrides, borides, carbides, silicides) as well as their internal 3D structure. In Tammann furnace upon reaching a temperature up to 2200-2300 ° C are sintered together items of high-melting metals (tungsten, molybdenum), composite materials (metal-methallylene) as well as graphitizations of polymeric materials for manufacture of safety and protective clothing.

Samples of iron basis for demonstrating the operational capabilities of high-temperature Tammann furnace have been sintered. Implemented was an experiment on sintering at a maximum temperature of 2300 ° C of articles of boron carbide. The samples of iron were pressed in the factory "Sinter-M" in Yambol. The used iron powder brand NC 100-24 was manufactured by the company Höganäs, Sweden and contained minor amounts of carbon / 0.01% /.
The particle size of the powder used is in the range +150 /up to 1% / and -48μm /up to 18%/. To the iron powder, by stirring in an atmosphere of absolute alcohol, were added micro powders of carbides /titanium carbide/ and borides /titanium diboride, dihrom pentaborid/. The content of the added powders depends on the purpose of the experiments. All produced items are from the actual production of the plant (Fig. 8). The pressing process is carried out at 500 MPa using 0.8% of zinc stearate as a plasticizer.
The composition of the starting powders was examined in advance by a laser nno granulometer in order to determine the particle size and its distribution.
Two types of iron powders were tested. For each one were made on several measurements. Fig 9. shows the average results.

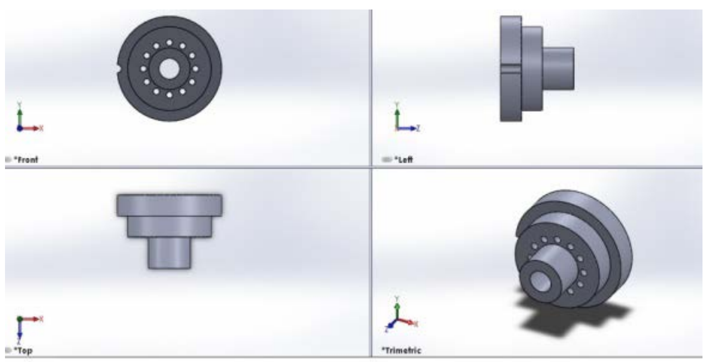
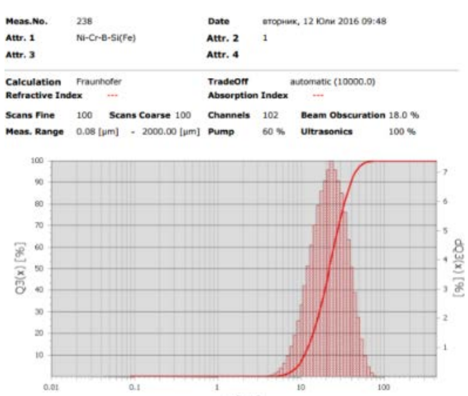


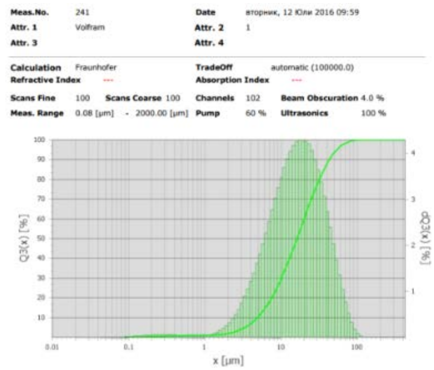
Fig. 8. Article of iron powder – nozzle



I50 1.30 **D[4,3]** 23.8 μm

Q3(x) [%]	x [μm]
5	9.2
10	**11.1**
25	15.3
50	**21.8**
75	30.4
90	**39.5**
95	45.5
99	57.3

a) Size - Experiment 1 b) Distribution by size - Experiment 1



d50 2.35 **D[4,3]** 20.6 µm

Q3(x) [%]	x [µm]
5	3.4
10	**4.9**
25	8.8
50	**16.2**
75	28
90	**42.9**
95	53.6
99	75.4

c) Size - Experiment 2 d) Distribution by size - Experiment 2

Fig. 9. Particle size of the used powders

The sintering of iron products, alloyed with micro powders, was carried out at a temperature of 1150 ° C - a temperature, which is used in production for sealing of the alloy articles up to a maximum density of 6,9-7,0 g / cm3 or about 90% of the density of the metal. In cases, when the carbonizing of the produced items was not necessary, was used packing boron nitride with a size up to 100 nm. For carrying out the carbonization of the products was used backfill of nano-sized powder of silicon carbide.

As a protective medium by the heating the furnace to 600 ° C was used nitrogen, above this temperature was used hydrogen. The used gases had a 99.8% purity. The heating time of the nacelle /graphite container/ was 45 minutes.

The composition of the various composite materials used in the experiments was as follows:

1. For the resulting preparations of the type "Ferotik" / company name of the instrument material - iron-titanium carbide/ was used as input titanium carbide with dimensions 4,6-5,1nm and a content of 12% relative to the iron base. To avoid any further carbonization due to the methane in the furnes was used a bedding of boron nitride. The sinter products were subjected to vacuum annealing to reduce the hardness in order to be to be finished with cutting tools.

2. For the densification and simultaneously alloying of the iron products were used borides of titanium and chromium in separate samples. The borides of transition metals /titanium and chromium/ form at the sintering temperature of the iron products, due to the presence of boron, an eutectic liquid, which seals the porous preform. This makes the production of iron powder metalurgical products for hydraulics and pneumatics.

The powder of titanium diboride is in the nano-size range of 100-120 nm. A small amount of boride /1.5% of the mass of iron/ was used, as the powder has a large surface above 100 m^2/g / and practically get into contact with almost all of the particles of iron. Dihrom pentoborid powder has a size of 500 nm. It was used a 2.5% addition to the iron powder.

Composite materials containing borides of titanium and chromium were packed in a powder of boron nitride. The sintered samples containing titanium have a density of 96-98%, and those with chromium boride have a theoretical density of 94-96%. All samples, however, have changed dimensions due to shrinkage, some are deformed.

3. The powder metallurgy has a practical interest in the simultaneous sintering and recarburising of iron products, which is normally separately done in specialized facilities. Combining the two processes leads to time and energy savings. For this purpose in a Tammann furnace were sintered without allowing compressed iron items packed in nano powder of silicon carbide. By the sintering in an environment of methane were obtained products with firmness, in the middle of the diameter cut, over 58-60 HRA.

When increasing the temperature up to 1270 ° C is obtained a surprising effect: surface coating of the products with nanoparticles of silicon carbide. The layer consisted of white cast iron with a high content of silicon. We will continue the experiments in order to create a new composite material.

4. Because of the absence of larger amounts of tungsten powder, which is used as an activator for sinterting of boron carbide, the tests by the high temperature /to 2300 ° C/ process of producing composite materials were restricted to small-scale devices, from the material used in nuclear energy, in the body armor and other articles. According to the instructions of Prof. Dr. Ing. Dimitar Radev sintered small devices allow the assumption that in Tammann furnace in the presence of tungsten can be conducted experiments for obtaining of nozzle, plates and protective elements.

Finished samples of high temperature produced materials and alloys containing nano-elements were examined in 3D industrial CT for 3D reconstruction and visualization inside a structure of studied objects in order to detect defects, pores, irregularities in the structure or in the distribution of constituents and others.

Examined were: Articles made from sintered boron carbide - Fig. 10

<u>Composite material "titanium carbide - iron" - Fig.11.</u>

<u>Silicon carbide on carburized iron - Figure 12.</u>

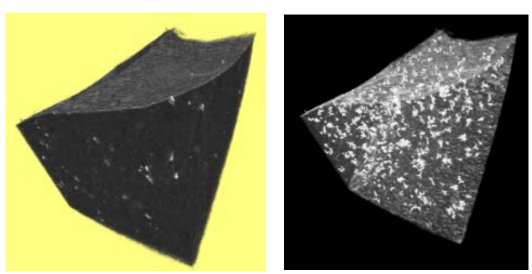


Fig 10. Flaw detection of articles of sintered boron carbide

Fig.11.Microstructure of titan carbide - iron

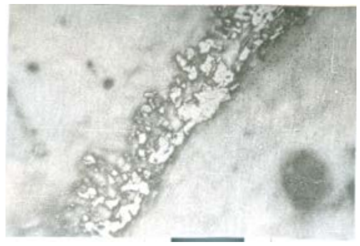


Fig.12 A layer of silico carbide on carbon iron

Other Experiments are as follows:

Sintering of Silicon Carbide and Boron Carbide in existing liquid phase (Fig. 13 - 20) with different percents of Si, SiC and B_4C.

Fig. 13 2% Si + SiC, T=1440℃

Fig. 14 6% Si + SiC, T= 1440℃

Fig. 15 6%Si + C, T= 1440℃

Fif. 16 2% Si + SiC, T=1650℃

Fig. 17 6% Si +SiC, T=1650℃

Fig. 18 %4 Si + C, T= 1650℃

Fig. 19 3% + B_4C, T= 1650℃ Fig. 20 10% + B_4C, T=1650℃

On the Fig. 21-24 are shown different diamond tools for granite processing, drilling, and polishing, as well as diamond particles fastened to the metal matrix.

Fif. 21 Diamond tool for granite processing Fig. 22 Diamond tool for drilling

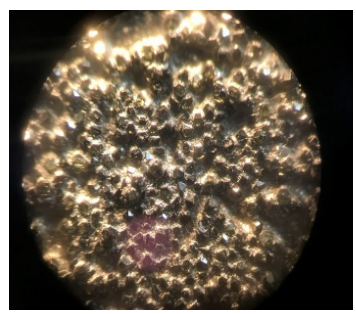
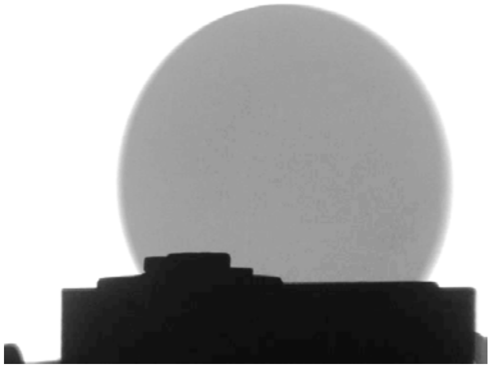


Fig. 23 Diamond tool for polishing Fig. 24 Diamond particles fastened to the metal matrix.

An investigation with X-ray 3D industrial tomograph of hot-pressed boron carbide was made (Fig. 25-27):



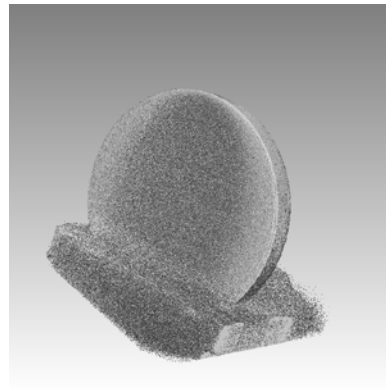


Fig. 25 Shape of the detail (the tile)   Fig. 26 Structure of the surface

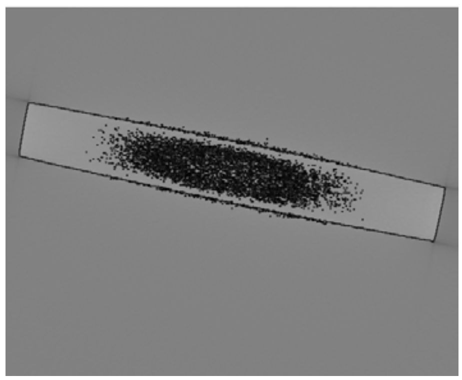


Fig. 27 Internal 3D structure of the tile

CONCLUSION

The high temperature methods are effective for obtaining materials and alloys with high hardness and wear resistance and still give the possibility of forming and processing in the production of industrial tools.

CONTRIBUTIONS:

The contributions to the dissertation work resulting from the research and development have mainly scientific-applied characteristics and are as follows:

- Review, analysis and systematization of high temperature technologies for obtaining materials and alloys and means for their realization,

- A review, analysis and systematization of types of materials in the micro- and nano scale,

- Existing high-temperature processes for the synthesis and sintering of metals are examined,

- The structure, organization and composition of a high-temperature technological line based on a Tamanova furnace is proposed,

- Optimization of technological processes and regimes in high temperature line using Tamanova furnace is made,

- Innovative high-temperature technology has been developed to produce diamond tools,

- Innovative high-temperature sintering technology for silicon carbide has been developed,

- Innovative high temperature technology for boring carbide bore has been developed,

- Innovative high temperature technology for sintering and pressing of solid materials has been developed,

- Experiments have been carried out to confirm the results of the developed developed innovative high-tech technologies. The results are analyzed.

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