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Fabrication of Powdery Composites Based Alumina and Its Consolidation by Hot Pressing Method in OXY-GON Furnace

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***Abstract*—**In this work, obtaining methods of ultrafine alumina powdery composites and high temperature pressing technology of matrix ceramic composites with different compositions have been discussed. Alumina was obtained by solution combustion synthesis and sol-gel methods. Metal carbides containing powdery composites were obtained by homogenization of finishing powders in nanomills, as well as by their single-step high temperature synthesis .Different types of matrix ceramics composites (α-Al_2O_3-ZrO_2-Y_2O_3, α-Al_2O_3-Y_2O_3-MgO, α-Al_2O_3-SiC-Y_2O_3, α-Al_2O_3-WC-Co-Y_2O_3, α-Al_2O_3-B_4C-Y_2O_3, α-Al_2O_3- B_4C-TiB_2 etc.) were obtained by using OXY-GON furnace. Consolidation of powders were carried out at 1550-1750°C (hold time - 1 h, pressure - 50 MPa). Corundum ceramics samples have been obtained and characterized by high hardness and fracture toughness, absence of open porosity, high corrosion resistance. Their density reaches 99.5-99.6% TD. During the work, the following devices have been used: High temperature vacuum furnace OXY-GON Industries Inc (USA), Electronic Scanning Microscopes Nikon Eclipse LV 150, Optical Microscope NMM-800TRF, Planetary mill Pulverisette 7 premium line, Shimadzu Dynamic Ultra Micro Hardness Tester DUH-211S, Analysette 12 Dynasizer.

***Keywords*—**α-Alumina, Consolidation, Matrix Ceramics, Powdery composites.

I. Introduction

TECHNOLOGIES, those imply obtainment of powdery composites and fabrication of functional ceramic materials by high temperature sintering have been used for obtaining new materials. At present, great attention is paid to the application of nanotechnologies for obtaining α-Al_2O_3 nanopowders and nanostructural ceramic materials based on them. For obtaining ultrafine α-Al_2O_3, several methods were used including sol-gel process, precipitation, chemical decomposition, plasma-chemical, electrochemical, microemulsion, hydrothermal, aerosol, corrosive, polymer-precursor, high temperature oxidation etc. During transformation of aluminum hydrate phases, different forms of Al_2O_3 (α, χ, η, δ, κ, θ, γ, ρ) are obtained. Only α-Al_2O_3 is thermodynamically stable, that is obtained by gradual heating of unsustainable intermediate phases of aluminum hydroxides or alumina above ~1200 ^oC temperature [1]-[4]. Alumina is widely applied material, for obtaining matrix ceramic composites, because they are characterized with high physical-mechanical properties, corrosion resistance, opportunity of operation at high temperatures (1400-1700 ^oC), radiation resistance, regulation of electrical properties in a wide range etc.

Physical-mechanical properties of ceramic targets depend on powders' sintering method. Many methods are used for consolidation of powders, including sintering of preliminary pressed powdery composite by gradual increasing of temperature, consolidation methods in micro-wave furnace, spark-plasma synthesis, sintering of powders in high frequency inductive furnace etc. [5]-[8]. In scientific researches and in practice, high temperature hot pressing furnaces with various modifications are used. Consolidation of powdery composites by hot-pressing method guarantees that materials with theoretical density will be used. One of the hot-pressing systems is high temperature (2000 ^oC) vacuum furnace OXY-GON (USA), which is equipped by press (30 tons). The furnace was used for consolidation of different powdery composites.

The present work deals with obtaining powdery composites based on α-Al_2O_3 and consolidation in high temperature vacuum furnace by hot-pressing method. For this purpose, simple technological scheme was developed for obtaining ultrafine alumina powders and pressing powdery composites from metal aluminum scrap and aluminum.

II. Experiment

A. Synthesis of alumina

Synthesis of α-Al_2O_3 was conducted by several methods:

a) 15g aluminum isopropoxide was diluted in 270 ml distilled water and was heated up to 80 ˚C with permanent stirring for 6-8 h. For peptization, 1-2 ml HNO_3 was added and stirring was continued during 3 hours at 110 ˚C. Obtained suspension was placed in to porcelain bowls and dried at 120 ˚C. For obtaining α-Al_2O_3, powder was annealed in muffle furnace at 1200˚C.

b) Aluminium nitrate ($Al(NO)_3 \cdot 9H_2O$) was dissolved in distilled water at a concentration of 0.5 mol $L^{-1}$and stirred

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for 20 min to achieve complete dissolution. NH_3H_2O solution of 4 mol L^{-1} was slowly added into the stirred $Al(NO)_3$ solution at room temperature. The pH values of the solution were adjusted to 5 by either HNO_3 or NH_3H_2O. Then, after additional stirring for 2 h, the obtained precursor, alumina hydrate gel, was centrifuged out and dried at 80 ˚C overnight. The dried bulks were rewashed with distilled water five times to remove NH_4NO_3 byproduct [9]. Annealing of obtained gel was conducted at 1200 ˚C for 2 hrs.

c) 4 g $Al(NO_3)_3{\cdot}9H_2O$ was added to 10 g (0.05 mol) urea. The mixture is stirred in the agate bowls for 10 min, as a result thick viscous mass is formed, and that is placed in porcelain (Quartz) bowl. The bowl is placed in muffle furnace heated up to ~500 ^oC, where reaction mixture is spontaneously ignited in ~2 min. Temperature of mixture achieves 1500 ^oC. Temperature is measured by IR thermometer. As a result, white volumetric powder is formed.

d) Obtaining of α-Al_2O_3-WC-Co-Y_2O_3 powdery composites: 12 g α-Al_2O_3 is added to 5 g $(NH_4)_{10}W_{12}O_{41}.nH_2O$, 3g $Co(NO_3)_2.6H_2O$ and 3 g $(CH_2)_6N_4$ (hexamethylenetetramine) and mixture is stirred in porcelain bowls for 20 min, as a result blue-colored mass is formed. Mixture is annealed on air at 170-190 ^oC for 10 min. Obtained black mass is homogenized in ball mill and is heated at 950 ^oC in hydrogen flow for 2 hrs for carbidization. Powder is cooled below room temperature in argon flow.

B. Materials and Reagents

Amorphous boron, $Y(CH_3COO)_3{\cdot}4H_2O$, $Mg(CH_3COO)_2{\cdot}4H_2O$, $ZrO(CH_3COO)_2{\cdot}2H_2O$, polyvinylalcohol, polyethylene glycol, hexamethylenetetramine, acetic acid, nitric acid are purchased from Sigma-Aldrich.

C. Fabrication of Powdery Composites

Pressing powdery composites were obtained by grinding of α-Al_2O_3 and other components (ZrO_2, SiC, TiC, B_4C, WC etc.) in nanomills. Furthermore, 0.05-10% dopants, in the form of dissolved salts, were added in suspension. Mass ration of balls and powdery was equal to 5:1. Nano mills (FRITCH planetary mill Pulverisette 7 premium line and RETCH PM 100) were used for grinding. Grinding process depends on content of powdery composites and grains sizes of initial powdery (1-24 h). The suspension was dried at 130 ˚C and further powders again dry grinded for 1 h in mill.

D. OXY-GON Furnace and Obtaining Ceramic Composites by Hot-Pressing Method

OXY-GON High Temperature Vacuum Furnace System (Fig. 1) consists of remote control, cooling (chiller) water system, hot-pressing chamber and press, which is equipped with a microprocessor. Treatment of pressure on samples is allowed by the software programmer pressing simultaneously two buttons of press. Hot-pressing chamber has double walls and it is cooled down by water flow. Heating samples has been carried out by using two-segment heater, made from tungsten net, which is screened by both vertically and horizontally with tungsten and molybdenum plates. Pressing and consolidating of the powdery composites have been carried out in high purity graphite moulds, inlayed with Graflex plates. Sintering powdery was placed in pressure shape of pre-annealing (1400 ˚C) graphite. First time the powdery was pressed with cold by furnace pressure at 2.5 MPa. When sintering chamber finishes vacuuming process, the samples are sintered by program regime. Simultaneous sintering-pressing with pressure 50 MPa was carried out for 20-60 min at maximum temperature [10].

Fig. 1 High temperature vacuum furnace OXY-GON

E. XRD

Samples phase analysis has been performed at XRD diffractometer DRON-3M (Cu-Kα, Ni Filter, 2°C/min.).

F. Nanosizer

Size of powdery particles are determined by Analysette 12 Dynasizer. 3% powdery composites suspension prepared in water by sonification during 30 min.

G. SEM and Optical Microscopes

Structural-morphologic investigation of ceramic composites has been performed by JEOL JSM-6510LV and Nikon ECLIPSE LV 150 microscope. Chemical content of these samples has been measured simultaneously with energy dispersive micro XRD analyzer.

H. Determination of Microhardness

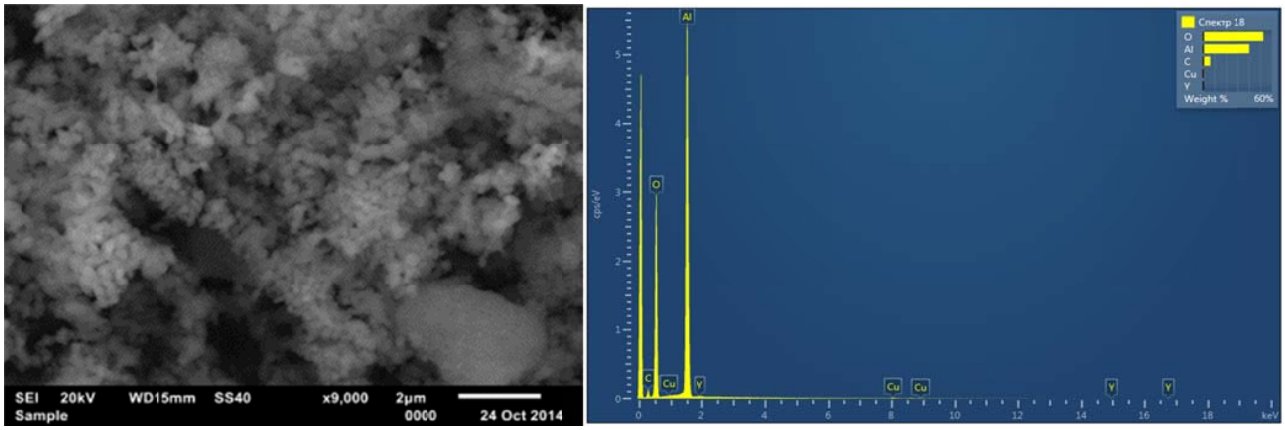
Microhardness and modulus of Al_2O_3 have been studied according to ISO-14577 international standard at dynamic ultra microhardness tester DUH-211S.

III. Results and Discussion

Researches were carried out step-by-step and they include: 1. Synthesis of α-alumina, carbides, borides and other components separately or in one process and obtaining powdery composites; 2. Homogenization of powdery composites in mills by wet and dry methods; 3. Preliminary thermal treatment of powdery composites (600-800 ^oC) for removing volatile compounds 3. High temperature consolidation of powdery composites; 4. Establishment of

phase composition of ceramic materials, investigation of physical-mechanical properties and structural-morphological researches.

α-Al_2O_3 powder has been obtained by several methods. Their doping was carried out by oxides, as well as, water-soluble salts and then by their homogenization in nanomills. Grinding cup and balls were made from corundum and zirconium. Powdery composites obtained in this way were not contaminated by other components. Scanning Electron Microscopy (SEM) Micrograph and Energy Dispersive micro-X-ray Spectrum (EDS) of α-Al_2O_3-Y_2O_3-MgO powder is given on Figs. 2 (a), (b). It is established by structural-morphological researches, that size of primary crystallites is 50-300 nm and they form big sizes easily breaking agglomerates (1-3 mcm).



(a) (b)

Fig. 2 SEM micrograph and EDS of powdery pressing composite Al_2O_3-Y_2O_3-MgO (a), (b)

For obtaining carbides containing powdery composites, two methods were used: I. Synthesis of components and homogenization of powders, obtained with relevant proportion in nanomills by wet and dry methods. α-Al_2O_3-ZrO_2-Y_2O_3, α-Al_2O_3-Y_2O_3-MgO, α-Al_2O_3-SiC-Y_2O_3 were obtained with this method; II. Tungsten and boron carbides containing pressing composites α-Al_2O_3-WC-Co-Y_2O_3, α-Al_2O_3-B_4C-Y_2O_3, α-Al_2O_3-B_4C-TiB_2 were obtained by one-step synthesis method. In this purpose, above mentioned methods were used [11], [12]. The essence of the method is synthesis of WC-Co, B_4C, B_4C-TiB_2 at presence of alumina and aluminum oxo-hydroxides. Tungsten, cobalt, boron, yttrium, titanium compounds or powders and carbidizing organic and carbon containing compounds were used as initial materials. Tungsten, molibden, titanium and boron carbides, oxy-carbides and mixed carbides were obtained by this method. Unstable oxides and oxyhydroxides of aluminum in a process of synthesis transfer in α-phase excludes necessity of its preliminary obtaining. Synthesis of multicomponent powdery composites α-Al_2O_3-WC-Co is described in experimental part. Homogenization of carbide containing powders was conducted in cup made from WC-Co, so certain amount of cup's and grinding balls material transfer in powdery composites.

As we mentioned above, high temperature vacuum furnace (OXY-GON) was used for sintering powdery composites. Obtaining of ceramic was conducted at 1600 ^oC temperature. Sintering was performed with certain temperature regime (Fig. 3). Consolidation of carbide containing powders was performed with relatively fast heating mode – hating velocity in this case achieves 20-25 °C/min. Maximum diameter of obtained samples is 75 mm.

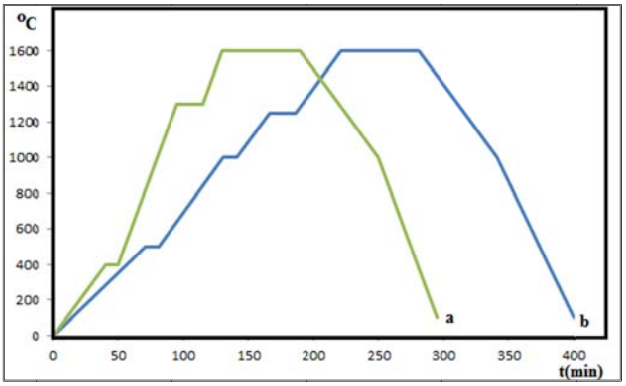


Fig. 3 Typical sintering temperature profile of powdery composites in high temperature vacuum furnace (OXY-GON)

As a result of sintering samples in vacuum, black-colored matrix ceramics have been obtained, because there have been thermal dissociation and formation defect lattice of Al_2O_3 in vacuum. Only α-Al_2O_3-SiC-Y_2O_3 ceramic material has dark green-color. Whitening ceramics is possible by their heating on air in muffle furnace at 1500-1600 ^oC for 1 h (Fig. 4). Because carbides are oxidized at this temperature, this method was used only for oxide ceramics. In inert atmosphere, white and gray ceramics are obtained.

Matrix ceramic enhanced with silicon carbide α-Al_2O_3-Y_2O_3(0.5%)-SiC(30%) was obtained in vacuum furnace by

sintering at 1600 ˚C during 1 h under pressure 50 MPa (Fig. 5) As it is shown from the diffractogram, formation of different phases does not take place. At the same time, $Y_3Al_5O_{12}$ is formed as a result of sintering of α-Al_2O_3-(WC-Co, 30%)-Y_2O_3 (5% mas.) containing powdery composite (Fig. 6, 7) that was expected, because this phase is form from Al_2O_3-Y_2O_3 system at lower temperature [13], [14].

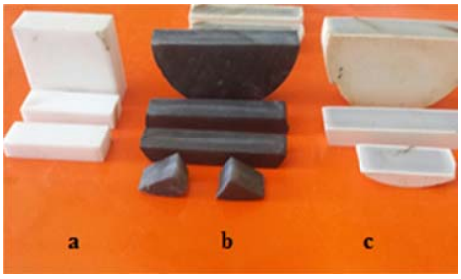


Fig. 4 Samples of α-Al_2O_3-ZrO_2-Y_2O_3 ceramics (a) Sintered in muffle furnace in air; (b) Black-colored samples, sintered in OXY-GON furnace in vacuum; (c) Same ceramic annealed on air at 1600 °C.

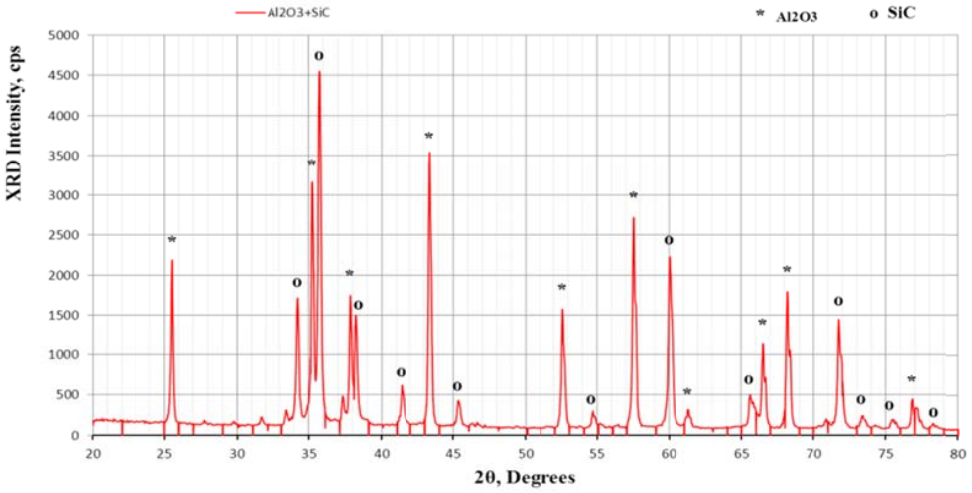


Fig. 5 X-ray diffraction analysis of matrix ceramic reinforced by silicon carbide α-Al_2O_3-Y_2O_3 (0.5%)-SiC (30%)

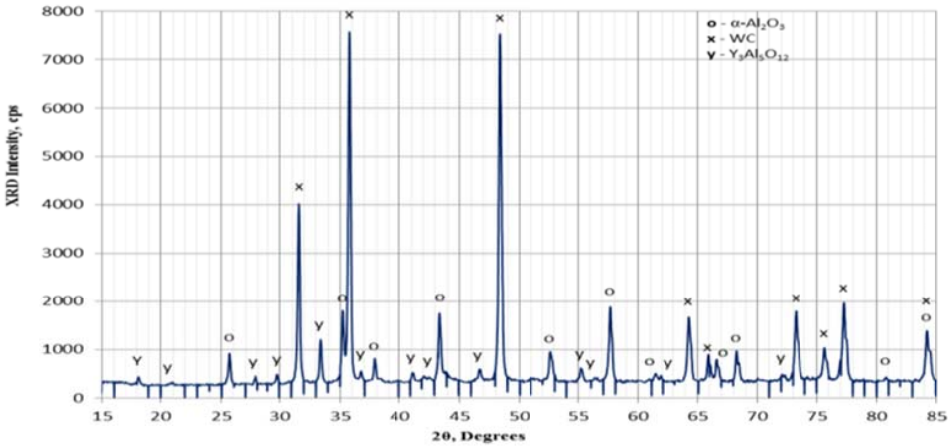
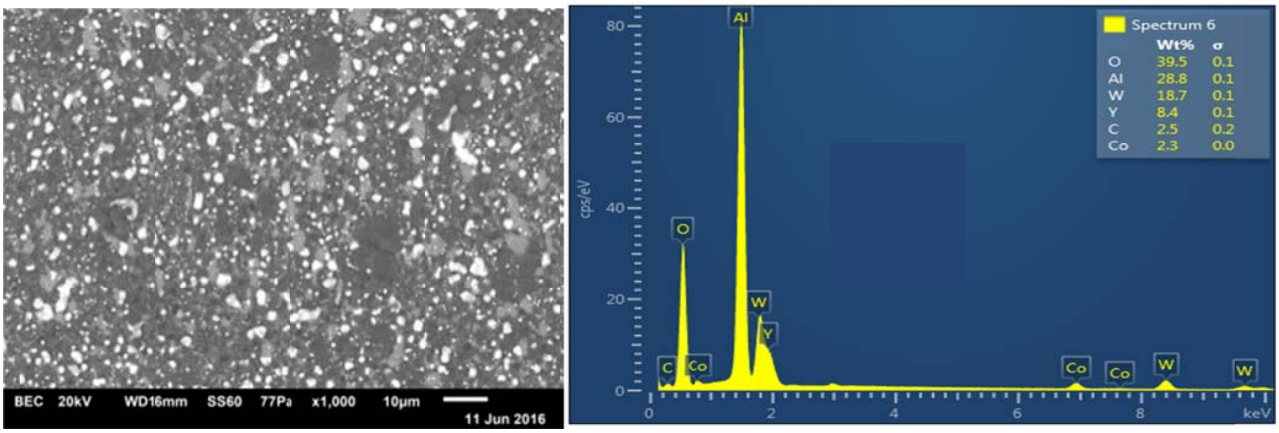


Fig. 6 X-ray diffraction analysis of α-Al_2O_3-WC-Co-Y_2O_3 matrix ceramic



(a) (b)

Fig. 7 SEM micrograph (a) and EDS (b) of ceramic composite (α-Al_2O_3-WC-Co-Y_2O_3) obtained at 1600°C

By using high temperature vacuum furnace at 1800 ˚C, from non-oxide ceramics B_4C-TiB_2 (20%) was obtained that is one of the most perspective nonoxide ceramic materials. Matrix ceramic α-Al_2O_3-B_4C-TiB_2, which consists of 30% (mas) B_4C-TiB_2 was obtained at 600˚C (Fig. 8).

Formation of new phase $9Al_2O_3{\cdot}2B_2O_3$ takes place (Fig. 9). For example, density of obtained ceramics based on α-Al_2O_3 reaches 99.5–99.6% of TD and they do not opening pores.

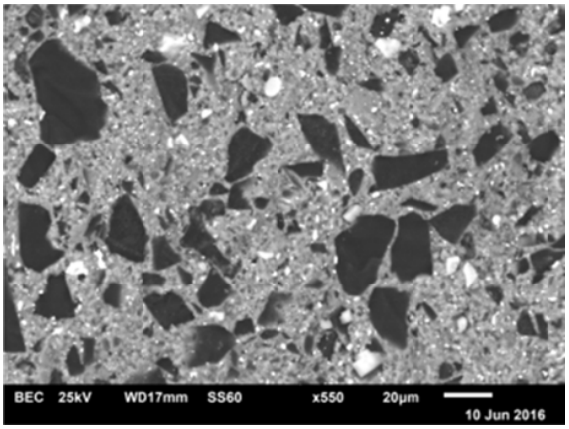


Fig. 8 SEM micrograph of matrix ceramics (α-Al_2O_3-B_4C-TiB_2) obtained at 1600°C

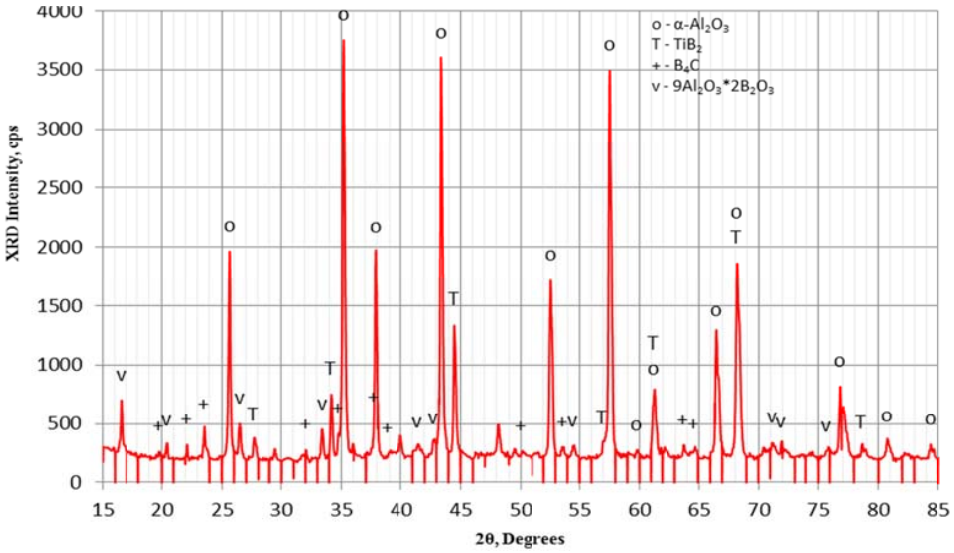


Fig. 9 X-ray diffraction analysis of α-Al_2O_3- B_4C-TiB_2 matrix ceramic

With variations of pressure and temperature in vacuum furnace, it is possible to obtain porous ceramic with low density. Determining of mechanical characteristics (static and dynamic micro-hardness, indentation modulus) was carried out by on Shimadzu dynamic ultra-micro hardness tester DUH-211S in loading-unloading test mode by Vickers indenter, for 50, 100 and 200GF loads. Holding time at maximum load was 10 s and 5 s at unload. Loading velocity was 7,1448 GF/sec. Static micro-hardness was determined by measuring diagonals of indenter's imprint and it does not contain elastic component, while in dynamic mode value of micro hardness is determined during loading process and it contains both the elastic and plastic components (Table I).

TABLE I
PHYSICAL-MECHANICAL PARAMETERS OF CERAMIC MATERIALS I. α-Al_2O_3-WC-Co-Y_2O_3; II. α-Al_2O_3-B_4C-TiB_2

Sample	P, gf	hmax (μm)	DHV	DHV, GPa	Eit, GPa	HV	HV, GPa
I	50	1.221	1672	16.386	43.00	1911	18.728
	100	1.725	1657	16.239	41.26	1811	17.748
	200	2.498	1573	15.415	38.99	1865	18.277
II	50	1.031	2329	22.824	48.54	3907	38.289
	100	1.518	2141	20.982	43.24	3579	35.074
	200	2.293	1880	18.424	36.17	3253	31.879

IV. CONCLUSION

Multicomponent pressing powders were obtained by two methods: I. Chemical synthesis of each component and homogenization of powder's mixture with relevant proportion in nanomill by wet and dry methods. α-Al_2O_3-ZrO_2-Y_2O_3, α-Al_2O_3-Y_2O_3-MgO, α-Al_2O_3-SiC-Y_2O_3, α-Al_2O_3-WC-Co-Y_2O_3 were obtained via this method; II. Tungsten and boron carbides containing pressing composite α-Al_2O_3-WC-Co-Y_2O_3, α-Al_2O_3-B_4C-Y_2O_3, α-Al_2O_3-B_4C-TiB_2 were obtained by one-step synthesis method. Sintering of composite powders was performed in vacuum and in inert atmosphere at different temperatures. Matrix ceramic α-Al_2O_3-Y_2O_3(0.5%)-SiC(30%) enhanced by silicon carbide were obtained by sintering in vacuum at 1600 ˚C for 1 h, under 50 MPa pressure. As a result of sintering, α-Al_2O_3-(WC-Co, 30%)-Y_2O_3 (5% mas) containing powdery composites new phase $Y_3Al_5O_{12}$ is formed. Density of obtained ceramics based on alumina reaches 99.5–99.6% of TD and they have not opening pores.

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