

ՀՀ ԳԱԱ Ա.Բ. ՆԱԼԲԱՆԴՅԱՆԻ անվ. ֆիզիկական ֆերմիոնային ինստիտուտ

ԴԱՎԻԹ ՀԱՅՐԱՊԵՏԻ ԴԱՎԹՅԱՆ

ԱՆՑՈՒՄԱՅԻՆ ՄԵՏԱՂՆԵՐԻ (Mo, W, Mn, Re) ԿԱՐԲԻԴՆԵՐԻ, ԲՈՐԻԴՆԵՐԻ ԵՎ
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Բ.00.04- ֆիզիկական քիմիա մասնագիտությամբ
քիմիական գիտությունների թեկնածուի գիտական աստիճանի հայցման
ատենախոսություն

ՍԵՂՄԱԳԻՐ

ԵՐԵՎԱՆ 2021

RA NAS INSTITUTE OF CHEMICAL PHYSICS after A.B. NALBANDYAN

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MICROWAVE IRRADIATION SYNTHESIS OF TRANSITIONAL METALS (Mo, W, Mn, Re)
CARBIDES, BORIDES AND BORON CARBIDE, THEIR PHYSICOMECHANICAL AND
CATALYTIC PROPERTIES

Dissertation of specialicity in 02.00.04 “Physical Chemistry” for the degree of
Candidate of Chemical Sciences

AFTOREFERAT

YEREVAN 2021

Ատենախոսության թեման հաստատվել է ՀՀ ԳԱԱ Ա.Բ. Նալբանդյանի անվան
Քիմիական ֆիզիկայի ինստիտուտի գիտական խորհրդի կողմից
Գիտական ղեկավար՝ քիմ. գիտ. թեկնածու Ռ. Ա. Մնացականյան
Պաշտոնական ընդդիմախոսներ՝ քիմ. գիտ. դոկտոր Պ.Ս. Ղուկասյան, տեխ. գիտ.
թեկնածու Վ.Վ. Բաղդամյան:

Առաջատար կազմակերպություն՝ Հայաստանի ազգային պոլիտեխնիկական
համալսարան, Երևան:

Պաշտպանությունը կայանալու է 2021թ. հոկտեմբերի 21-ին ժ. 14:00-ին, ՀՀ ԳԱԱ Ա. Բ.
Նալբանդյանի անվան Քիմիական ֆիզիկայի ինստիտուտում գործող ՀՀ ԲՈԿ-ի 017
<<Ֆիզիկական և անօրգանական քիմիա>> մասնագիտական խորհրդի նիստում (0014,
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Ատենախոսությանը կարելի է ծանոթանալ ՀՀ ԳԱԱ Ա.Բ. Նալբանդյանի անվան
Քիմիական ֆիզիկայի ինստիտուտի գրադարանում:

Սեղմագիրն առաքված է 2021թ. սեպտեմբերի 10-ին:

Մասնագիտական խորհրդի գիտական քարտուղար, ֆիզ-մաթ. գիտությունների
թեկնածու՝



Հ.Պ. Սարգսյան

The dissertation theme is approved by the scientific council of the RA NAS Chemical physics
institute after A.B. Nalbandyan

Scientific supervisor: Candidate of chemical sciences R.A. Mnatsakanyan

Official opponents: P.S. Ghukasyan, Doctor of chemical sciences, V.V. Baghrmryan,
Candidate of technical sciences

Leading organization: National Polytechnic University of Armenia Yerevan.

The dissertation defense will take place on 21st of October 2021 at 14:00 o'clock, during the
"Physical and inorganic chemistry" professional council's session of RA SCC 017 acting
within the Institute of Chemical Physics after A.B. Nalbandyan RA NAS (0014, Yerevan, P.
Sevak str., 5/2).

The dissertation can be accessed at the library of the RA NAS Institute of Chemical Physics
after A.B. Nalbandyan.

The aforeferat is delivered on September 10, 2021.

Scientific secretary of the professional council, candidate of physical-mathematical sciences:



H.P. Sargsyan

INTRODUCTION

The relevance of the paper

The synthesis of active catalysts and hard materials is one of the main issues of contemporary material science. Materials with new structures need to be synthesized and up-to-date methods of synthesis to be used in order to solve those issues. Considering the papers existent in literature during last years, which concern the solutions of the abovementioned issues, the study of the transitional metals carbides and borides represents particular interest from the practical point.

The transitional metals carbides, especially tungsten and molybdenum carbides as catalysts and co-catalysts, are studied in numerous reactions, which are the following: hydration, dehydration, reforming and isomerization of hydrocarbons, catalytic degradation of hydrazine, oxidation of hydrogen, electrocatalysis, reactions ongoing in different types of fuel and electrochemical cells, hydrodesulfurization of petroleum containing organic sulfur compounds.

As practical materials, the transitional metals borides and the boron carbide represent a huge interest due to the following characteristics: high hardness, high durability, mechanical firmness, chemical stability, unique physical properties.

Based on the mentioned, those materials are being used in incisive and abrasive tools, are often used in semi-transmitter physics, electronic techniques, in astronomy and military industry due to unique, super mechanical characteristics.

One of the contemporary effective methods of organic and inorganic compounds' synthesis in material science is the method of microwave irradiation. The requirements for the synthesis methods of organic and inorganic materials are becoming stricter during the last years. The requirements read as follows: high selectivity for the obtainment of target material, one of the highest conversion, minimum requirements for the raw material purity with the aim of obtaining pure products, synthesis of nanoscale powder with narrow particles' size distribution in case of solid material powders, high velocity of increase and decrease of the temperature during the synthesis, minimum energy consumption, minimum heating volumes, simplification of the synthesis process and decrease of the sub-stages' quantity.

Moreover, one of the important issues in material science is the synthesis of nanosize materials, as the nanoscale allows maintaining the stoichiometry of the obtained materials having chemical and targeted convertible physicochemical characteristics.

The aim of the paper

The aim of the paper is the following:

- through microwave irradiation method synthesize nano-powders transitional metals carbides, borides and boron carbide with microstructure, concrete chemical and phase compositions,
- use different physicochemical and mechanical methods of research in order to study the structure of the obtained materials,

- optimize the synthesis conditions based on the data obtained as a result of studies,
- study the mechanical characteristics of the obtained materials: microhardness by Vickers, compressibility, erosion durability, etc.,
- study the catalytic activity of the obtained materials in the following reactions: hydration and dehydration of hydrocarbons, catalytic degradation of hydrazine, hydrodesulfurization of diesel fuels,
- test of the obtained catalysts in the conditions of microwave irradiation.

The issues of the study (research)

- design and prepare reactor with maximum microwave permeability, ensuring high temperature and inert hermetic environment,
- modify the domestic microwave oven in order to secure maximum convenience and effectiveness of the synthesis and an opportunity to remotely measure the temperature,
- optimize the obtainment of the nanoscale narrow size distribution material powders through domestic microwave irradiation,
- synthesize transitional metals borides: rhenium borides, manganese borides and boron carbide,
- select and optimize the sintering conditions of the obtained borides,
- study the physicochemical characteristics of the sintered samples,
- synthesize the molybdenum and tungsten carbides,
- synthesize molybdenum carbide combined with different carriers and doping of nickel atoms,
- study the structure of the obtained powders,
- study the catalytic activity of the obtained pure, combined and doped carbides and borides.

The scientific novelty of the paper

- for the first time in the presented paper simple, compact, easily used and cleaned quartz microwave reactor has been designed and prepared,
- for the first time boride phases rhenium diboride (ReB_2), rhenium diboride boron carbide ($\text{ReB}_2\text{-B}_4\text{C}$) composite, manganese diboride (MnB_2) have been synthesized through microwave irradiation method,
- for the first time in the literature the phase of boron carbide with the highest microhardness ($\approx 35\text{GPa}$) currently, accessible super light ($\approx 3,2\text{g/cm}^3$) and super hard ($\approx 50\text{GPa}$) composites (27%w $\text{ReB}_2\text{-B}_4\text{C}$) has been synthesized and sintered,
- for the first time the molybdenum carbide doped by the nickel atoms synthesized through microwave method has shown highest catalytic activity in the reactions of diesel fuel's hydrodesulfurization,
- for the first time the microwave irradiation and also the domestic microwave oven have been used in the process of catalysts' activation.

The practical importance of the paper

The method of the microwave irradiation presented in this paper can be used for both laboratory and industrial quantities of the homogenous, nanoscale powders with narrow distribution particles' size synthesis. By the suggested method, a production of boron carbide (B₄C) and composite rhenium diboride boron carbide (ReB₂-B₄C) can be organized. The microwave irradiation method can be used in the process of catalytic reactions' activation.

The publications of the paper

The main part of the dissertation is published in seven scientific articles. Two of them are published in local journals (in English), two in Russian journals (in Russian) and three in international journals (in English) having more than 3 IF, the reference rate is increasing and up-to-date, increasing h-index of mine is 3 at the moment. The results of the studies have been reported in international and local scientific conferences.

The structure and volume of the dissertation

The present dissertation consists of the content, introduction, 4 chapters: literary hints, methodical part and 2 experimental chapters, conclusions and list of used literature. The dissertation is composed within 149 pages, includes 23 charts, 45 pictures and 293 references.

Brief description of the dissertation

In the introduction section the relevance of the theme is reasoned, the aim, scientific novelty, clauses being presented for defense, practical importance and obtained results are composed.

In the first chapter the literary hint is presented, which is devoted to microwave physics, heating mechanism, synthesis of transitional metals carbides and borides and their catalytic activity in different reactions.

In the second chapter the experimental methods and their reasoning used in the dissertation are presented.

In the third and fourth chapters the microwave irradiation synthesis of transitional metals carbides, borides and boron carbide and their physicochemical, catalytic characteristics' study results are presented.

After each chapter discussion of the results is presented and corresponding conclusions are made.

THE MAIN CONTENT OF THE DISSERTATION

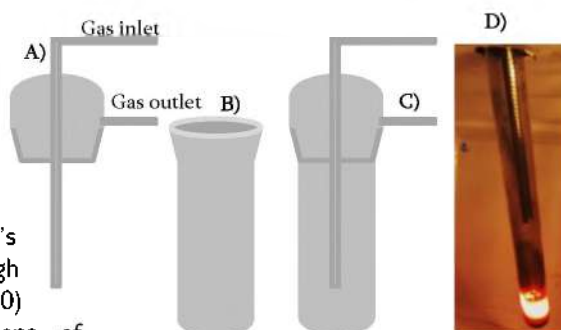
The primary description, clauses, reasoning and aim of the paper, its relevance, scientific novelty, practical importance, obtained results, their discussion and corresponding conclusions are presented in the dissertation.

Chapter 1: Accessible literature's analytical research is presented in the paper related to the following: used microwave irradiation (especially 2.45 GHz frequency) heating mechanism, features of interaction with solid materials, heating possibility of the studied compounds depending on their dielectric permeability, evaluation of the advantages and

disadvantages compared to other methods, features of obtaining different compounds of transitional metals through this method, its possible advantages and difficulties. As a result of the mentioned analysis the unique and effective influence of microwave irradiation on the reactions' activation in solid phases has been substantiated. Transitional metals carbides and borides usage in different catalytic reactions is discussed. Moreover, the difficulties of their nanoscale particles' obtainment when using other heating methods are presented.

Chapter 2: The descriptions of the following are presented: the used methods and the quartz streaming simple reactor (Fig. 1), which is for the first time designed, constructed and used by us, particularly modified domestic microwave oven, which gives an opportunity to ensure highest irradiation (maximum 1300°C) of the reaction mixture and constant inert streaming environment.

Figure 1: Quartz flow reactor A) Quartz lid equipped with gas purging system, B) quartz reactor, C) Quartz reactor equipped with gas purging system, D) photo of quartz reactor in the reactor containing raw mixture during microwave heating.



The calibrated process of the sample's temperature measurement through remote infrared (Dostman HT 1800)

radial thermometer in the conditions of

microwave irradiation conducted by us for the first time is presented. The study methods of the obtained materials' compositions, structures and characteristics identification are presented: XRD, SEM, TEM, XPS, densitometry, SPS, microhardness by Vickers. Moreover, the description of catalytic reactors is presented. Before the experimental studies, thermodynamic and thermokinetic calculations have been conducted through HSC 5.0 Thermo computer calculation programs, based on which the stoichiometric composition of raw reaction mixtures and the optimal quantities of additives.

Chapter 3: The obtainment, description and studies of the characteristics of the manganese diboride (MnB_2), rhenium diboride (ReB_2), rhenium diboride boron carbide (ReB_2-B_4C) composite and boron carbide (B_4C) are presented.

Manganese diboride (MnB_2): For the first time in the literature, manganese diboride has been synthesized through microwave heating method. The stoichiometric correlation of the raw mixture has been calculated considering that the manganese (IV) oxide must be restored together with magnesium and boron, the residual boron quantity must be enough for obtaining manganese diboride. Chemical reaction's equation is the following:



The products have been subjected to acidity basic washing and further drying.

Washed and dried products have been described through the XRD analyze method. Obtained diffractogram is shown in the Fig. 2A,B the full transformation of raw materials: MnO₂ and MgB₁₂, to final product manganese diboride: MnB₂:

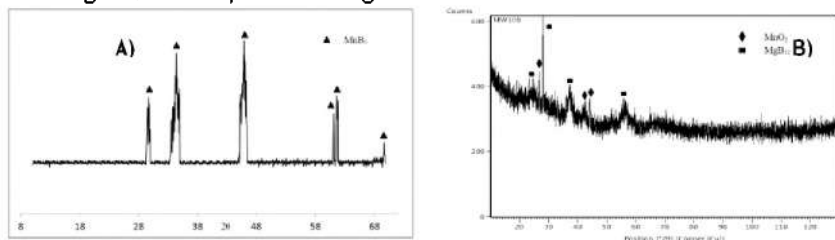


Figure 2: XRD diffractograms of A) washed and dried products, B) initial mixtures.

Boron carbide (B₄C): Raw mixture's stoichiometric correlation of the boron carbide obtainment through microwave method has been calculated according to the following chemical equation: $MgB_{12} + 3C(O) = 3B_4C + Mg(O)$

The products have been subjected to acidity washing, further drying and spark plasma sintering (SPS). The products and sintered samples have been described through XRD method. The diffractograms are shown in the Fig. 3. The particles' size of the obtained products has been calculated by the Scherrer equation and described through the SEM (Fig.

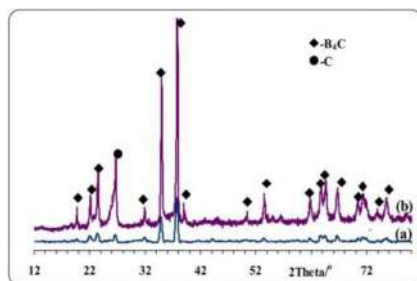
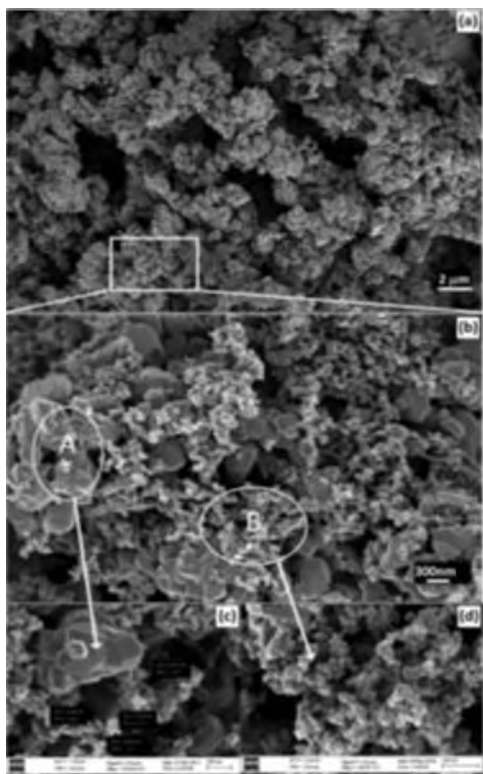


Figure 3: XRD patterns of MW synthesized B₄C boroncarbide: (a) before sintering, (b) after sintering.

4) analyze method. It composes 40-50nm on average.

Figure 4: SEM images of B₄C powder after MW synthesis (a, b, c, d-different magnifications).

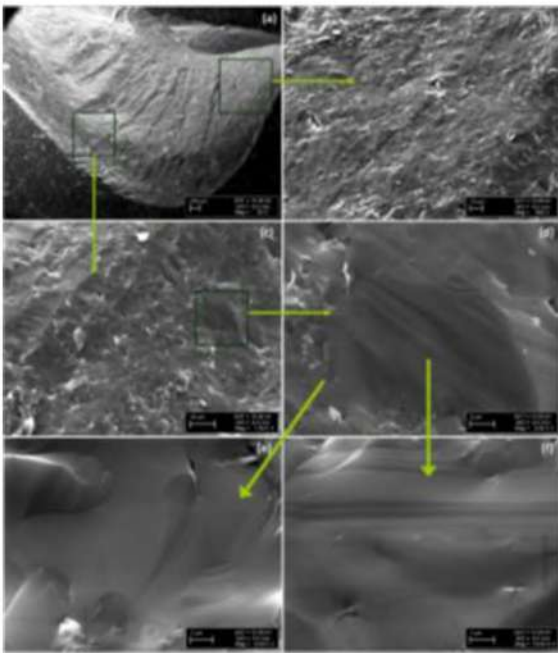


Figure 5: SEM images of fractured surface of B₄C compacts (sample 3, T_{sintering}= 1900 °C).

Based on the studies of microstructural and other parameters the optimal conditions of sintering have been created, as a result of which the geometrical and Archimedian densities of the sintered B₄C samples have been measured accordingly 2,510 and 2,499g·cm⁻³. Thus, the comparative density composes >99%. The microhardness of the obtained SPSed samples has been measured through the Vickers indentation and it has been shown that HV5 composes 34,5±2,3Gpa for B₄C, which is currently one of the highest values combined with the existent data in the literature. Indentation fracture toughness (IFT) has been decided based on the radial cracks derived from the corners of the indents. The highest value calculated by the Median, Evans and Palmqvist methods composes 5,7MPam^{1/2}, which is obviously the highest value existent in the literature. The results of the EDS analysis has shown the presence of B₄C after SPS sintering, which confirms that the main product is boron carbide, despite that there were oxygen traces' quantities in the surface. As an outcome of the combination of XRD, SEM, EDS analysis' results, microhardness by Vickers of the sintered samples and the evaluation of the Indentation fracture toughness (IFT), it can be stated that through SPS sintering of the boron carbide nanopowder obtained by the microwave method, sintered samples with high density and improved mechanical characteristics are obtained. Those are obtained in less than 2000°C temperature and without any additives, but through decreasing the defect of the boron carbide nanostructure obtained by the microwave method.

In the Fig. 5 the SEM images of sintered samples and their fractures are presented. The erosion experiments conducted for the boron carbide have shown that the values obtained in case of B₄C exceed the values of many hard materials used for incisive and abrasive water jet nozzles. The erosion experiment of the sintered B₄C has been conducted by using quartz erodent and the type of obtained erosion and its erosion

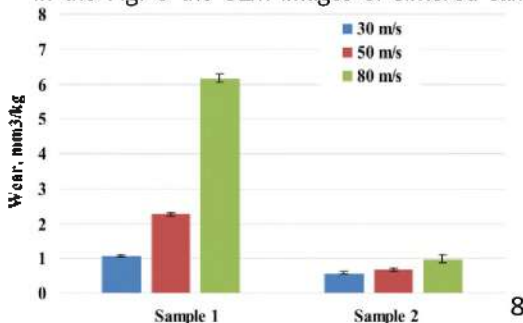


Figure 6: Erosive wear rate of B₄C sintered at different temperatures.

wear level depending on the speed of erodent have been studied.

The Fig. 6 shows the level of volumetric erosion of the B₄C samples sintered through spark plasma method, which has been displayed during the erosion experiment of the centrifugal solid particles in a room temperature. Regardless of the sintering temperature, the main mechanisms of the erosion wear functioning in the given conditions are similar, e.g. fracture and/or fragmentation of the carbide and removal of the complete ceramic particles as a result of intercrystalline cracking combined with concrete plastic deformation.

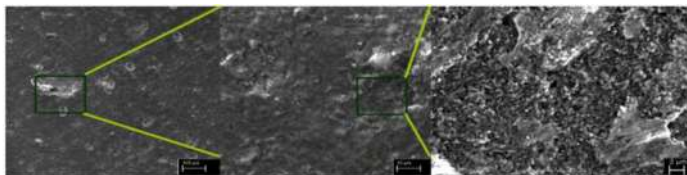


Figure 7: SEM micrographs of B₄C (sample 2) after the erosion test at 80

The microstructural images (Fig. 7) show that as a result of erosion experiment the appearance of surface porosity strictly differs from the case of sintering in much higher temperature, and the existence of much smaller holes and scratches is obvious. That means, the microwave heating method allows synthesizing the nanoscale described with having narrow particles' size distribution, which as an outcome of sintering ensures high density of materials using reasonable temperature regime. The SPS process contributes to the increase of the intensity of boron carbide diffraction lines and decrease of the width of those lines' half-height at the expense of quantitative reduction of the defects present in the nanoscales. The free carbon present in the boron carbide powder is migrating through formed nanoscales' surface during the sintering process and is intensifying the highest density securement process.

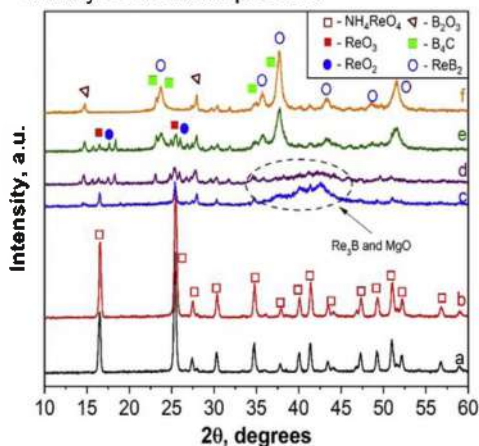


Figure 8: XRD patterns of initial NH₄ReO₄ +MgB₁₂ +C mixture (a) and irradiated materials with different microwave power and duration: (b)– 180W for 80 s, (c) – 450W for 80 s, (d) – 600W for 80 s, (e) – 900W for 80 s, (f) – 900W for 600 s.

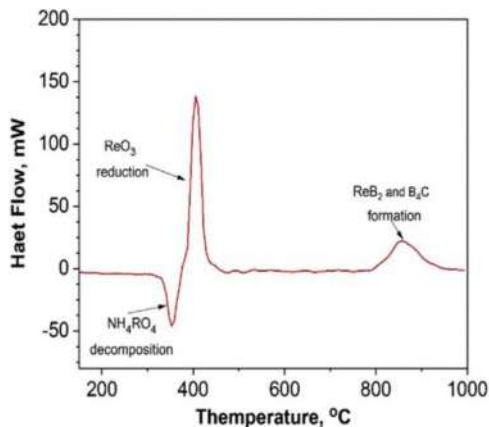


Figure 9: DSC curve for the NH₄ReO₄ +MgB₁₂ +C mixture heated in helium.

Based on the studies of the microstructural Fig. 5 and descriptive parameters, the sample

sintered in 10 minutes and in 1900°C temperature under 50Mpa pressure has >99% comparative density and much higher microhardness by Vickers compared to B₄C prepared in ordinary methods, which is conditioned by the maintenance of the nanostructure during the SPS processing.

Rhenium diboride: Raw mixture's stoichiometric correlation of the rhenium diboride obtainment through microwave method has been calculated based on the securement of the raw materials' complete conversion. The products have been subjected to acidity basic washing and further drying. Dried samples were characterized by XRD (Fig. 8). In order to study the characteristics of the raw mixture in linear heating conditions, differential scanning calorimetry (DSC, Mettler-Toledo) has been used. The composition, morphology and atomic structure of the products have been studied through SEM and TEM methods. As we can notice, in the diffractograms of the samples irradiated 600s by 900W power there are present only ReB₂ and B₄C phases' characteristic peaks and the lines of ReO₂ and ReO₃ become almost invisible. DSC study of the raw mixture has been conducted and the curve (Fig. 9) shows endothermic peak in 330-380°C temperature, which corresponds to the degradation of NH₄ReO₄ and the obtainment of ReO₃, and strong exothermic peak concentrated in ~430°C temperature. Comparing to XRD diffractogram (Fig. 8) it can be concluded that ReO₃ phase reacts with MgB₂ through heat generation, which leads to B₂O₃, MgO and Re₃B phases obtainment. As the process develops, Re₃B is transformed into ReB₂ phase, and B₄C is obtained in much higher temperatures, which is proved by the DSC curve's exothermic peak in 800-850°C temperatures.

SEM studies of the raw mixtures and samples irradiated by microwave have been conducted in order to discover the critical modifications of the microstructure during the ReB₂

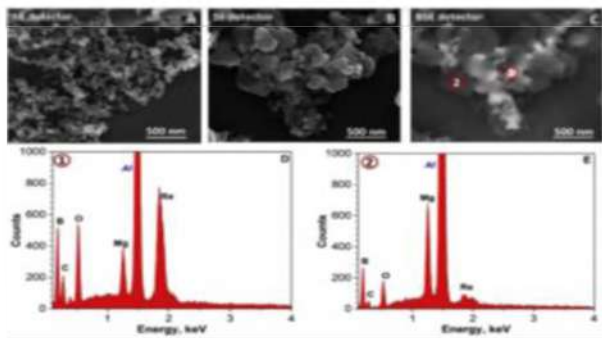


Figure 10: SEM images of initial carbon power (A), and NH₄ReO₄ +MgB₂ +C mixture (B and C) and EDXS spectra (D and E) taken from different particles.

50nm). The increase of the irradiation power until 600W leads to “spread” (Fig. 11C) of the compounds containing Re.

It is assumed that the exothermic recovery of ReO_3 happens within 450-600W power and originates B_2O_3 , MgO and intermediate Re_3B compounds. This process leads to the origination of Re_3B , which is then transformed into ReB_2 phase in higher temperatures. In the SEM image (Fig. 11D) of sample irradiated by 900W nanoscale (less than 100nm) light

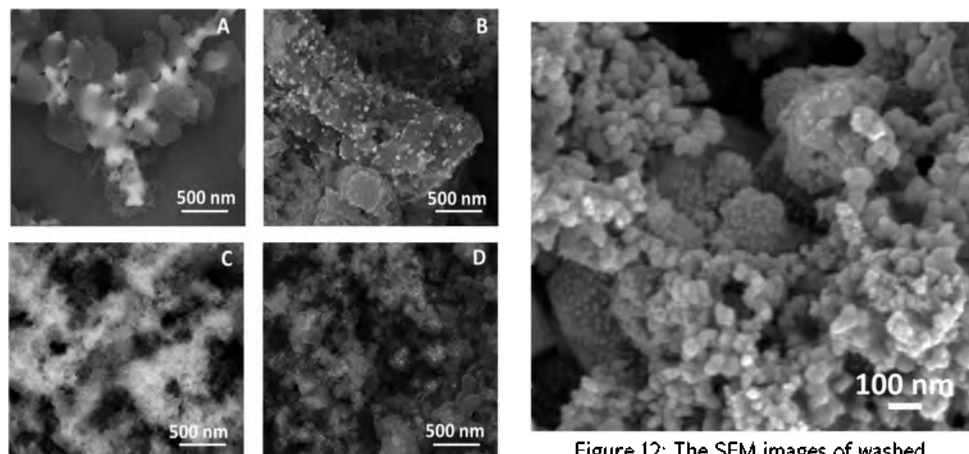


Figure 11: SEM images taken by backscattering electron detector of initial $\text{NH}_4\text{ReO}_4 + \text{MgB}_{12} + \text{C}$ mixture (A), irradiated samples at 450W (B) 600W (C), and 900W(D).

Figure 12: The SEM images of washed and dried product.

shade particles are present embedded in darker phase. The diffractogram of the washed and dried powder product shows that ReB_2 is the primary phase, whereas in the product there are present some quantity of B_4C and graphitized carbon. It is worth mentioning, that most of the B_4C diffraction lines coincide with the ReB_2 lines. The graphitized carbon's wide and low intensity line can be seen in $\sim 26^\circ$ temperature, which assumes that high temperature irradiation and exothermic reactions improve the crystalline structure of carbon. Using the widening of the diffraction peaks within $50-90^\circ$ corner, the average crystalline size of ReB_2 phase is evaluated $\sim 30\text{nm}$. The SEM image of washed powder shows that the average diameter of the product particles is 50nm (Fig. 12). That disparity can be explained by the existence of many defects in nanoscales, which contribute to additional expansion of XRD lines.

Rhenium diboride-boron carbide composite: The initial mixture's stoichiometric correlation has been calculated according to the following chemical equation: $2\text{NH}_4\text{ReO}_4 + 7\text{MgB}_{12} + 20\text{C} = 2\text{ReB}_2 + 20\text{B}_4\text{C} + 7\text{MgO} + 2\text{NH}_3 + \text{H}_2\text{O}$.

The products have been subjected to acidity basic washing, further drying and describing through XRD method. The diffractogram contains lines, which correspond to only ReB_2 and B_4C . Crystalline graphite carbon's diffraction peaks can be seen in $2\theta \sim 26^\circ$ temperature (Fig. 13A). The SEM study of B_4C -27wt.% ReB_2 composite has shown formation of nanoscale particles, significant lessening (from $\sim 100\text{nm}$ to dozens nm) of the particles' size compared

to raw mixture (Fig. 13D,E) is noticed. Through XRD diffractogram Scherer method (Fig. 13A) the average size of the crystals has been decided: ~30nm.

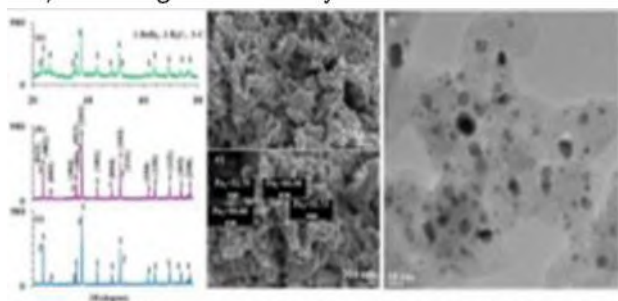


Figure 13: XRD patterns of powder (A), compacted sample 1 (B), compacted sample 2 (C), SEM images (D,E) and TEM image (F) of MS B4C-27wt.%ReB₂ nanopowder.

This difference between particles' size can be conditioned by the existence of many defects in nanoscales, which contributes to the expansion of XRD lines.

The TEM analysis of the product has shown crystal phases, which are presented with dark fields in/on an equally distributed (approximately with 10-20nm sizes) light contrast phase (Fig. 13F).

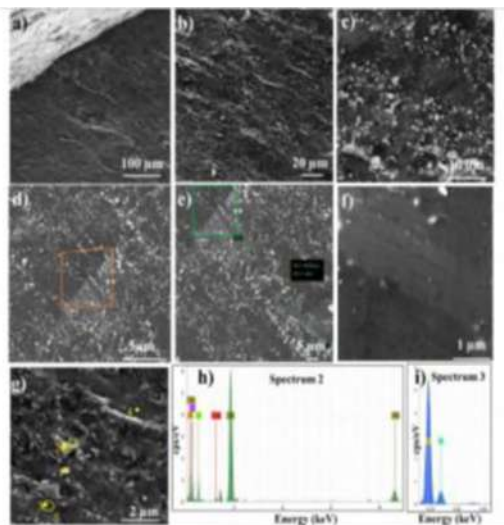


Figure 14: SEM images of fracture surfaces (A,B,C,F), indentation marks (D,E) and EDS spectra (H,I) produced at the surface of sample 2.

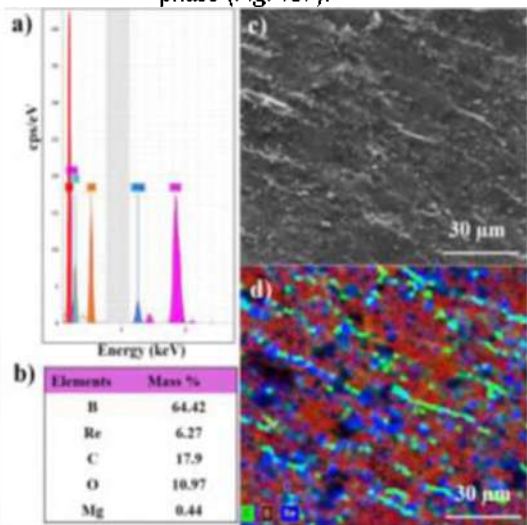


Figure 15: EDS mapping of sample 2.

The composites sintered 5 minutes in 1750°C temperature are described with high porosity (up to 8%), because of which they have not been studied furtherly.

The XRD patterns of materials sintered through SPS technique have shown only ReB₂ and B₄C diffraction peaks (Fig. 14B,C), which present that there is no modification of phase compound regardless of the sintering temperature. The intensity of 27wt.%ReB₂-B₄C diffraction peaks is increasing and the width is significantly decreasing in parts of half-height

(Fig. 14B,C) emphasizing the order of composite's crystallinity structure and growth of the small particles.

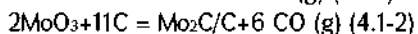
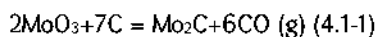
The highest density of samples has been obtained in case of sintering 10 minutes in 1900°C temperature (sample 2). In the Fig. 14, it can be seen from the SEM images of sample 2 fracture area that there are no obvious pores and not sintered parts. The EDS spectrum and mapping, Fig. 14, Fig. 15 show that in bright parts there is much bigger quantity of oxygen in more striking area, which is conditioned by the existence of approximately 30% oxygen in raw nanoscales. It coincides with the XPS analysis, where it has become clear that Re(VII)/Re(0) evaluated correlation in the surface layer composes ~30/70.

For the B₄C-27wt%ReB₂ composite 50±3GPa: sample 2. The value of hardness has been measured depending on SPS conditions. The distribution of indentation trace and cracks in sample 2 are presented in Fig. 14D,E. Due to the combination of ultra-small size of the particles and high degree of density as a result of sintering, the sample 2 has shown considerably high microhardness by Vickers with the value of 50±3GPa compared to pure ReB₂ or B₄C. The origination of firm interphase near ReB₂ unit cell, the quantity of boron atoms is increasing, which leads to additional sigma bonds and consequently, to the increase of microhardness by Vickers.

The high value of hardness (~50GPa) classifies the obtained composite as a super-hard material. Unlike pure ReB₂, which mainly contains Re-Re metal bonds, the light atoms of boron and carbon contribute to the covalent nature of the B-B and Re-B-C atoms' cohesion. According to the density's functional theory (DFT), the covalent bond has a decisive role in case of super-hard materials. Conditioned by that, the hardness of 27wt.% ReB₂-B₄C composite classifies as asymptotic hardness type in conditions of corresponding load, which is used for super-hard materials. Nevertheless, many papers tend to classify ReB₂ as super-hard material using small load (0.49N). The increase of applied power from 0.49N to 4.9N leads to significant decrease of hardness up to 30GPa, which is 40% low compared to B₄C-27wt.%ReB₂ composite presented as a result of current study. Compared to B₄C material (density: ~2,52gcm⁻³, HV5~30GPa) with high strategic importance, the composite obtained from the combination of B₄C with ReB₂ has shown much higher hardness combined with low density. It is obvious that the combination of microwave heating synthesis and SPS sintering secures reliable route for fabrication of super-hard and light material.

Chapter 4: In the Chapter 4 the molybdenum and tungsten carbides obtained by us through the microwave method are characterized, and they have been studied with different carriers and doping materials in different catalytic reactions.

Molybdenum carbide: The synthesis has been conducted according to the following chemical reactions:



For the synthesis of the Mo₂C/ZSM12 and Mo₂C/γ-Al₂O₃ systems accordingly MoO₃/zeolite(ZSM12)/C and MoO₃/γ-Al₂O₃/C have been taken.

In the Fig. 16 the XRD diffractogram of Mo₂C product is presented. As it is clear from the diffractogram, within the sensitivity of X-ray analysis raw mixture's conversion (100%) is present. The molybdenum carbide particles' sizes have been evaluated through XRD diffractogram Scherrer's equation: 30-50nm (Chart 2). From the calculated crystals' sizes the specific surface of Mo₂C in Mo₂C/carrier(Mo₂C, Mo₂C/C, Mo₂C/ZSM12 and Mo₂C/γ-Al₂O₃) systems has been evaluated (Chart 2).

In the Fig. 17 the XRD diffractograms of the raw ZSM12 and synthesized product are presented. Raw zeolite is described with 2θ=7 and 9° corner (Fig. 17A). After the synthesis the XRD characteristic peaks of zeolites have disappeared, which assumes that initial zeolite

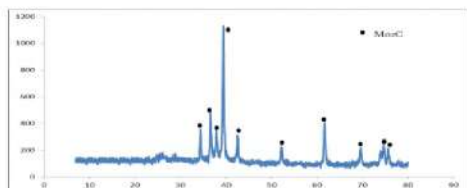


Figure 16: XRD diffractograms of molybdenum carbide (Mo₂C).

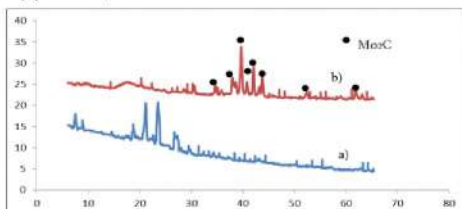


Figure 17: XRD diffractograms of A) initial ZSM12, B) synthesized product.

has been subjected to phase conversion in the conditions of high temperature (Fig. 17B).

An attempt has been made to increase the catalytic activity of molybdenum carbide using different carriers. In order to do that, carriers with different physicochemical characteristics (from light to hard acid surfaces) have been selected for the synthesis. The studies have shown that the percent of hydrazine conversion depends on the used carrier. In our case, the catalytic activity of molybdenum carbide in different carriers can be presented in the following order: Mo₂C/Al₂O₃ > Mo₂C/C > Mo₂C > Mo₂C/ZSM-12

Hydrazine in its nature is basic molecule, thus it can be assumed that the first steps of its conversion with the catalyst are acid centers, which in some cases can be a restrictive stage:



where S is the acid center of the surface. The acid center can be in the surface of the carbide or in the carrier. The carriers almost do not have catalytic activity (Chart 1), so the catalytic degradation of hydrazine is attributed to molybdenum carbide. The highest value of conversion has been displayed in case of Mo₂C/γ-Al₂O₃+N₂H₄·H₂O reaction (Chart 1). It is assumed that γ-Al₂O₃ having clearly expressed acid feature secures the high concentration of basic hydrazine in the catalytic surface, which in its turn ensures good absorption of microwave irradiation in corresponding temperature leading to such high value of conversion (approximately 95%).

Chart 1				
Sample	Conv., %	d _{Mo₂C} , nm	S, m ² /g of Mo ₂ C	Conv.,%/m ² Mo ₂ C
70%Mo ₂ C/ZSM12	41	23	28.4	1.44

70%Mo ₂ C/C	61.15	25	23.3	2.62
70%Mo ₂ C/ Al ₂ O ₃	95.4	21	31.1	3.07
Mo ₂ C	52.5	30	21.8	2.41
C	8.03	-	-	-
Al ₂ O ₃	0	-	-	-
ZSM12	0	-	-	-

Despite the fact that ZSM type zeolite systems are described with surface hard acidity, within the frames of the current study Mo₂C/ZSM12+N₂H₄°H₂O reaction has shown the lowest level of conversion

(Chart 1). It is known, that the degradation temperature of the ZSM12 zeolites containing low SiO₂ is approximately 700°C, which assumes that during the carbide synthesis, as already mentioned, the zeolite degradation leads to loss of surface acidity. The catalytic activity of individual carriers without the existence of the catalyst has been studied too. It has become clear that γ-Al₂O₃ and zeolite ZSM12 carriers show absolute catalytic inertia (Chart 1). Nevertheless, carbon shows insignificant catalytic activity (approximately 8%, Chart 1), which can be explained by the formation of active centers in the carbon surface when it interacts with microwave irradiation. As it has been shown in previous papers, Mo₂C, Mo₂C/C has catalytic activity conditioned by the existence of acid surface centers. However, our studies have shown that the carriers have an important role during catalytic process and lead to 100% selectivity.

Molybdenum, tungsten carbides: Molybdenum carbide 70%Mo₂C/C has been synthesized through microwave irradiation method according to the following chemical reaction:

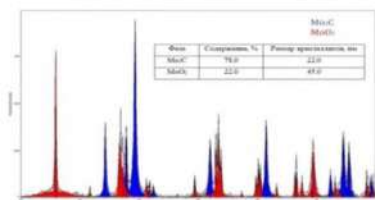
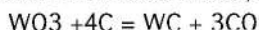
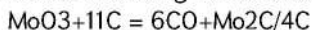


Figure 18: Synthesized molybdenum carbide XRD diffractograms.

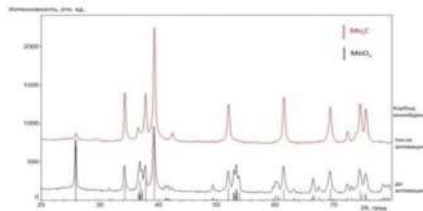


Figure 19: Molybdenum carbide XRD diffractograms before and after activation by reducing mixture of hydrogen/methan.

As model alkenes the following reactives have been used: cyclohexane (99%, Sigma Aldrich), decen-1 (97%, Sigma Aldrich), hexadecen-1 (99.8%, Sigma Aldrich), okten-1 (98%, Sigma Aldrich). The supervision of products' composition and purity of raw materials has been conducted through the method of gas chromatography.

The oxides' contents in molybdenum and tungsten carbides have been studied after one week from the synthesis of the samples. As it is shown in the Fig. 18, molybdenum carbide contains considerable amount of oxides, which shows its high passivation while keeping in the air. Similar data has been obtained for tungsten carbide.

The synthesized molybdenum and tungsten carbides almost immediately become passive in the air, thus the catalysts have been activated in the conditions of hydrogen/methane mixture's flow. The removal of the oxide layer has been confirmed through XRD (Fig. 19). It is important to mention that the recovery of the carbides in hydrogen flow (with the absence of methane) leads to the origination of MoC phase. In this regard, it is more expedient to recover the catalysts in the conditions of methane/hydrogen mixture's flow.

Chart 2: Hydration of alkenes: 2h, 40atm H₂, 50mg Mo₂C, 300°C conditions.

Substrate	Conversion, %
Cyclohexane	40.5
Okten-1	1.8
Hexadecen-1	2.3
Decen-1	8.0

As substrates for the transitional metal carbides' hydration the following have been used: cyclohexene, okten-1, decen-1 and hexadecen-1. Corresponding alkenes are considered to be the reaction product, which has been confirmed through gas chromatography-spectrometry.

As it is shown in the Chart 2, in the present conditions highest effectiveness of hydration is displayed by cyclohexene, which has been chosen

Chart 3: The influence of catalyst's composition in the hydration of cyclohexane. Hydration conditions: 300°C, 40atm, 2h, m(catalyst) = 50 mg.

Catalyst	Conversion, %
Mo ₂ C (activation with hydrogen)	37
Mo ₂ C (activation with hydrogen/methane mixture)	41
WC (activation with hydrogen)	28
WC (activation with hydrogen/methane mixture)	33
WC (industrial)	11

for further study.

In the first stage of the paper, the influence of the catalyst's nature on the hydration of cyclohexene has been studied. As catalysts tungsten (WC) and molybdenum (Mo₂C) carbides have been used. The results are presented in the Chart 3.

The results of the studies

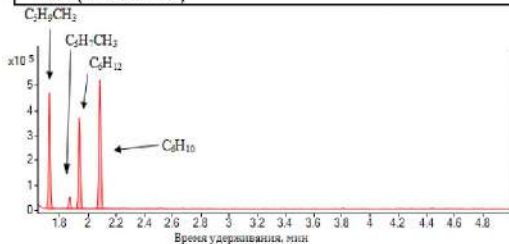


Figure 20: The GC-MS chromatograms of products obtained under 20atm hydrogen and 2 hours duration.

have shown the effectiveness of the catalysts used during the recovery of alkenes compared to the commercial carbide. As it is shown in the Chart 3, the molybdenum carbide, which has been recovered in hydrogen/methane mixture's flow, has displayed the best results; consequently, all further experiments have been conducted with the existence of this catalyst. The addition of methane during the recovery of the catalyst is needed to exclude the opportunity of the MoC phase

origination. The temperature, pressure, time and amount of catalyst influence on the cyclohexene hydration has been studied. It is worth mentioning that 20atm pressure

contributes to the isomerization of cyclohexene to methylcyclopentene, which has been confirmed through chromatography with mass spectrometer (Fig. 20).

Hydrodesulfurization of molybdenum carbide: The catalysts Mo_2C , $\text{Mo}_2\text{C}/\gamma\text{-Al}_2\text{O}_3$, $\text{Ni-Mo}_2\text{C}/\text{C}$ have been synthesized. As model alkenes, hydrodesulfurization substrates and standards the following reactives have been used: naphthalene (99%, Sigma Aldrich) cyclohexene (99%, Sigma Aldrich), decen-1 (97%, Sigma Aldrich), hexadecen-1 (99.8%, Sigma Aldrich), okten-1 (98%, Sigma Aldrich), dibenzothiophene (DBT 98%, Sigma Aldrich), dibenzylsulfide (Bn2S 98%, Sigma Aldrich), benzothiophene (BT 98%, Sigma Aldrich), 4,6-dimethyldibenzothiophene (Me_2DBT 95%, Acros Organics), thiophene (T 99%, Sigma Aldrich). Decalin (99%, Sigma Aldrich) has been used as solvent for the model mixtures of

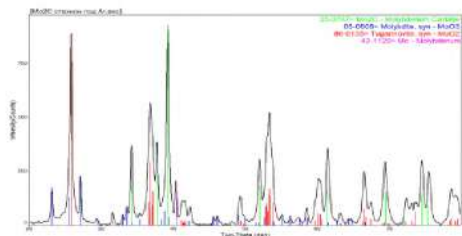


Figure 21: The XRD diffractogram of stoichiometric molybdenum carbide.

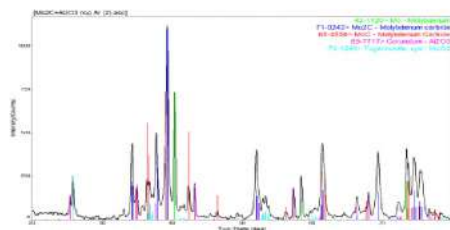


Figure 22: The XRD diffractogram of molybdenum carbide as a carrier used aluminum oxide.

sulfur compounds, and benzol has been used for naphthalene (99,6%, ЭКОС-1).

X-ray phase analysis has confirmed the existence of target product Mo_2C phase in synthesis compounds (Fig. 21, Fig. 22).

Chart 4: The comparison of molybdenum carbides catalytic activities in naphthalene recovery reactions. Process conditions: H_2 40atm, catalyst 100mg, 400°C, 4 h.

N ^o	Catalyst	Naphthalene conversion, %
1	Mo_2C	82
2	Mo_2C^*	85
3	$\text{Mo}_2\text{C}/\text{Al}_2\text{O}_3$	91
4	$\text{Ni-Mo}_2\text{C}$	97

* - Repetition of the experiment in the same conditions

All diffractograms (Fig. 21, Fig. 22) show the existence of molybdenum oxide in the sample, which confirms the high sensitivity of synthesized catalytic systems against the oxidation through atmospheric oxygen, as a result of which further catalytic reactions have been

conducted on the newly recovered samples. The surface layer of the carbide nanocatalysts is rapidly oxidizing in the air, as a result of which in that layer the transitional metals are in oxidized state, which negatively impacts on their catalytic activity. The usage of microwave

irradiation for the synthesis of the catalysts has shown that this method can be used also for the activation of catalytic reactions. In the same conditions of temperature, compared to ordinary heating, in case of the microwave heating the reaction undergoes several times faster.

After the activation of the catalyst, the characterized peaks of MoO₂ phase in the diffractogram disappear (Fig. 21, Fig. 22). In order to determine the catalytic activity of the catalysts containing molybdenum during the hydration process of the condensed aromatic compounds naphthalene 10% solution in benzol has been used. Initial experiments have shown that benzol has not been subject to any changes in the conditions of naphthalene conversion within the temperature and pressure studied. According to the obtained results (Chart 4), Ni-Mo₂C catalyst has shown the highest activity during the naphthalene conversion. Such high activity is conditioned by the existence of nickel atoms, which coincides with the literature data: increase of molybdenum carbide activity when doped by nickel atoms. Using all catalysts, according to the data of chrom-mass spectrometry, in all described cases, the main product of naphthalene hydration is tetraline, which origination selectivity is more than 90%. Side product is the obtained small amount decalin (not more than 2-3%). Through using Mo₂C/Al₂O₃, Ni-Mo₂C and stoichiometric Mo₂C catalysts hydration of cyclohexene and decen-1 has been conducted (Chart 5).

The high catalytic activity of carbides doped with nickel atoms, compared to other catalysts, gives an opportunity to completely hydrate the studied alkenes in 300°C temperature, moreover for the complete hydration of cyclohexene the needed reaction time is 4 hours, but for decen-1 it is up to 8 hours.

The obtained catalysts have been used in the reactions of the hydrodesulfurization of the

Chart 5: The influence of catalyst nature on alkenes' conversion in hydration reactions. Hydration conditions: H₂ 30atm, catalyst 50mg, 300°C, 2h.

Substrate	Catalyst		
	Mo ₂ C	Mo ₂ C/Al ₂ O ₃	Ni-Mo ₂ C
	Alkene conversion, %	Alkene conversion, %	Alkene conversion, %
Cyclohexene	66	71	80
Decen-1	26	38	52

Chart 6: The influence of temperature on the conversion of dibenzothiophene. Conditions of the process: H₂ 40atm, catalyst' 50mg, 2h.






Catalyst	Hydration temperature, °C			
	250	300	350	400
Mo ₂ C/Al ₂ O ₃	14%	35%	50%	89%
Ni-Mo ₂ C	27%	42%	63%	96%

dibenzothiophene 1,5% mixture in decalin solution as a model of diesel fraction. In the autoclave initially cleaned by argon 1ml model mixture and newly recovered catalyst's calculated quantity are filled, then the autoclave is closed and filled with hydrogen securing

the required pressure. Ni-Mo₂C and Mo₂C/Al₂O₃ have been used as catalysts. It is clear from the Chart 6 that during the hydrodesulfurization reaction Ni-Mo₂C is more active catalyst than Mo₂C/Al₂O₃. If we follow the assumption that hydrogen's activity and acid centers are needed for reactions with hydrogen, then such high activity of Ni-Mo₂C can be explained by the co-action of the nickel atoms and acid centers on carbide surface.

The comparative activity evaluation of compounds containing sulfur that exists in different diesel fractions during hydrodesulfurization reactions has shown that not mixed dibenzothiophene in these conditions has the smallest activity (Chart 15).

Chart 15: Hydrodesulfurization conversion of organic compounds containing sulfur with the presence of Ni-Mo₂C catalyst. Hydration conditions: H₂ 40atm, catalyst 50mg, 350°C, 6h

Substrate	Structural formula	Conversion, %
Dibenzylsulfide		100
Thiophene		100
Benzothiophene		99
Dibenzothiophene		92
4,6- Dimethyldibenzothiophene		96

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Conclusions

1. For the first time simple, easily used and cleaned, compact quartz microwave reactor and modified microwave oven with an opportunity of remote temperature measurement have been designed and prepared.
2. For the first time through microwave irradiation method rhenium diboride (ReB_2), rhenium diboride boron carbide ($\text{ReB}_2\text{-B}_4\text{C}$) composite, manganese diboride (MnB_2) boride nanophases have been synthesized.
3. Through microwave irradiation method nanophases of boron carbide, molybdenum and tungsten carbides, molybdenum carbide combined with different carriers and molybdenum carbide doped by nickel atoms have been synthesized.
4. For the first time in the literature the phase of boron carbide with the highest microhardness ($\approx 35\text{GPa}$), accessible super light ($\approx 3,2\text{g/cm}^3$) and super hard ($\approx 50\text{GPa}$) composites (27%w $\text{ReB}_2\text{-B}_4\text{C}$) has been synthesized by microwave heating and sintered by SPS methods, which is comparable to the hardness of c-BN. Also, those materials display high erosion durability.
5. Basis for the accessible, easy and energy saving industrial methods' creation and realization of super light and super hard materials have been made.
6. The synthesized tungsten and molybdenum carbides and the latter's phases combined with different carriers, compared to commercial analogies, have displayed high catalytic activity in the reactions of carbohydrate hydration, dehydration and degradation of hydrazine.
7. For the first time the molybdenum carbide doped by nickel atoms synthesized through microwave method has shown highest catalytic activity in the reactions of diesel fuel's hydrodesulfurization.
8. For the first time the microwave irradiation and the domestic microwave oven have been used in the process of catalyst reactions' activation. The study was shown higher efficiency of applied method compared with conventional.

Դավիթ Հայրապետի Դավթյան

ԱՆՅՈՒՄԱՅԻՆ ՄԵՏԱՂՆԵՐԻ (Mo, W, Mn, Re) ԿԱՐԲԻԴՆԵՐԻ, ԲՈՐԻԴՆԵՐԻ ԵՎ ԲՈՐԻ ԿԱՐԲԻԴԻ ՄԻԿՐՈԱԼԻԲԱՅԻՆ ՃԱՌԱԳԱՅԹՄԱՄԲ ՄԻՆԹԵՂԸ, ԴՐԱՆՑ ՖԻԶԻԿԱՄԵԽԱՆԻԿԱԿԱՆ ԵՎ ԿԱՏԱԼԻՏԻԿ ՀԱՏԿՈՒԹՅՈՒՆՆԵՐԸ
Ամփոփագիր

Աշխատանքի նպատակն է եղել միկրոալիքային ճառագայթման կիրառմամբ սինթեզել անցումային մետաղների՝ Mo, W, Mn, Re, կարբիդներ և բորիդներ, ինչպես նաև բորի կարբիդ: Կիրառված սինթեզի մեթոդը թույլ է տվել ստանալ վերջիններիս նանոֆազերը, բյուրեղիկների չափերի նեղ բախշվածությամբ: Ստացված նյութերը փորձարկվել են երկու ուղղությամբ՝ որպես հետերոգեն կատալիզատորներ և որպես կարծր նյութեր:

Սինթեզի համար առաջին անգամ նախագծվել, կառուցվել և կիրառվել է քվարցային պարզ ռեակտորը՝ հազեցած գազահոսքային համակարգով, հատուկ ձևափոխվել է կենցաղային միկրոալիքային վառարանը, որը հնարավորություն է տվել ապահովելու ռեակցիոն խառնուրդի առավելագույն ճառագայթում (առավելագույնս 1300°C), իներտ հոսքային միջավայրում: Ռեակցիոն խառնուրդի ջերմաստիճանը միկրոալիքային ճառագայթման պայմաններում չափվել է հեռահար ինֆրակարմիր (Dostman HT 1800) ջերմաչափով:

Ստացված նյութերի կառուցվածքը և տեքստուրային առանձնահատկություններն ուսումնասիրվել են բազմաթիվ ֆիզիկոմեխանիկական և ֆիզիկոքիմիական եղանակներով (XRD, SEM, TEM, XPS, խտաչափություն, SPS, միկրոկարծրություն ըստ Վիկերսի, BET և այլն): Ավելին, ստացված նմուշների կատալիտիկ ակտիվությունը հետազոտվել է ինչպես դասական տաքացման պայմաններում, այնպես էլ միկրոալիքային ճառագայթման պայմաններում:

Աշխատանքի արդյունքում սինթեզվել են հետևյալ նյութերի նանոֆազերը՝ MnB₂, B₄C, ReB₂, ReB₂-B₄C, WC, Mo₂C, Mo₂C/C, Mo₂C/ZSM12, Mo₂C/γAl₂O₃, Ni-Mo₂C:

Ստացված նյութերը որպես կատալիզատորներ փորձարկվել են հետևյալ ռեակցիաներում՝ ալկենների հիդրում, դեհիդրում, հիդրազինի քայքայում, դիզելային վառելիքում պարունակվող ծծումբօրգանական միացությունների հիդրոծծմբազրկում և այլն:

Ստացվել են հետևյալ արդյունքները.

1. Առաջին անգամ նախագծվել և պատրաստվել է պարզ, հեշտ կիրառելի, դյուրամաքրվող, կոմպակտ քվարցային միկրոալիքային ռեակտոր և ձևափոխված միկրոալիքային վառարան՝ հազեցած ջերմաստիճանի հեռահար չափման հնարավորությամբ:
2. Միկրոալիքային ճառագայթման եղանակով առաջին անգամ սինթեզվել է ռենիումի դիբորիդ(ReB₂), ռենիումի դիբորիդ, բորի կարբիդ(ReB₂-B₄C), մանգանի դիբորիդ(MnB₂) բորիդային նանոֆազերը:
3. Միկրոալիքային եղանակով սինթեզվել են բորի կարբիդի, մոլիբդենի և վոլֆրամի կարբիդների, մոլիբդենի կարբիդի համակցված տարբեր կոմպոզիցիաներով, նիկելի ատոմներով դոպացված մոլիբդենի կարբիդի նանոֆազեր:
4. Գրականության մեջ առաջին անգամ եռակալվել է այս պահին ամենաբարձր միկրոկարծրությամբ(≈35GPa) բորի կարբիդ ֆազը, մատչելի գերթեթև(≈3,2g/cm³) և գերկարծր(≈50GPa) կոմպոզիցիոն(27%wReB₂-B₄C), վերջինս համեմատելի է c-BN-ի կարծրության հետ: Ինչպես նաև նշված նյութերը ցուցաբերում են բարձր էրոզիոն մաշակայունություն:

5. Հիմք է դրվել գերթեթև և գերկարծր նյութերի մատչելի, հեշտ և էներգախնայող արտադրական եղանակների ստեղծման և իրագործման համար:
6. Սինթեզված վոլֆրամի և մոլիբդենի կարբիդները և վերջինիս տարբեր կրիչների հետ համակցված ֆազերը, համեմատած կոմերցիոն անալոզների հետ, ցուցաբերում են բարձր կատալիտիկ ակտիվություն ածխաջրածինների հիդրման, դեհիդրման, հիդրազինի քայքայման ռեակցիաներում:
7. Առաջին անգամ միկրոալիքային եղանակով սինթեզված նիկելի ատոմներով դոպացված մոլիբդենի կարբիդը դիզելային վառելիքի հիդրոծծմբազրկման ռեակցիաներում ցուցաբերել է առավելագույն կատալիտիկ ակտիվություն՝ համեմատած կոմերցիոն անալոզների հետ:
8. Առաջին անգամ միկրոալիքային ճառագայթումը, ինչպես նաև կենցաղային միկրոալիքային վառարանը կիրառվել են կատալիտիկ ռեակցիաների ակտիվացման պրոցեսում:

Давид Айрапетович Давтян

**СИНТЕЗ КАРБИДОВ И БОРИДОВ ПЕРЕХОДНЫХ МЕТАЛЛОВ (Mo, W, Mn, Re) И
КАРБИДА БОРА С ПОМОЩЬЮ МИКРОВОЛНОВОГО ИЗЛУЧЕНИЯ – ИХ
ФИЗИКОМЕХАНИЧЕСКИЕ И КАТАЛИТИЧЕСКИЕ СВОЙСТВА**

Резюме

Целью работы было с помощью микроволнового излучения синтезировать карбиды и бориды переходных металлов Mo, W, Mn, Re, а также карбид бора.

Примененный метод синтеза позволил получать нанофазные кристаллики с узким распределением размера. Полученные вещества тестированы в двух направлениях - в качестве гетерогенных катализаторов и на механическую твердость. Для синтеза впервые проектирован, построен и испытан кварцевый проточный реактор. Специально модифицирована бытовая микроволновая печь, которая позволила в реакторе получить температуру 1300°C в проточной инертной атмосфере. Температура реакционной среды измерялась с помощью дистанционного инфракрасного термометра (Dostman HT 1800).

Структуру и текстурные особенности полученных веществ исследованы различными физикохимическими и физикомеханическими методами (SEM, TEM, XPS, денситиметрия, SPS, микротвердость по Викерсу, BET и т.д.) Каталитическая активность исследовалась как в условиях классического нагрева так и в условиях микроволнового излучения. В результате работ синтезированы следующие соединения MnB₂, B₄C, ReB₂, ReB₂-B₄C, WC, Mo₂C, Mo₂C/C, Mo₂C/ZSM12, Mo₂C/ γ -Al₂O₃, Ni-Mo₂C.

Полученные вещества в качестве катализаторов испытаны в реакциях: гидрирование и дегидрирование алкенов, разложения гидразина, гидрообессеривания сероорганических соединений в дизельном топливе.

Получены следующие результаты:

1. Впервые разработаны и приготовлены простые, легко применимые, легко очищаемые компактный кварцевый микроволновый реактор и модифицированная микроволновая печь, оснащенные возможностью измерения температуры на расстоянии.
2. Впервые методом микроволнового излучения были синтезированы боридные нанофазы диборида рения (ReB_2), диборида рения - карбида бора ($\text{ReB}_2\text{-B}_4\text{C}$), диборида марганца (MnB_2).
3. Методом микроволнового излучения синтезированы нанофазы карбидов молибдена и вольфрама, карбида молибдена в сочетании с различными носителями, карбида молибдена, легированного атомами никеля.
4. Впервые в литературе представлены данные о фазе карбида бора с наивысшей микротвердостью ($\approx 35 \text{ GPa}$), о доступном сверхлегком ($\approx 3,2 \text{ g/cm}^3$) и сверхтвердом ($\approx 50 \text{ GPa}$) композите (27%w $\text{ReB}_2\text{-B}_4\text{C}$): последний по показателю твердости сопоставим с c-BN. Кроме того, вышеуказанные материалы обладают высокой устойчивостью к эрозии.
5. Была заложена основа для создания и внедрения доступных, нетрудных и энергосберегающих методов производства сверхлегких и сверхтвердых материалов.
6. Синтезированные карбиды вольфрама и молибдена и их фазы в сочетании с различными носителями проявляют высокую каталитическую активность в реакциях гидратации и дегидратации углеводов, разложения гидразина по сравнению с коммерческими аналогами.
7. Впервые синтезированный микроволновым методом легированный атомами никеля карбид молибдена, показал высокую каталитическую активность в реакциях гидрообессерования соединений дизельного топлива.
8. Впервые микроволновое излучение, а также бытовая микроволновая печь были использованы для активации каталитических реакций. Метод показал высокую эффективность по сравнению с обычным нагревом

