

ՀՀ ԳԱԱ Ա.Բ. ՆԱԼԲԱՆԴՅԱՆԻ ԱՆՎԱՆ ՔԻՄԻԱԿԱՆ ՖԻԶԻԿԱՅԻ ԻՆՍՏԻՏՈՒՏ

ԶԱՔԱՐՅԱՆ ՄԱՐԻԵՏԱ ԿԱՐԵՆԻ

ՄԻ ՇԱՐՔ ՄԵՏԱԴՆԵՐԻ ԹԹՎԱԾՆԱՎՈՐ ՄԻԱՑՈՒԹՅՈՒՆՆԵՐԻ
ՄԱԳՆԵԶԻՈՒՄԱ-ԿԱՐԲՈԹԵՐՄ ՎԵՐԱԿԱՆԳՆՈՒՄՆ ԱՅՐՄԱՆ ՌԵԺԻՄՈՒՄ
ԵՎ W-Me (Cu, Ni, Ag) ՀԱՄԱՁՈՒԼՎԱԾՔՆԵՐԻ ՍԻՆԹԵԶԸ

Բ.00.01 - «Անօրգանական քիմիա» մասնագիտությամբ քիմիական
գիտությունների թեկնածուի զիտական աստիճանի հայցման ատենախոսության

Ս Ե Ղ Մ Ա Գ Ի Ր

ԵՐԵՎԱՆ 2020

A.B. NALBANDYAN INSTITUTE OF CHEMICAL PHYSICS NAS RA

ZAKARYAN MARIETA

MAGNESIO-CARBOTHERMAL REDUCTION OF OXYGENOUS COMPOUNDS
OF A NUMBER OF METALS IN COMBUSTION MODE AND SYNTHESIS
OF W-Me (Cu, Ni, Ag) ALLOYS

A B S T R A C T

of Dissertation in 02.00.01 – “Inorganic chemistry” presented for the degree of
candidate of chemical sciences

YEREVAN 2020

Ատենախոսության թեման հաստատվել է Երևանի պետական համալսարանում

Գիտական ղեկավար՝

ՀՀ ԳԱԱ թղթակից անդամ,
ֆիզ-մաթ. գիտությունների դոկտոր,
պրոֆեսոր Ս.Լ. Խառատյան

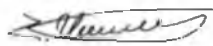
Պաշտոնական ընդդիմախոսներ՝

քիմ. գիտ. դոկտոր, պրոֆեսոր Ն.Հ. Զուլումյան
քիմ. գիտ. թեկնածու, Ա.Բ. Հարությունյան

Առաջատար կազմակերպություն՝ Տալլինի տեխնոլոգիական համալսարան

Պաշտպանությունը կայանալու է 2020 թ. դեկտեմբերի 24-ին, ժամը 14³⁰-ին ՀՀ ԳԱԱ Ա.Բ. Նալբանդյանի անվան Քիմիական ֆիզիկայի ինստիտուտում գործող ՀՀ ԲՈԿ-ի 017 «Քիմիա» մասնագիտական խորհրդում (0014, Երևան, Պ Սևակի փ. 5/2): Ատենախոսությանը կարելի է ծանոթանալ ՀՀ ԳԱԱ Ա.Բ. Նալբանդյանի անվան Քիմիական ֆիզիկայի ինստիտուտի գրադարանում: Սեղմագիրն առաքված է 2020 թ. նոյեմբերի 13-ին:

017 Մասնագիտական խորհրդի
գիտական քարտուղար,
ֆիզ-մաթ գիտությունների թեկնածու



Հ.Պ. Սարգսյան

The subject of the dissertation is approved at Yerevan State University

Scientific advisor:

Correspondent member of NAS RA,
Doctor of Sciences in Physics and Mathematics
professor S.L. Kharatyan

Official opponents:

Doctor of Chemical Sciences, professor N.H. Zulumyan
Candidate of Chemical Sciences, A.B. Harutyunyan

Leading organization:

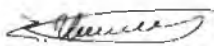
Tallinn University of Technology

Defense will take place on 24th of December 2020 at 14³⁰ on meeting of the special council of the SCC RA 017 “Chemistry”, acting at A.B. Nalbandyan Institute of Chemical Physics NAS RA (0014, Yerevan, st. P. Sevak 5/2).

The PhD thesis is available at the library of A.B. Nalbandyan Institute of Chemical Physics NAS RA.

The abstract is sent out on November 13, 2020.

Scientific secretary of the 017 special council,
Candidate of Sciences in Physics and Mathematics



H.P. Sargsyan

GENERAL DESCRIPTION OF THE WORK

Work timeline

Driven by the worldwide needs in the key areas of electronics, spaceflight, energy and security, the demand for the tungsten-copper (W-Cu), tungsten-nickel (W-Ni) and tungsten-silver (W-Ag) composite materials of high performance has greatly increased in recent years. These tungsten-based composites offer a valuable combination of functional and structural properties, including superior thermal management properties, high microwave absorption capacity, high tensile strength, superior abrasion resistance, high thermal and electrical conductivity. In particular, refractory metals (e.g. W, Mo) are intended to ideally combine the low thermal expansion coefficient with the high thermal and electrical conductivity of transition metals (eg. Cu, Ag). However, a huge challenge still lies in the non-availability of sufficient quality (high relative density, homogeneous microstructure, ultrafine and finely dispersed composing phases) materials impeding the technological advancement for tungsten-based composites in a variety of applications.

The preparation of refractory metal based alloys by conventional metallurgical methods is challenged by the large differences in the specific gravity and melting points of the constituents: ($T_W=3422$ °C, $T_{Cu}=1085$ °C, $T_{Ag}=962$ °C, $T_{Ni}=1455$ °C). This is further complicated by the limited mutual solubility of the metals in the both solid and liquid states.

The distinct particles of one metal are dispersed in a matrix of the other one, producing of a so called "pseudoalloy". The microstructure therefore becomes a metal matrix composite in contrary to an ordinary alloys or solid solutions. It should be noted that unlike W-Cu, W-Ag pseudoalloys, tungsten with nickel forms an ordinary alloy and could form intermetallic compound with specific molar ratio of metals.

In order to produce high-density parts with net shape components, homogeneous structure and enhanced physicomechanical properties, very fine dispersion of both metals should be attained. Thus, the development of cost-effective techniques of production of homogenous and fine-grained composite materials (W-Cu, W-Ni, W-Ag), as well as the optimization of their preparation conditions is targeted in the current research.

Taking into account the difficulties in obtaining a homogeneous composite material with desired microstructure, purity and grain size distribution, one-stage in-situ process is proposed for nanopowders' synthesis. Our findings are directed to the synthesis of fine-grained composite powders from available precursors (metal oxides and/or salts mixture) with high homogeneity and enhanced sinterability.

Self-propagating high-temperature synthesis (SHS) via thermo-kinetic coupling is the proposed approach, which allows control over the combustion process parameters, regulation of the powder grain size, and maintainance of compositional homogeneity. By controlling the combustion process, optimal conditions for the synthesis of target materials can be examined and developed, and furtherly commercially upscaled.

The synthesized powders were subjected to consolidation by spark plasma sintering (SPS) technique to manufacture compacts with high relative density and promising mechanical properties.

Aim and problems of the work

The aim of this work is to develop new technological procedure for the synthesis of fine powders of W-Cu, W-Ni, W-Ag composite materials based on magnesio-carbothermal reduction of oxygenous compounds by means of controlled combustion processes. Optimization of thermal regimes made it possible to regulate the composition and microstructure of the materials obtained directly in the combustion process.

To achieve the above-mentioned goals:

- Thermodynamic analysis in the $\text{WO}_3\text{-CuO-Mg-C}$, $\text{CuWO}_4\text{-Mg-C}$, $\text{WO}_3\text{-NiO-Mg-C}$, $\text{NiWO}_4\text{-Mg-C}$, $\text{WO}_3\text{-Ag-Mg-C}$, $\text{Ag}_2\text{WO}_4\text{-Mg-C}$ systems was performed to explore the possibility to synthesize W-Cu, W-Ni, W-Ag composite materials in combustion mode and to find out the optimal conditions.
- The influence of initial mixture composition and process parameters on the combustion temperature, phase composition and microstructure of target materials was studied.
- Solution combustion synthesis (SCS), chemical precipitation and furnace methods were utilized for the preparation of nanoscale starting materials with controllable microstructure for the combustion synthesis of W-Cu, W-Ag, W-Ni composite materials.
- The regularities of combustion, phase and structure formation laws were revealed for the $\text{WO}_3\text{-CuO-Mg-C}$, $\text{CuWO}_4\text{-Mg-C}$, $\text{WO}_3\text{-NiO-Mg-C}$, $\text{NiWO}_4\text{-Mg-C}$, $\text{WO}_3\text{-Ag-Mg-C}$, $\text{Ag}_2\text{WO}_4\text{-Mg-C}$ systems based on the preliminary thermodynamic calculations for defining the optimal conditions for W-Cu, W-Ni, W-Ag materials' preparation.
- Kinetic regularities and phase formation mechanisms were explored in the studied systems using thermal analysis method at low (DTA/TG; $V_{\text{H}}=2.5\text{-}30$ °C/min) and high (HSTS; $V_{\text{H}}=100\text{-}1200$ °C/min) heating rates for assessing the effect of the heating rate on the conversion process.
- The obtained materials were thoroughly characterized by different physicochemical analysis methods.
- SHS synthesized powders were consolidated by spark plasma sintering technique and were studied physico-mechanical properties of the obtained compact samples.

Novelty of the work

- For the first time, W-Cu, Ni-W, W-Ag composite materials were obtained in combustion mode.
- Simultaneous utilization of magnesium and carbon as reducing agents mitigated the violent nature of combustion process allowing to perform SHS synthesis under controllable and moderate temperature modes.

- The interaction pathway was outlined and the kinetic parameters of the $\text{WO}_3\text{-CuO-Mg-C}$, $\text{CuWO}_4\text{-Mg-C}$, $\text{WO}_3\text{-NiO-Mg-C}$, $\text{NiWO}_4\text{-Mg-C}$, $\text{WO}_3\text{-Ag-Mg-C}$, $\text{Ag}_2\text{WO}_4\text{-Mg-C}$ systems were deduced at low ($V_h=2.5\text{-}30\text{ }^\circ\text{C/min}$) and high ($V_h=100\text{-}1200\text{ }^\circ\text{C/min}$) heating rates.
- The utilization of salts as precursors containing both metals in the same crystalline structure showed to be contributing to the homogeneous distribution of metals in the product.
- The use of fine-grained reagents allowed synthesizing composite nanopowders with enhanced chemical homogeneity.

Practical value of the work

- Single-stage, effective approaches of in-situ production of nanopowders of W-Cu and W-Ag pseudoalloys, as well as W-Ni alloys with average particle size 10-50 nm have been developed.
- In addition to the oxide raw materials, salt precursors, containing both metals in the same crystal lattice were used as starting materials, providing the synthesis of target alloys with higher homogeneity.
- Using thermo-kinetic coupling approach allowed the preparation of W-Cu, W-Ni, W-Ag composite materials by the magnesio-carbothermal reduction of (WO_3+CuO) , CuWO_4 , (WO_3+NiO) , NiWO_4 , (WO_3+Ag) , Ag_2WO_4 precursors in combustion mode under the controllable and mild temperature conditions.
- The optimal conditions to obtain target alloys from oxygenous compounds have been determined by studying the possible mechanisms of alloys synthesis in combustion processes under non-isothermal conditions.
- The nanopowders obtained in the combustion mode were consolidated and compacted by SPS technique with providing high relative density and mechanical properties.

Content and structure of the work

The PhD thesis consists of an introduction, five chapters, conclusions and a reference list. The PhD thesis is written on one hundred and forty-nine (148) pages, contains fourteen (14) tables, eighty-eight (87) figures and one hundred and fifty-seven (157) references.

Publications

The main part of the PhD thesis is published in nine (9) articles, four (4) of which are in international peer-reviewed journals, five (5) in the local journals, as well as in nine (9) theses.

Chapter 1. Literature review

The literature review consists of three main sections.

In the first section the properties and applications of tungsten-copper, tungsten-nickel and tungsten-silver composite materials, as well as the main ways and difficulties of obtaining of these nanomaterials are discussed.

The second section provides description of self-propagating high-temperature synthesis, its features, types and advantages, as method of obtaining inorganic substances (metals, alloys, composites, etc.). Besides, it includes comprehensive description of thermo-kinetic coupling approach and the advantages and importance of the coupling of chemical reactions in SHS processes.

In the third section the considerable advantages and characteristics of solution combustion synthesis method is presented, as well as the preparation of various metals and alloys by SCS.

Chapter 2. Experimental part

To produce target W-Cu, W-Ni, W-Ag composite materials in the combustion mode the experiments were carried out in a constant pressure reactor. Thermodynamic calculations were performed to find out the optimal conditions for joint and complete reduction of oxygenous compounds by using "ISMAN-THERMO" software package. The calculation is based on the principle of minimizing the thermodynamic potential of the system. Combustion temperatures were registered using micro-thermocouple technique. The phase composition of the samples was analyzed by X-ray diffraction method. To identify the products from the XRD spectra, the data were processed using the ICDD database. Morphologies and microstructures of the samples were examined by high-resolution scanning electron microscope equipped with a topographic imaging and energy selective backscattered detector for compositional contrast. For identifying and quantifying elemental composition of the samples energy dispersive X-ray spectroscopy (EDS) was used. Specific surface areas of materials synthesized by SHS method were measured by adsorption analysis (BET method). IR method was used to detect the structural features of materials synthesized in different ways, as well as differences in the absorption intensities of the functional groups. The gaseous products were analyzed by gas-chromatography method. The obtained powders were consolidated using SPS technique. The density of consolidated parts was measured by Archimedes technique and Vickers micro-hardness - by Vickers microhardness tester.

The mechanism and kinetics of reduction reactions by Mg+C combined reducers was studied by Differential Thermal Analysis/Thermogravimetry (DTA/TG) method utilizing Q-1500 instrument ($V_h=2.5-30$ °C/min, $T_{max}=1000$ °C), as well as high-speed temperature scanner (HSTS). The latter provides an advanced opportunity to disclose the step-wise nature of complex reactions in the multicomponent systems at high heating rates (V_h - up to 1200 °C/min, $T_{max}=1300$ °C).

Chapter 3. Preparation of W-Cu pseudoalloys by magnesio-carbothermal reduction of tungsten and copper oxides, copper tungstate

It is well known that magnesiothermal reduction of tungsten and copper oxides are extremely exothermic ($T_{ad} \geq 3000$ °C) with violent combustion. This method of metal synthesis, akin to thermite reactions, is accompanied by intensive gas release, melting the intermediate or final products, and generally produces low yields. In order to mitigate the reaction conditions it is coupled with metal oxide carbothermal reduction process, which is low exothermic one. Furthermore, the use of (Mg + C) combined reducers will allow the control of the reaction temperature in a wide range at synthesis of composite powders.

The properties of W-Cu pseudoalloys and therefore the spheres of application primarily depend on their composition. The physical and mechanical properties of the pseudoalloys can be adjusted by changing the ratio of metals.

Prior to experimental procedure, thermodynamic calculations were carried out for the $2WO_3$ -CuO-yMg-xC and WO_3 -3CuO-yMg-xC systems. The goal being to optimize conditions for the joint and complete reduction of tungsten and copper oxides, aimed at obtaining W-Cu pseudoalloys with different compositions (W:Cu=2:1; 1:3). The amount of Mg was determined as to provide complete reduction at comparatively low temperatures. To define the effect of carbon on the combustion parameters (temperature and wave propagation velocity), a series of experiments were performed versus carbon content. The obtained results revealed that the increase of carbon amount leads to a decrease in both the combustion temperature and velocity (Fig. 1) conditioned by the growth in the portion of low-caloric carbothermal reaction in the system.

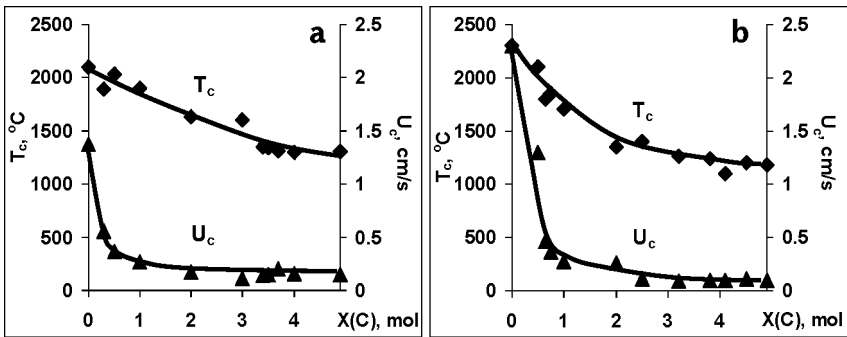


Fig. 1. Combustion temperature (T_c) and velocity (U_c) vs carbon amount for the $2WO_3$ -CuO-2.7Mg-xC (a) and WO_3 -3CuO-1.7Mg-xC (b) systems

To determine the phase composition of combustion products, XRD analyses were performed. Considering the thermodynamic calculations and XRD of the combusted samples, the optimal ranges for obtaining the target 2W-Cu and W-3Cu pseudoalloys were selected as $2WO_3+CuO+2.7Mg+(3.5-4)C$ and $WO_3+3CuO+1.7Mg+(4.5-8)C$.

Microstructural examinations testify that an increase in carbon concentration leads to significant grain refinement, as the process proceeds in relatively moderate conditions and grain growth is inhibited at lower temperatures.

To remove the magnesia byproduct from the yielded metals, the reaction products were subjected to hydrochloric acid treatment ($\omega=10\%$) at room temperature. According to the results, the combustion product after acid treatment represents target material (Fig. 2). SEM analyses of acid treated samples revealed that the products contain only fine snowflake-like particles with 30-50 nm in size.

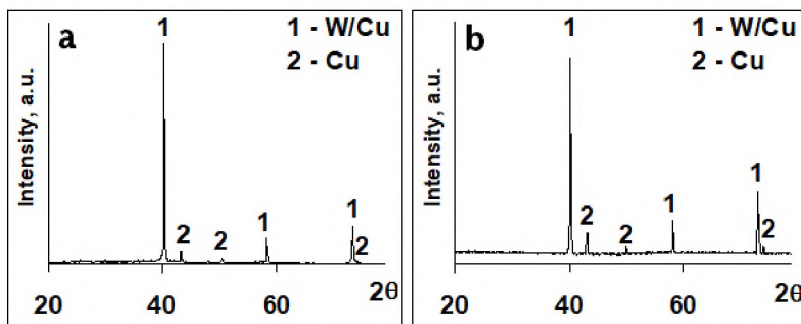


Fig. 2. XRD patterns of combustion products for the $2\text{WO}_3+\text{CuO}+2.7\text{Mg}+3.7\text{C}$ (a) and $\text{WO}_3+3\text{CuO}+1.8\text{Mg}+4.7\text{C}$ (b) mixtures after acid treatment

The obtained ultrafine structured W-Cu powders were exposed to hot explosive consolidation (HEC) for the fabrication of dense compacts. According to microhardness and density measurement results, W-Cu nanocomposites obtained by SHS method and consolidated by HEC technology demonstrated enhanced microhardness and density (up to 85 %) compared to conventional methods. Further optimization of consolidation process lead to preparation of almost fully dense samples.

For the synthesis of nanocomposite powders with homogenous metal distribution and microstructure, the use of copper tungstate is suggested, as it yields a final product with excellent chemical homogeneity and purity thanks to the presence of the both metals in the same crystalline structure. Moreover, high surface area and additional reactivity generated from the thermal decomposition of salt precursors promoted the overall interaction between particles.

It is widely acknowledged that the selection of the starting materials (e.g. particle size, preparation technique) can highly contribute to enhancing the structure and properties of the final products. Regarding to that, fine precursors were synthesized by SCS (a), chemical precipitation (b) and furnace methods (c).

The oxygen containing raw material prepared by SCS produced the finest alloys' particles at ~ 50 nm, while chemically precipitated one yielded ≈ 100 nm, and the salt obtained by furnace method comprised particles ≈ 400 nm, respectively (Fig. 3).

W-Cu powders, synthesized from different raw materials, were characterized by different particle sizes. In particular, the powder obtained from the reduction of copper tungstate prepared by the furnace method possesses the largest grains: 200-400 nm, while the powder obtained from the SCS synthesized initial reactant is the finest: 10-20 nm (Fig. 4).

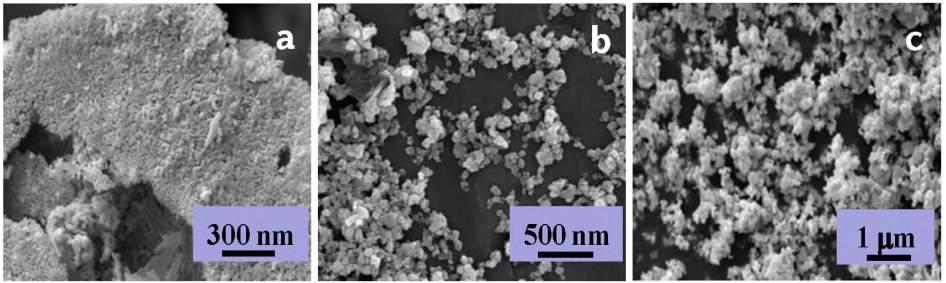


Fig. 3. SEM images of CuWO_4 obtained by SCS (a), chemical precipitation (b) and furnace (c) methods

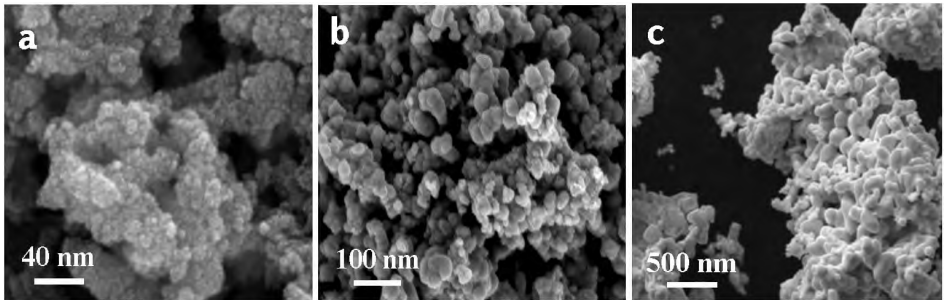


Fig. 4. SEM images of W-Cu pseudoalloys obtained by the reduction of CuWO_4 prepared by SCS (a), chemical precipitation (b) and furnace (c) methods

W-Cu composite powders produced by SHS were consolidated by SPS technique, which allowed preparing compact specimens with 95 % relative density. This is 10 % higher than that obtained for the compact sample prepared by the powders reduced from oxides. In Figure 5, the results of EDS mapping analyses for the W-Cu product (from salt precursor) are depicted. The blue color corresponds to tungsten phases and the pink color to copper phases illustrating the homogeneous distribution of W and Cu phases throughout the sample.

It follows that the presence of two metals in the crystal lattice of the same material contributes to the homogeneity of the distribution of metals in the reduced powder, which in turn has a positive effect on the powders' densification behavior.

To explore the sequence of processes occurring in the combustion wave, the combustion process was performed in the section of bulk copper wedge. As the front approaches the apex specific heat losses increase and at some critical point combustion wave propagation stops. After the process, products thus obtained were analyzed layer-by-layer by X-ray examinations. According to the obtained data, firstly the copper oxide carbothermal reduction into copper takes place and then magnesio-carbothermal reduction of the tungsten oxide into tungsten over WO_2 .

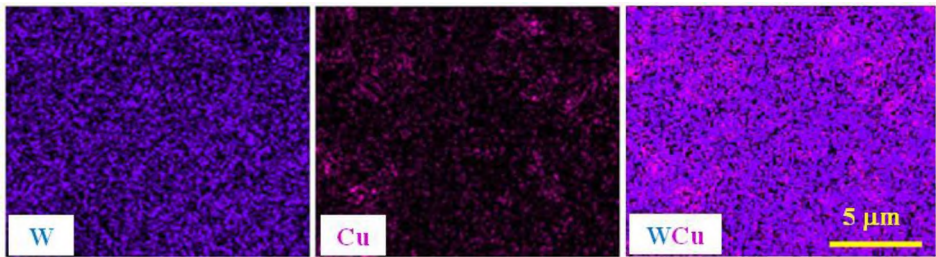


Fig. 5. EDS mapping of the combustion product (W-Cu) after SPS consolidation

Chapter 4. Preparation of W-Ni alloys by magnesio-carbothermal reduction of tungsten and nickel oxides, nickel tungstate

For the preparation of W-Ni alloys, 1:1 molar ratio of metals was chosen as the model-version. A careful analysis of the system will give insights into the synthesis of alloys with other compositions. Stemming from the thermodynamic calculations, magnesio-carbothermal co-reduction of tungsten and nickel oxides was performed in $\text{NiO-WO}_3\text{-1.7Mg-xC}$ system yielding Ni-W alloy. It is worthy to note that in the $\text{CuO-WO}_3\text{-Mg-C}$ system, combustion temperatures are comparably higher than the melting point of the fusible metal (copper, 1083 °C). In contrary, for the $\text{NiO-WO}_3\text{-1.7Mg-xC}$ system, combustion temperatures in optimal conditions don't surpass the melting point of Ni; hence, the reduction process occurs without melting the reduced metallic components, which can increase the homogeneity of the obtained product. In contrast to the above-mentioned W-Cu pseudoalloys, in the Ni-W system, Ni and W metals form nickel rich intermetallic compound with specific molar ratio of metals Ni_{17}W_3 .

It is worth noting that in the $\text{NiO-WO}_3\text{-1.7Mg-xC}$ system with high molar fraction of carbon ($x > 4.5$ mol), combustion wave propagates in a non-steady regime. The registered thermograms for carbon rich $\text{NiO-WO}_3\text{-1.7Mg-xC}$ mixtures are essentially different showing anomalous fast cooling zone (Fig. 6b). As observed visually, the combustion process is shown to have a wave propagation in spin-combustion mode.

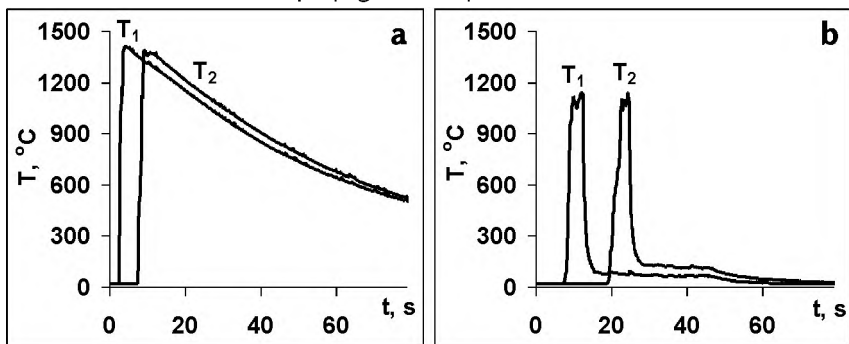


Fig. 6. Temperature-time histories at combustion of the $\text{NiO+WO}_3\text{+1.7Mg+2.2C}$ (a) and $\text{NiO+WO}_3\text{+1.7Mg+5C}$ (b) mixtures

After cooling the reacted samples were crushed into a powder, subjected to acid leaching for removing byproduct magnesia. The XRD analyses of acid treated samples showed, that MgO was completely removed from the mixture by dilute solution of hydrochloric acid, as no characteristic peaks of MgO were detected (Fig. 7).

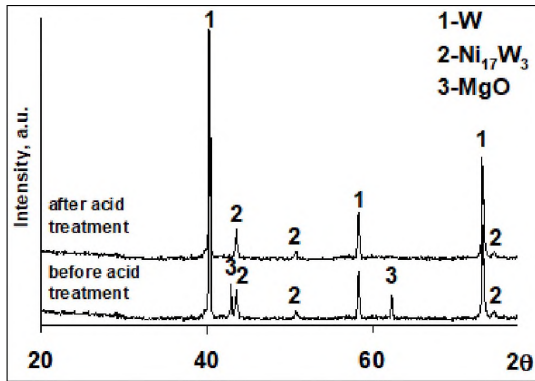


Fig. 7. XRD patterns of combustion products of the $\text{WO}_3+\text{NiO}+1.7\text{Mg}+2.2\text{C}$ mixture before (a) and after (b) acid treatment

The relative density of the SPS compacted ($T=1350\text{ }^\circ\text{C}$, $P=50\text{ MPa}$, dwell time=3 min) specimen was 95 %. The average Vickers microhardness was measured to be $590\pm 60\text{ kg/mm}^2$, which collaborates with the hardness of W-Ni alloy prepared by electrodepositing method ($530\text{-}570\text{ kg/mm}^2$).

Parallel to experiments with oxide precursors, the synthesis of W-Ni alloy was studied from $\text{NiWO}_4\text{-Mg-C}$ mixture as well. The microstructural analysis of NiWO_4 , synthesized by two different routines (SCS (a) and furnace (b) methods), revealed that the salt prepared by the furnace method possesses larger grains (Fig. 8). Prolonged exposure at high temperatures ($850\text{ }^\circ\text{C}$ for ≈ 7 hours) resulted in grain coarsening. In case of the SCS method, the temperature of the system reaches up to $1000\text{ }^\circ\text{C}$ for only few seconds.

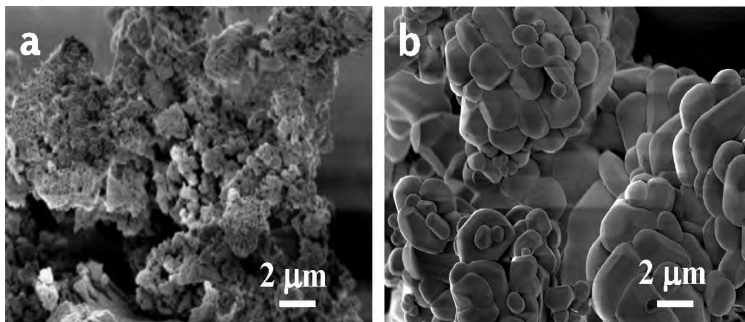


Fig. 8. SEM images of NiWO_4 obtained by SCS (a) and furnace (b) methods

The chemical homogeneity of the W-Ni alloy was examined by EDS mapping to determine the spatial distribution of metals in the sample. As can be seen from the Figure 9, the sintered material has a significantly high homogeneity compared to compact specimen prepared from the powders by the reduction of oxide precursors.



Fig. 9. EDS mapping of the combustion product (W-Ni) after SPS consolidation

Considering that combustion processes are characterized by high temperatures and high self-heating rates of substances in the combustion wave, the investigation of the interaction mechanism and optimization of synthesis conditions become challenging. To tackle the challenge, the reduction process was modeled at controllable heating conditions tuning the process within the time and exploring the Ni-W formation pathway under programmed heating rates by thermal analysis methods. XRD analyses of the quenched products together with the kinetic data of the co-reduction of WO_3 and NiO oxides by Mg+C combined reducer at various stages are used to elucidate the reduction mechanism under non-isothermal conditions by Differential Thermal Analysis/Thermogravimetry (DTA/TG, $V_h=2.5-30$ °C/min) and high speed temperature scanner (HSTS, $V_h=$ up to 1200 °C/min). According to the data obtained by DTA/TG technique, the reduction process starts by magnesiothermal reduction of NiO ($T_{max}=615$ °C; solid+solid mechanism) and afterwards WO_3 ($T_{max}=660$ °C; solid+liquid mechanism). The reduction process continues by carbon, which reacts with the remaining oxides (Fig. 10).

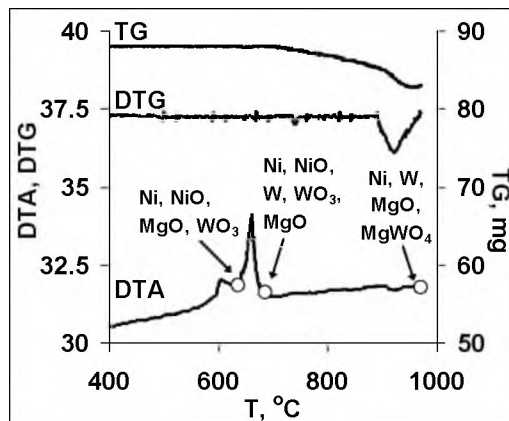


Fig. 10. DTA/TG/DTG curves of the NiO+ WO_3 +Mg+2C mixture, $V_h=20$ °C/min

The thermogravimetric examinations performed at various heating rates (2.5-20 °C/min) allowed calculating the effective activation energy values (E_a) for the reduction stages of the studied reactions (Table 1) using Kissinger and Ozawa methods. These methods are based on the Arrhenius' equation modulated for the non-isothermal conditions of the reaction in such a way where temperature is a linear function of time.

Table 1. Activation energy values for the reactions (Ni & W containing systems)

Reaction	Heating rate, °C/min	Activation energy value, kJ/mol
NiO+WO ₃ +4Mg	2.5-20	152
NiO+WO ₃ +3C	2.5-20	232
NiO+WO ₃ +Mg+2C	2.5-20	149
NiO+WO ₃ +4Mg	300-1200	146±10
NiO+WO ₃ +2.5Mg+1.5C	300-1200	141±10
NiWO ₄ +4Mg	300-1200	216±10
NiWO ₄ +2.5Mg+1.5C	300-1200	148±10

The mechanism and kinetics of tungsten and nickel oxides joint reduction (as well as NiWO₄) by Mg+C combined reducer were also studied at high heating rates (up to 1200 °C/min: closer to the heating rates in combustion wave).

Figure 11 depicts the heating curves of the reduction processes of (NiO+WO₃) mixture (a) and NiWO₄ (b) by combined (Mg+C) reducers at $V_h=300$ °C/min. In both cases the interaction starts after the melting of Mg and proceeds by a solid+liquid mechanism.

It was revealed that complete reduction of NiWO₄ takes place at 1000 °C, while in the case of oxides mixture only the nickel oxide completely reduced, but the complete reduction of WO₃ was not achieved at the studied temperature range (up to 1300 °C).

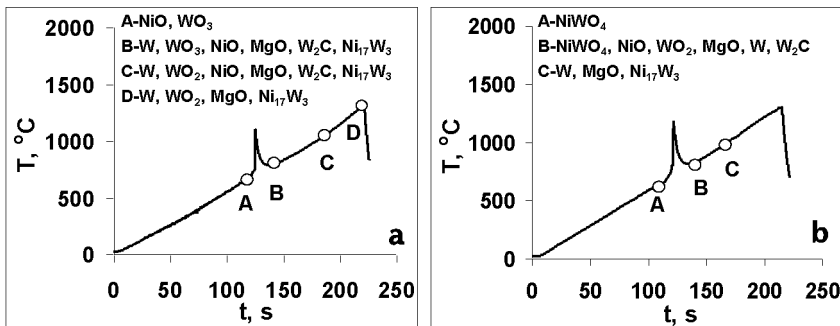


Fig. 11. Heating curves of the NiO+WO₃+2.5Mg+1.5C (a; A-725, B-800, C-1060, D-1300 °C) and NiWO₄+2.5Mg+1.5C (b; A-720, B-830, C-1000 °C) mixtures, $V_h=300$ °C/min

Thus, by combining the results obtained, it can be proved, that the reduction reactions of NiWO₄ by Mg and (Mg+C) combined reducer started earlier and it was possible to achieve complete reduction at comparatively lower temperatures compared to the (NiO+WO₃) mixture. In addition, the magnesio-carbothermal reduction reactions of nickel and tungsten

oxides and nickel tungstate began by ~20 and 30 °C earlier, than magnesiothermal ones and about ~300 and 370 °C earlier, than carbothermal processes, evidencing on the synergetic effect at utilization of combined reducers in the ternary and quaternary mixtures.

To reveal the influence of the heating rate on the interaction mechanism, HSTS studies were performed in a wide range of heating rates (100-1200 °C/min). An increase in heating rate shifts the exothermic peaks of magnesiothermal reduction to the higher temperature zones. Using the temperature data of exothermic peak's maximum deviation at different heating rates, the values of the effective activation energies for magnesiothermal reduction stages are calculated by Kissinger's method (Table 1).

The heating rate has a decisive effect not only on the interaction pathway, but also on the reduction degree. XRD analysis of the products of the NiO+WO₃+1.5Mg+2.5C mixture heated at 100 °C/min and higher (300-1200 °C/min) revealed that at 100 °C/min heating rate the reaction proceeded completely. When the heating rate is 300 °C/min or higher and heating continues to 1300 °C without holding at the maximum temperature, then complete reduction of oxides does not take place, and partially reduced WO₂ remains in the products.

Chapter 5. Preparation of W-Ag pseudoalloys by magnesio-carbothermal reduction of tungsten oxide-silver mixture and silver tungstate

In this chapter a new pathway for the preparation of W-Ag composite nanopowder by energy-saving combustion synthesis using reactions thermo-kinetic coupling approach is reported. Silver tungstate (prepared by chemical precipitation) and Ag+WO₃ (prepared by SCS) were used as initial precursors.

In Figure 12, combustion thermogram (a) and XRD pattern (b) of the SCS product are depicted.

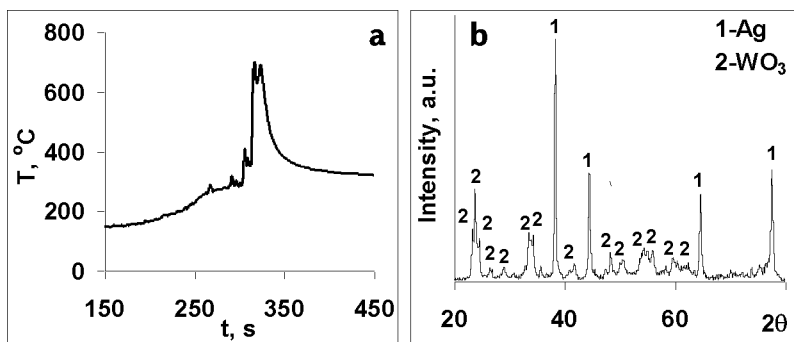


Fig. 12. Combustion thermogram of $(\text{NH}_4)_{10}(\text{H}_2\text{W}_{12}\text{O}_{42}) \cdot 4\text{H}_2\text{O} + 12\text{AgNO}_3 + 8\text{C}_6\text{H}_8\text{O}_7 + 25\text{NH}_4\text{NO}_3$ mixture (a) and diffractogram of as-received product (b)

Figure 13 represents XRD pattern (a) and SEM images (b, c) of the chemically precipitated $\alpha\text{-Ag}_2\text{WO}_4$. Microstructural examinations reveal that the final product possesses fine-grained rod-like particles.

It was established that the reduction of Ag+WO₃ mixture and silver tungstate under the combustion mode using Mg+C combined reducer (Ag-WO₃-yMg-xC; Ag₂WO₄-yMg-xC) enables the preparation of target W-Ag composite powders with high-purity under moderate thermal conditions.

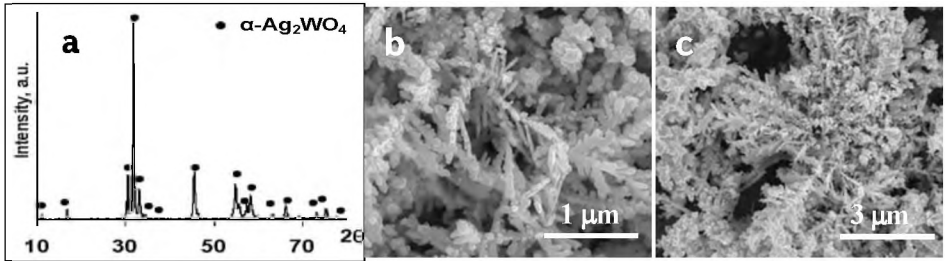


Fig. 13. XRD pattern (a) and SEM images (b, c) of the chemically precipitated Ag₂WO₄

The target W-Ag pseudoalloy (purified from magnesia) represented a porous powder with 20-30 nm particulates. The synthesized W-Ag powders were consolidated by SPS (T=1020 °C, P=50 MPa, dwell time=3 min) yielding a compact sample with 92 % relative density and excellent homogeneity (Fig. 14). The Vickers microhardness measured for this sample was 180±10 kg/mm² being in the same order with the ones reported in literature (prepared by blend sintering method; 165 kg/mm²).

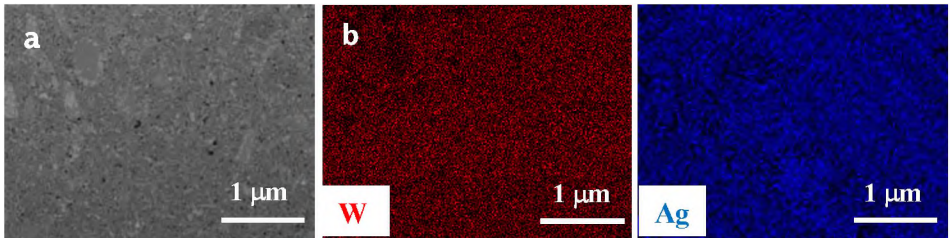


Fig. 14. SEM image (a) and EDS mapping (b) of the acid treated combustion product (W-Ag) after SPS consolidation

The mechanism for silver tungstate reduction with combined (Mg+C) reducer (Ag₂WO₄-xMg-yC) was studied under linear heating conditions both at low ($V_h=2.5-30^\circ\text{C}/\text{min}$) and high heating rates (100-1200 °C/min⁻¹).

At low heating rates for both the cases using separate reducing agents and a combined reducer, the reaction began before the reaching melting point of magnesium. An increased heating rate shifted the value of T_{max} towards the high-temperature region (Fig. 15b).

It was revealed that the magnesio-carbothermal reduction of silver tungstate by carbon starts at 410 °C, followed by simultaneous reduction by magnesium and carbon at 640 °C ($V_h=10^\circ\text{C}/\text{min}$). The reaction starts with a solid+solid interaction and proceeds transfers to into a solid+liquid mechanism (Fig. 15a).

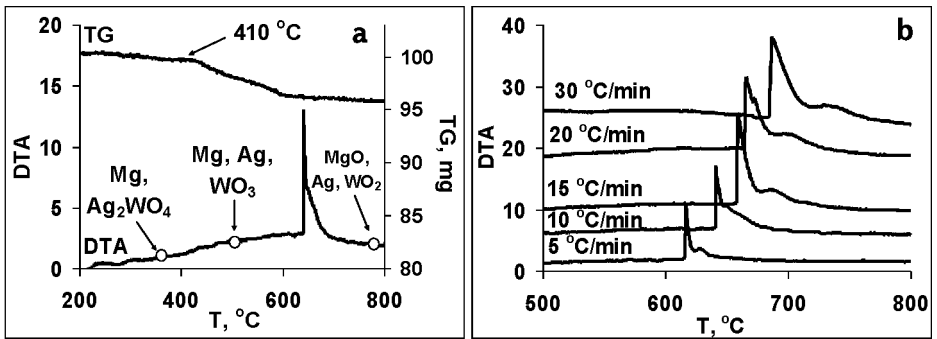


Fig. 15. DTA and TG curves of the $\text{Ag}_2\text{WO}_4+2\text{Mg}+2\text{C}$ mixture, $V_h=10^\circ\text{C}/\text{min}$ (a) and DTA curves of the $\text{Ag}_2\text{WO}_4+2\text{Mg}+2\text{C}$ mixture at various heating rates, $V_h=5-30^\circ\text{C}/\text{min}$ (b)

The effective values of activation energy (E_a) for the magnesiothermal reduction stages for binary ($\text{Ag}_2\text{WO}_4\text{-Mg}$) and ternary ($\text{Ag}_2\text{WO}_4\text{-Mg-C}$) systems were determined (Table 1). In the case of high heating rates (HSTS technique) a weak exothermic effect was observed in the heating curve of the $\text{Ag}_2\text{WO}_4+2\text{Mg}+2\text{C}$ mixture ($300^\circ\text{C}/\text{min}$) between $450-670^\circ\text{C}$, followed by the strongly expressed exothermic (magnesiothermal) reaction (Fig. 16a).

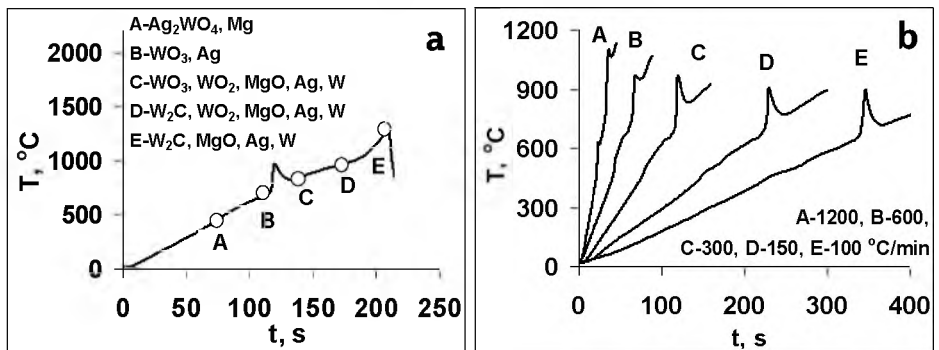


Fig. 16. Heating curve of the $\text{Ag}_2\text{WO}_4+2\text{Mg}+2\text{C}$ mixture at $300^\circ\text{C}/\text{min}$ (a) and heating thermograms for various heating rates, $V_h=100, 150, 300, 600, 1200^\circ\text{C}/\text{min}$ (b)

According to XRD analyses, the reduction process in $\text{Ag}_2\text{WO}_4+2\text{Mg}+2\text{C}$ mixture starts with carbon; the weak exothermal domain observed between $450-670^\circ\text{C}$ corresponds to the carbothermal reduction reaction of silver. The second exothermic peak corresponds to the magnesiothermal reduction of tungsten.

From Figure 16b, when switching to a higher heating rate, the exothermal peaks of the interaction deviate to a higher temperature range allowing to determine effective E_a values by the Kissinger method (Table 2).

Table 2. Activation energy values for the reactions (Ag & W containing systems)

Reaction	Heating rate, °C/min	Activation energy value, kJ/mol
$\text{Ag}_2\text{WO}_4+4\text{Mg}$ (I stage)	2.5-20	58
$\text{Ag}_2\text{WO}_4+4\text{Mg}$ (II stage)	2.5-20	36
$\text{Ag}_2\text{WO}_4+2\text{Mg}+2\text{C}$	2.5-20	39
$\text{Ag}_2\text{WO}_4+4\text{Mg}$	300-1200	119 ± 10
$\text{Ag}_2\text{WO}_4+2\text{Mg}+2\text{C}$	300-1200	77 ± 10

The calculations reveal that there is a difference in effective activation energy values at low ($V_h=2.5-30$ °C/min) and high ($V_h=100-1200$ °C/min) heating rates, which may be caused by the fact that in contrast to high heating rates, at low heating rates the magnesiothermal reduction reaction begins before the melting point of magnesium and proceeds by solid+solid mechanism.

Conclusion

1. Based on the principle of thermo-kinetic coupling of combustion reactions and the use of a combined reducing agent (Mg+C), it became possible to organize the reduction of oxygenous compounds of tungsten, copper, nickel and silver at moderate and controlled temperatures and synthesize W-Me(Cu, Ni, Ag) nanocomposite materials with a particle size of 10-50 nm.
2. It was shown that the use of salts (copper, nickel and silver tungstates) in comparison with oxides, increases the homogeneity of metals' distribution in the target material, reducing residual porosity in SPS consolidated samples.
3. It was revealed that the alloys obtained from SCS derived tungstates are more fine-grained (10-30 nm) and beneficial for further consolidation process.
4. It is shown that both at low and high heating rates, the reduction of oxygenous compounds by (Mg+C) combined reducer takes place at a significantly lower temperature, compared to the reduction process with solely by magnesium or carbon, evidencing on the synergetic effect at utilization of combined reducer.
5. The increase of the heating rate in the $\text{WO}_3\text{-NiO-Mg-C}$, $\text{NiWO}_4\text{-Mg-C}$, $\text{WO}_3\text{-Ag-Mg-C}$, $\text{Ag}_2\text{WO}_4\text{-Mg-C}$ systems, shifts the reduction stages to the higher temperature area, which makes it possible to identify the mechanism of multistage reactions.
6. For the first time the values of the effective activation energy of a number of magnesiothermal and carbothermal reduction reactions have been determined.

The main results of the dissertation were published in the following works

Articles:

1. **M.K. Zakaryan**, A.S. Arzumanyan, S.L. Kharatyan, Magnesium-Carbothermic Reduction of Ag_2WO_4 . DTA/TG Study, Chemical Journal of Armenia, 2020, vol. 73, No. 4, in Press
2. **M.K. Zakaryan**, Kh.T. Nazaretyan, S.V. Aydinyan, S.L. Kharatyan, NiO reduction by Mg+C combined reducer at high heating rates, Journal of Thermal Analysis and Calorimetry, 2020, <https://doi.org/10.1007/s10973-020-10148-5>
3. **M.K. Zakaryan**, Reduction of Silver Tungstate in Combustion Mode and Synthesis of W-Ag Pseudoalloy, Chemical Journal of Armenia, 2019, vol. 72, No. 4, pp. 401-408
4. **M.K. Zakaryan**, O.M. Niazyan, S.V. Aydinyan, S.L. Kharatyan, Reaction Pathway in the WO_3 -NiO-Mg-C System. DTA/TG Study, Chemical Journal of Armenia, 2019, vol. 72, No. 3, pp. 223-232
5. **Marieta Zakaryan**, Sofiya Aydinyan, Suren Kharatyan, Combustion Synthesis and Consolidation of Ni-W Nanocomposite Material, Ceramics in Modern Technologies, 2019, vol. 1, pp. 67-74
6. **M.K. Zakaryan**, O.M. Niazyan, S.V. Aydinyan, S.L. Kharatyan, DTA/TG Study of NiO Reduction by Mg+C Combined Reducer, Chemical Journal of Armenia, 2018, vol. 71, No. 4, pp. 473-485
7. S.V. Aydinyan, H.V. Kirakosyan, **M.K. Zakaryan**, L.S. Abovyan, S.L. Kharatyan, A. Peikrishvili, G. Mamniashvili, B. Godbadze, E.Sh. Chagelishvili, D.R. Lesuer, M. Gutierrez, Fabrication of Cu-W Nanocomposites by Integration of Self-propagating High-temperature Synthesis and Hot Explosive Consolidation Technologies, Eurasian Chemico-Technological Journal, 2018, vol. 20, pp. 301-309
8. **M.K. Zakaryan**, H.V. Kirakosyan, L.S. Abovyan, S.V. Aydinyan, S.L. Kharatyan, Magnesium-Carbothermal Reduction of CuWO_4/MeO Nanostructured Precursors & Synthesis of W/Cu Composite Materials, Chemical Journal of Armenia, 2017, vol. 70, No. 4, pp. 450-461
9. **M. Zakaryan**, H. Kirakosyan, S. Aydinyan, S. Kharatyan, Combustion synthesis of W-Cu composite powders from oxide precursors with various proportions of metals, International Journal of Refractory Metals and Hard Materials, 2017, vol. 64, pp. 176-183

Theses:

1. **M.K. Zakaryan**, A.A. Baldryan, S.L. Kharatyan, Preparation of W-Ag pseudoalloys by combining SHS with SCS, VI Scientific Conference of Armenian Chemical Society, October 7-12, 2019, Yerevan, Armenia, pp. 81
2. **M.K. Zakaryan**, Kh.T. Nazaretyan, S.V. Aydinyan, S.L. Kharatyan, Joint Reduction of $\text{NiO}+\text{WO}_3$ Oxides by Combined Mg/C Reducer. Synergetic Effect, XV International

Symposium on Self-Propagating High Temperature Synthesis, September 16-20, 2019, Moscow, Russia, pp. 546-548, DOI: 10.24411/9999-0014A-2019-10198

3. **M.K. Zakaryan**, A.A. Baldryan, S.L. Kharatyan, W-Ag Nanocomposite Preparation by Combining SCS and SHS, XV International Symposium on Self-Propagating High Temperature Synthesis, September 16-20, 2019, Moscow, Russia, pp. 543-545, DOI: 10.24411/9999-0014A-2019-10197

4. **M.K. Zakaryan**, A.S. Grigoryan, A.A. Hovhannisyan, S.L. Kharatyan, Combustion Synthesis of Ni-W Composite Powders by Using Nickel Tungstate as a Precursor, V International Conference "Current Problems of Chemical Physics", 25-29 September, 2018, Yerevan, Armenia, pp. 158-159

5. **M.K. Zakaryan**, Kh.T. Nazaretyan, O.M. Niazyan, S.L. Kharatyan, Kinetics of Nickel Oxide Reduction by Mg/C Combined Reducer at Non-Isothermal Conditions, V International Conference "Current Problems of Chemical Physics", 25-29 September, 2018, Yerevan, Armenia, pp. 78-79

6. **M.K. Zakaryan**, S.V. Aydinyan, S.L. Kharatyan, Synthesis of Ni-W Nanopowders from Oxide and Salt Precursors in Combustion Mode by Using Thermo-Kinetic Coupling Approach, XIV International Symposium on Explosive Production of New Materials: Science, Technology, Business and Innovations (EPNM-2018), 14-18 May, 2018, St. Petersburg, Russia, pp. 298-300, DOI: 10.30826/EPNM18-103

7. **M.K. Zakaryan**, L.S. Abovyan, H.V. Kirakosyan, S.V. Aydinyan, S.L. Kharatyan, Combustion Synthesis of W/Cu Nanopowders from $\text{CuWO}_4/\text{WO}_3$ & CuWO_4/CuO Precursors Derived by SCS Method, ArmCS-5: "Actual Problems of Fundamental and Applied Chemistry", 3-7 October, 2017, Yerevan, Armenia, pp. 110

8. **M.K. Zakaryan**, S.L. Kharatyan, Combustion Synthesis of Ni-W Composite Nanopowders from Oxide Precursors, XIV International Symposium on Self-Propagating High Temperature Synthesis, September 25-28, 2017, Tbilisi, Georgia, pp. 318-319

9. **M.K. Zakaryan**, H.V. Kirakosyan, S.V. Aydinyan, S.L. Kharatyan, B.A. Godibadze, G.I. Mamniashvili, A.B. Peikrishvili, Combustion Synthesis of 2W-Cu & W-3Cu Composite Nanopowders from Oxide Precursors, Chemistry Today-2016, 5-th International Conference of Young Scientists, September 18-21, 2016, Tbilisi, Georgia, pp. 20-23

ՀԱՔԱՐՅԱՆ ՄԱՐԻԵՏԱ ԿԱՐԵՆԻ

ՄԻ ՇԱՐՔ ՄԵՏԱՂՆԵՐԻ ԹԹՎԱԾՆԱՎՈՐ ՄԻԱՑՈՒԹՅՈՒՆՆԵՐԻ ՄԱԳՆԵԶԻՈՒՄԱ-ԿԱՐԲՈԹԵՐՄ ՎԵՐԱԿԱՆԳՆՈՒՄՆ ԱՅՐՄԱՆ ՌԵԺԻՄՈՒՄ ԵՎ W-Me (Cu, Ni, Ag) ՀԱՄԱՁՈՒԿԱԾՔՆԵՐԻ ՍԻՆԹԵԶԸ

ԱՄՓՈՓԱԳԻՐ

Աշխատանքը նվիրված է այրման ռեժիմում (Mg+C) համակցված վերականգնիչով վոլֆրամի, պղնձի, նիկելի և արծաթի թթվածնավոր միացությունների միափուլ վերականգնման պրոցեսների ուսումնասիրմանը ղեկավարվող այրման պրոցեսների միջոցով և վոլֆրամ-պղնձ (W-Cu), վոլֆրամ-նիկել (W-Ni), վոլֆրամ-արծաթ (W-Ag) կոմպոզիտային նյութերի նուրբ փոշիների ստացմանը:

Ֆունկցիոնալ և կառուցվածքային հատկությունների (մեծ հարաբերական խտություն, կարծրություն և առաձգական ամրություն, բարձր դիմադրողականություն, մաշակայունություն, ճկունություն և այլն) արժեքավոր համադրմամբ բնութագրվող W-Cu, W-Ni և W-Ag կոմպոզիտային նյութերի նկատմամբ աճող հետաքրքրությունը պայմանավորված է մի շարք առաջատար ոլորտներում (կիսահաղորդչային և հզոր էլեկտրոնային սարքերի, պաշտպանիչ վահանակների և եռակցման էլեկտրոդների, միկրոէլեկտրոնային սարքավորումների արտադրություն և այլն) վերջիններիս արդյունավետ կիրառմամբ: Ուստի, անընդհատ աճող մեծ պահանջարկն անհրաժեշտություն է ստեղծում կատարելագործելու այս նյութերի ստացման տեխնոլոգիան և մշակելու նոր, առավել արդյունավետ ու տնտեսապես շահավետ մոտեցումներ:

Հաշվի առնելով ղեկավարելի կառուցվածքով և հատիկների համասեռ բաշխվածությամբ նանոփոշիների ստացման հետ կապված դժվարությունները (աշխատատարություն, մեծ էներգաձախսեր, բազմափուլ պրոցեսներ, փոքր արտադրողականություն), առաջարկվում է ստացման միափուլ in-situ պրոցես, որի համար ավանդական եղանակում կիրառվող մետաղափոշիների փոխարեն օգտագործվում են մետաղների օքսիդների և/կամ աղերի խառնուրդ՝ որպես առավել մատչելի ելանյութեր: Դրված խնդիրը լուծելու համար առաջարկվում է բարձր ջերմաստիճանային ինքնատարածվող սինթեզի (ԲԻՍ) միջոցով, կիրառելով ռեակցիաների ջերմ-կինետիկական զուգորդման մոտեցումները, կառավարել այրման պրոցեսի պարամետրերը և կարգավորել ստացվող նյութի փոշու հատիկի չափսը, մետաղների բաշխման աստիճանը: Այրման պրոցեսի պայմանների և նպատակային արգասիքների բնութագրերի կառավարման հնարավորությունը կարևորվում է բարձր հարաբերական խտությամբ և բարելավված մեխանիկական հատկություններով կոմպակտ նմուշների ստացման համար:

Իրականացված հետազոտություններից ստացվել են հետևյալ հիմնական արդյունքները՝

- Ելնելով այրման ռեակցիաների ջերմ-կինետիկական զուգորդման սկզբունքից և օգտագործելով (Mg+C) համակցված վերականգնիչ՝ վոլֆրամի, պղնձի, նիկելի և արծաթի թթվածնավոր միացությունների վերականգնման պրոցեսը կազմակերպվել է

մեղմ ու կառավարելի ջերմաստիճանային պայմաններում և սինթեզվել 10-50 նմ մասնիկի չափս ունեցող W-Me (Cu, Ag, Ni) նանոկոմպոզիտային նյութեր:

- Պղնձի, նիկելի և արծաթի վոլֆրամատների կիրառումը, ի համեմատ օքսիդների, նպաստել է նպատակային նյութում մետաղների բաշխման համասեռության մեծացմանը և էլեկտրակայծային եռակավման եղանակով ստացված կոմպակտ նմուշի մնացորդային ծակոտկենության զգալի նվազմանը:
- ԼԱՍ եղանակով սինթեզված վոլֆրամատներից ստացված համաձուլվածքները առավել մանրահատիկ են (10-30 նմ) և շահեկան հետագա կոմպակտավորման համար:
- Եվ՝ դանդաղ, և՛ արագ տաքացման պայմաններում ելային թթվածնավոր միացությունների վերականգնումը (Mg+C) համակցված վերականգնիչով տեղի է ունենում զգալիորեն ավելի ցածր ջերմաստիճանում՝ ի համեմատ առանձին վերականգնիչներով վերականգնման պրոցեսի, ինչը վկայում է արտահայտված սինթեզետիկական էֆեկտի մասին:
- WO_3 -NiO-Mg-C, $NiWO_4$ -Mg-C, WO_3 -Ag-Mg-C, Ag_2WO_4 -Mg-C համակարգերում տաքացման արագության մեծացմանը զուգընթաց տեղի է ունենում ռեակցիայի փուլերի տեղաշարժ դեպի բարձրջերմաստիճանային տիրույթ, ինչը թույլ է տվել բացահայտել բազմափուլ ռեակցիաների մեխանիզմը:
- Առաջին անգամ որոշվել են մի շարք մագնեզիումաթերմ և կարբոթերմ ռեակցիաների էֆեկտիվ ակտիվացման էներգիայի արժեքները դանդաղ և արագ տաքացման պայմաններում:

ЗАКАРЯН МАРИЕТА КАРЕНОВНА

МАГНИЙ-КАРБОТЕРМИЧЕСКОЕ ВОССТАНОВЛЕНИЕ КИСЛОРОДНЫХ СОЕДИНЕНИЙ РЯДА МЕТАЛЛОВ В РЕЖИМЕ ГОРЕНИЯ И СИНТЕЗ W-Me (Cu, Ni, Ag) СПЛАВОВ

РЕЗЮМЕ

Работа посвящена изучению процессов восстановления кислородных соединений вольфрама, меди, никеля и серебра в режиме горения с применением (Mg+C) комбинированного восстановителя и получения тонких порошков композитных материалов вольфрам-медь (W-Cu), вольфрам-никель (W-Ni) и вольфрам-серебро (W-Ag) для дальнейшего электроискрового компактирования.

Растущий интерес к композиционным материалам W-Cu, W-Ni и W-Ag, которые характеризуются ценным сочетанием функциональных и структурных свойств (высокая относительная плотность, твердость и эластичность, превосходная стойкость к истиранию, износостойкость, гибкость и т.д.), обусловлен эффективным использованием этих материалов в ряде ведущих областей (полупроводниковая техника, производство мощных электронных устройств и защитных панелей, сварочные электроды, микроэлектронные оборудования и др.). Растущий спрос

порождает необходимость совершенствования технологии получения этих материалов, разработки новых, более эффективных и экономичных подходов. Учитывая трудности, связанные с получением нанопорошков с однородной, управляемой структурой, необходимой чистотой и распределением зерен (трудоемкость, высокие затраты энергии, многоступенчатые процессы, низкая производительность), предлагается одноэтапный *in-situ* процесс производства, для которого вместо металлических порошков, используемых в традиционном методе, в качестве наиболее доступных исходных материалов можно использовать смесь оксидов металлов и/или солей.

Для решения поставленной задачи предлагается с применением самораспространяющегося высокотемпературного синтеза (СВС) и использованием термо-кинетического сопряжения реакций, управлять параметрами процесса горения, регулировать размер частиц и степень распределения металлов в получаемом материале. Возможность управления характеристическими параметрами целевых материалов используется для получения компактных образцов с высокой относительной плотностью и улучшенными механическими свойствами.

В результате проведенных исследований были получены следующие основные результаты:

- На основе принципа термо-кинетического сопряжения реакций горения и использования комбинированного восстановителя ($Mg+C$), процесс восстановления кислородных соединений вольфрама, меди, никеля и серебра реализован при умеренных и контролируемых температурах горения, и синтезированы нанокompозитные материалы $W-Me$ (Cu, Ag, Ni) с размером частиц 10-50 нм.
- Использование солей ($CuWO_4, NiWO_4, Ag_2WO_4$), по сравнению с оксидами, увеличивает однородность распределения металлов в целевом материале, и способствует уменьшению остаточной пористости в консолидированных образцах.
- Сплавы, полученные из вольфрамов меди, никеля и серебра, синтезированных методом горения раствора, более мелкозернистые (10-30 нм) и эффективны для дальнейшего уплотнения.
- Как в условиях медленного, так и при быстром нагревании восстановление кислородных соединений с помощью ($Mg+C$) комбинированного восстановителя происходит при значительно более низких температурах по сравнению с процессом восстановления с отдельными восстановителями, что указывает на выраженный синергетический эффект.
- В системах $WO_3-NiO-Mg-C, NiWO_4-Mg-C, WO_3-Ag-Mg-C, Ag_2WO_4-Mg-C$ по мере увеличения скорости нагрева отдельные стадии реакций смещаются в высокотемпературный диапазон, что позволяет выявить механизм многостадийных реакций.
- Впервые определены эффективные значения энергии активации ряда магнийтермических и карботермических реакций восстановления оксидных соединений вольфрама, меди, никеля и серебра в условиях медленного и быстрого нагрева.