Combustion Synthesis and Consolidation of Ni-W Nanocomposite Material

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Ni-W nanocomposite material was synthesized by self-propagating high temperature synthesis method from the NiO-WO\textsubscript{3} oxides mixture using Mg+C combined reducers via thermo-kinetic coupling approach. Thermodynamic modeling was performed to design combustion synthesis in the NiO-WO\textsubscript{3}-yMg-xC system to find optimum values for x and y in a moderate temperature conditions. Combustion peculiarities and reduction mechanism were explored using copper wedge technique combined with XRD analysis of the quenched products disclosing the preferential participation of magnesium rather than carbon in the primary stage of reduction process. The obtained Ni-W nanocomposite material with up to 50 nm average particle size subjected to spark plasma sintering exhibited high relative density and improved microhardness.

Keywords: Ni-W nanocomposite, Combustion synthesis, Oxide precursor, Thermo-kinetic coupling, Spark plasma sintering.

1. Introduction

The fortuitous discovery in 1907-1909 conveys the situation of early days of nickel-tungsten powder metallurgy which has formed the basis for a manufacturing process of the first Ni-W alloys composed from the mixture of 90 to 94\% fine tungsten powder and 10 to 6\% nickel powder [1]. The content/ratio of particles in the alloy fundamentally affects its properties which are controlled not only by the content of incorporated particles, but also by the hardness of the matrix [2]. By the incorporation of tungsten into nickel the refinement of nanocrystalline structure occurs promoting the hardness, lubricity, wear and corrosion properties of the sintered bodies and coatings [3,4]. These composites exhibit a unique combination of high strength, dumping capability, good conductivity and relatively high ductility making them attractive for radiation shields, welding electrodes, armour penetrators, as electrocatalysts for hydrogen evolution and substrate of superconducting materials [5-10]. Future applications of Ni-W crystalline and amorphous alloys (13-76 wt.\% W) include microelectromechanical systems, magnetic heads and relays, environmentally safe substitutes for hard chromium plates [11-13]. The advantage of tungsten composites is the combination of radiographic density, machinability, good corrosion resistance, high radiation absorption, and, what is always emphasized, lack of toxicity [14-15]. It is already reported that tungsten-nickel alloys might be obtained by joint reduction of their oxides [16-19] under heating in a hydrogen atmosphere or by carbon monoxide [20]. Rodriguez et al. [21], Mangnus et al. [22], Richardson et al. [23] and Okamoto et al. [24] studied the kinetics and the mechanism of tungsten and nickel oxides reaction with $\text{H}_2$.

It is well known that refractory metal containing alloys are difficult to prepare by conventional methods due to large differences in melting points and limited mutual solubility [25]. The ductility and strength of tungsten composites strongly depend on their microstructure, which in turn can be controlled by trace impurity content and thermal conditions of the synthesis procedure. The use of low-cost and convenient preparation technique of powders may expand and addresses the major challenge of achieving high levels of homogeneity of particles. Hence, self-propagating high-temperature synthesis (SHS) [26-27] as a simple, cheap technique with controllable temperature conditions can be proposed as an alternative method for the production of Ni-W composite powders. To prepare the W-Ni alloy by a controllable temperature route, namely by the reduction of oxide precursors, we proposed in-situ preparation of Ni-W composite powders in combustion mode by applying reaction’s coupling approach [28-29]. Such a technique was already proven to provide very fine, nano and submicron powders of W-Cu, Mo-Cu composite materials [30-33]. In this research combustion peculiarities of NiO-WO\textsubscript{3}-yMg-xC system were disclosed and Ni-W composite powder was prepared from the oxide precursors by means of Mg-C reducing mixture.

2. Experimental

2.1. Materials and methods

The following raw materials were used in experiments: tungsten (VI) oxide (Pobedit Company, Russia, pure, high grade, $\mu < 40$ µm), nickel (II) oxide (pure), magnesium (MPF-3, Russia, pure, particle size $0.15 \text{ mm} < \mu < 0.3 \text{ mm}$), carbon (P-803, Russia, $\mu < 0.1$ µm).

The mixture of initial materials was homogenized in a ceramic mortar for 10 minutes and cylindrical samples with 1.5-2.5 g cm$^{-3}$
density. 30-50 mm height and 20 mm in diameter were prepared. The prepared samples were placed in a reaction chamber CPR-3l which was sealed, evacuated, purged with nitrogen (purity 99.97%, oxygen content less than 0.02%) and filled to the desired pressure (0.1-1.0 MPa). The combustion process was initiated with short heating of tungsten spiral (18 V, 2 s) from the upper surface of the sample. Combustion temperatures (Tc) and combustion velocity (Uc) were measured using two C-type tungsten-rhenium thermocouples, each 100 µm in diameter (W-5Re/W-20Re). The thermocouples were inserted into the sample at a depth of 10 mm with a distance 15 mm between each other. The standard measurement errors for Tc and Uc were ± 20 °C and 5% respectively. The output signals of thermocouples were transformed by a multichannel acquisition system and recorded by a computer with up to 2 KHz frequency. The average of maxima for two temperature profiles was calculated as the combustion temperature (Tc). The average value of combustion velocity is calculated by the following formula: 

\[ U_c = \frac{L}{D_{t} - 1} \]

where L is the distance between the thermocouples, Δt is time distance between the signals of thermocouples.

Phase compositions of the samples were analyzed by X-ray diffraction (XRD; D5005, Bruker, USA) using CuKα radiation (λ = 1.5406 Å) with a step of 0.02° (2θ) and a count time of 0.4 s. To identify the products from the XRD spectra, the data were processed using the JCPDS database. Morphologies and microstructures of the samples were examined by high-resolution scanning electron microscope (HR-SEM Zeiss Merlin) at an accelerating voltage of 2 kV. HR-SEM was equipped with an In-Lens SE detector for topographic imaging and In-Lens energy selective backscattered detector for compositional contrast. The gaseous products were analyzed by gas-chromatography (LKHM-72 apparatus). The obtained powders were subjected to a high energy ball milling with a ball/composite weight ratio of 4:1 for 60 min and consolidated using spark plasma sintering technique (SPS furnace combined with KCE®-FCT HP D 10-GB equipment by FCT System GmbH (Rauenstein, Germany) in vacuum at temperature of 950-1350°C with simultaneous application of 50-100 MPa pressure for a dwell time of 3 to 10 min. The powder was loaded into a 10-20 mm inner diameter graphite die with a sheet of graphitic paper placed between the punch and the powder and heated up to sintering temperature with a heating rate of 100 to 200°·min⁻¹. The Vickers microhardness (HV) was measured on the polished surface using hardness tester Indentec 5030 SKV applying 1 kgf force for 10 s.

2.2. Thermodynamic consideration

Thermodynamic calculations were performed for the NiO-WO3-yMgyxC system to find out optimum conditions for joint and complete reduction of nickel and tungsten oxides by using “ISMAN-THERMO” software package [34]. The latter enables to calculate adiabatic combustion temperature (Tad) and equilibrium composition of combustion products. As a result, corresponding phase diagram was constructed depending on magnesium and carbon amounts (Fig. 1). As it can be seen there are different areas of products formation depending on the amount of magnesium and carbon. The formation of target product is achievable in a definite area of magnesium (from 1.7 to 2.2 moles) and carbon (from 1.6 to 2.3 moles) amounts (cross marked on the Fig. 1): at that adiabatic temperature makes 1000-2000 °C. It is worthy to note, that thermodynamic calculations were performed with excluding the possible formation of WC and W2C carbides. The latter is based on the results of [35-36], where it was shown, that at least 1700 °C and more is necessary to form considerable amount of tungsten carbides when duration of interaction is less than few seconds (comparable with characteristic time of combustion wave propagation). Preliminary experiments confirmed this hypothesis and showed that metals reduction seems possible at lower temperature region of cross marked area. According to thermodynamic calculations, within the whole interval of reducers’ amount the main gaseous products are CO and CO2. At that the ratio of carbon oxides depends on the temperature and with the increasing of temperature CO ↔ CO2 equilibrium shifts to the side of CO formation. Moreover, at high amounts of magnesium (high temperatures), gaseous Mg, WO2 and (WO3)n are present too.

The main calculations were carried out for pressure 0.5 MPa which was found as optimum for complete and joint reduction of tungsten and nickel oxides without evaporation of Mg and tungsten oxides.

2.3. Combustion laws

Based on the results of thermodynamic consideration, firstly the amount of strong reducer-magnesium was chosen (1.7-1.8...
mol). The choice was based on the preference of implementing the combustion synthesis and providing complete reduction at comparatively moderate temperatures. Then, to find out the optimum NiO+WO₃+yMg+xC composition for preparing Ni-W alloy and to reveal the effect of carbon amount on the combustion parameters (combustion temperature and combustion wave propagating velocity), magnesio-carbothermic co-reduction of tungsten and nickel oxides was performed with changing carbon amount within certain interval.

In Figure 2 are presented combustion thermograms for NiO+WO₃+1.8Mg+2C mixture, on the basis of which combustion temperature and velocity were determined. According to the results obtained the increase of carbon amount leads to a decrease the combustion temperature and velocity conditioned by growth of portion of low-caloric carbothermal reactions in the system (Fig. 3).

As it can be seen from the Figure 3, with the increase of carbon amount from 0 to 3, the combustion velocity decreases from 0.73 to 0.10 cm·s⁻¹. Simultaneously, a significant decline is registered for the combustion temperature (from 2100 °C up to 1250 °C). The initial comparatively fast decrease of U_c (from 0.73 to 0.3 cm·s⁻¹) stipulated by the addition of small amount of carbon (0.5 mol) can be explained by the following: at x = 0 combustion temperature (2100 °C) exceeds the melting point of NiO (T_m = 1955 °C), while at x > 0.5 it’s lower (T_c < 1850 °C). This means, that at x = 0, the reduction reaction occurs with melted NiO and at x > 0.5 with solid NiO, which can significantly decrease the combustion velocity.

According to reaction scheme:

\[
\text{NiO} + \text{WO}_3 + y\text{Mg} + x\text{C} \rightarrow \text{Ni} + \text{W} + \text{MgO} + \text{CO/CO}_2
\]

the interaction is accompanied by mass loss due to formation of gaseous products. In the Figure 4 the experimental and calculated mass losses for the NiO-WO₃-1.8Mg-xC system vs carbon amount are illustrated. Note that the experimental mass losses were estimated by weight measurements of samples before and after SHS, and theoretical ones - from thermodynamic calculations by “ISMAN THERMO” software package. In the case of carbon amount up to 1 mol, it is evident that the experimental mass loss is higher than the calculated one by 10-12 %. In the case of more amount of carbon (> 1 mol) the difference between experimental and calculated data was reduced up to 3-4%. This fact may be caused by incomplete conversion of reagents and the mismatch of experimental and calculated compositions of combustion products. Besides, at small amounts of carbon by the fact of high combustion temperature the release of mechanical emissions of solid components can be high too.

To determine the composition of gaseous products gas-chromatography analysis was conducted. It was found that at combustion of WO₃+NiO+1.8Mg+1.9C mixture the CO/CO₂ molar ratio is 4.7 and T_c=1380 °C. At that the calculated value of the CO/CO₂ molar ratio for the same mixture is about 5.3. Then the reaction can be presented by the following equation:

\[
\text{NiO} + \text{WO}_3 + y\text{Mg} + x\text{C} \rightarrow \text{Ni} + \text{W} + \text{MgO} + \text{CO/CO}_2
\]
WO₃ + NiO + 1.8Mg + 1.9C = W + Ni + 1.8MgO + 1.56CO↑ + 0.33CO₂↑

The optimum conditions for the preparation of Ni-W alloys have been determined on the basis of products’ XRD analysis results. The latter showed that the reduction degree increases with the increase of carbon amount (Fig. 5). Besides, XRD studies confirmed that at small amounts of carbon magnesium tungstate forms as undesired byproduct. However, the amount of magnesium tungstate decreases in parallel with the increase of carbon amount and disappears in the combustion products beginning at x = 2.2 moles. As it can be seen from the Figure 5, when the amount of carbon is x = 2.2-3, optimum area was found for the preparation of Ni-W composite powder.

The absence of Ni and NiO in XRD, on the one hand, and the lack of magnetic properties of obtained powder, on the other hand, proves the formation of Ni-W composite powder. As we can see from the Figure 5, besides of Ni₁₋₁₁₇ W₃ alloy, metallic tungsten is detected too.

Similar experiments were performed also with mixtures containing 1.7 mol magnesium (NiO-WO₃-1.7Mg-xC). XRD analyses showed that optimum area for the complete reduction of metals with 1.7 mol Mg becomes possible in a very narrow range of carbon amount (y = 2.15-2.2 mol), in contrast to 1.8 mol of Mg (y = 2.2-3 mol).

It is worthy to note, that the mixtures NiO-WO₃-1.8Mg-xC are able to combust also at relatively high carbon content. It was revealed that at x > 4.5 mol combustion wave propagation behavior is going to the non steady regime, which is not observed in the CuO-WO₃-yMg-xC and CuO-MoO₃-yMg-xC systems [29-32]. In this case the registered thermograms for carbon rich mixtures are essentially differred from thermograms presented in Fig. 2 by their disparate fast cooling nature (Fig. 6).

In the Table 1 experimental parameters of combustion reactions of initial mixtures for both regimes are represented: 1) stationary regime with carbon amount 2.2 mol and 2) non steady regime with carbon amount 5 mol. As it can be seen: a) combustion temperatures differ by 270 °C, b) the dwelling time at maximum temperature for mixture 1 is 2.5 times higher than that for mixture 2, c) heating rate of reagents in combustion wave propagation differ by the factor of ~2, d) cooling rates are differ significantly, about 50 time.

Based on visual observations of combustion wave propagation it is assumed, that in this case we are dealing with spin-combustion mode. Note that this phenomenon is observed in the both mixtures (y = 1.7 & 1.8). Besides, for the NiO-WO₃-1.8Mg-xC and NiO-WO₃-1.7Mg-xC systems at respectively x > 6.25 and x > 6 moles combustion wave does not propagate and therefore combustion limits were observed (Table 2).

For disclosing the influence of ambient gas (N₂) pressure on combustion behaviour, experiments were performed for the optimum composition (WO₃ + CuO + 1.8Mg + 2.2C) at different inert gas pressure (0.1-1 MPa). It was shown that pressure affect on the combustion temperature only at P < 0.2 MPa, meanwhile the combustion wave propagation velocity monotonically decreases about 4 times (Fig. 7).

At pressures of 0.1 and 0.3 MPa the mass loss is about 20% higher than the calculated values, while at higher pressures (from 0.5 up to 1 MPa) the difference between registered and calculated mass change decreases practically 2 times (Fig. 8).

XRD patterns indicate the complete reduction of both Ni and W during combustion at 0.5-1 MPa pressure (part II - W, Ni₁₋₁₁₇ W₃, MgO), while at P < 0.5 MPa combustion process is accompanied also by the formation of magnesium tungstate (part I - W, Ni₁₋₁₁₇ W₃, MgO, MgWO₄). Accordingly, P = 0.5 MPa was chosen as optimal for further studies.
2.4. Characterization of the final product

For removing the byproduct magnesia from target metals the reaction products after cooling were crushed into a powder, subjected to acid treatment by hydrochloric acid \((\omega = 10\%)\) at room temperature, washed with deionized water and dried in vacuum oven \((90^\circ C, 2 \text{ hours})\). According to XRD and SEM analysis results, after acid leaching the product contains only target materials with an average particle size up to 50 nm (Fig. 9, 10).

In the Figure 11 EDS mapping analyses results for the same product are depicted. The blue color corresponds to tungsten phase and the red color to nickel phase illustrating the homogeneous distribution of W and Ni phases throughout the sample.

Powders produced by SHS were consolidated using spark plasma sintering (SPS) technique. Powder was sintered at 950-1350 °C with simultaneous application of 50-100 MPa pressure for a dwell time of 3-10 min. SPS of Ni-W nanocomposite powder at 950 oC allow to achieve only 80 % density, while the samples sintered at 1350 °C at 50 MPa pressure within 3 min. were characterized by 95% of relative density and the average value for Vickers microhardness was 5.8±0.6 GPa.

Figure 12 illustrates SEM results for the SPS compacted material (combustion product of NiO+WO3+1.8Mg+2.2C mixture after acid treatment).

2.5. Exploring the reduction mechanism by copper wedge technique

To explore the mechanism of processes occurring in the combustion wave, the NiO+WO3+1.7Mg+2.2C mixture was selected and the combustion process was realized in the section of bulk copper wedge (the height - 47 mm, vertex angle of 10°). Temperature profiles of the combustion wave were registered by thermocouples located in two different zones.
Ni-W alloy was synthesized by the coreduction of oxide precursors in combustion mode using thermo-kinetic coupling approach. Similar approach was used by our research group for the preparation of tungsten-copper and molybdenum-copper pseudalloys [30-33]. Despite the fact that the behavior of combustion velocities (sharp decline) depending on the amount of carbon in these three systems has an extrinsic similarity, however, the arguments of reduction mechanism in the NiO-WO₃-Mg-C system are significantly different from the previous cases where the reduction begins with carbon, then continues by Mg. In the NiO-WO₃-Mg system thermal and chemical coupling occurs together and here also we deal with so-called thermo-chemical or thermo-kinetic coupling of reactions [27-29]. The simultaneous utilization of magnesium and carbon facilitates to the reduction of NiO and WO₃ under the controlled self-sustaining regime and the preparation of fine W-Ni composite powders. Note, that the solely magnesiothermic reaction of the both oxides is characterized by high values of enthalpy (NiO+Mg = 427.29 kJ·mol⁻¹; WO₃ + Mg = -842.94 kJ·mol⁻¹) and reaction temperature (about 3000 °C). These highly exothermic reactions proceed in a vigorous uncontrollable combustion mode leading to evaporation of significant amount of initial reactants, as well as incomplete conversion. In order to moderate the reaction conditions the reduction temperature was decreased by coupling with the oxides reduction by carbon, which is low exothermic process. The investigation of reaction mechanism showed that in contrast to CuO-WO₃-Mg-C and CuO-MoO₃-Mg-C systems, the reaction in the NiO-WO₃-Mg-C system starts with magnesiothermic reduction of NiO, which is responsible for heat generation and combustion wave propagation. The reduction continues with magnesiothermic/magnesiocarbothermic reduction of WO₃ and Ni₇W₃ formation occurs. Residual amount of oxide(s) converts to metals and unlike to previous ones, the reduction process occurs without melting of reduced metallic component, which can increase the homogeneity of the obtained product. Besides, in contrast to the above mentioned W-Cu and Mo-Cu pseudalloys, in this case, Ni and W metals forms nickel rich intermetallic compound with specific molar ratio of metals Ni₇W₃. In the XRD pattern of final product the respective peaks of metallic tungsten and Ni₇W₃ were detected.

It is worthy to note, that in the NiO-WO₃-Mg-C system at high x values (x > 4.5 mol) combustion wave propagation behavior is going to the non steady regime. Such phenomenon was not
observed in the CuO-WO$_3$-yMg-xC and CuO-MoO$_3$-yMg-xC systems, and where at higher amount of carbon (x > 5 mol) two stage character of the combustion wave becomes apparent disclosing the proceeding of two sequential exothermic reactions (splitting regime).

Coming to the influence of reactions’ coupling on the microstructure features one may observe that the addition of carbon with simultaneous decrease of combustion parameters promotes the nanostructure formation and the preparation of Ni-W nanocomposite powder at mild and controlled conditions. Our studies showed that spark plasma sintering of Ni-W nanocomposite powder allow to consolidate samples even at 950 °C (80%), while the highest density was achieved at 1350 °C (95%). Microstructure and composition of the alloy was preserved during the sintering process having a small grain size (less than 1 μm) mainly composed of the W phase and the Ni$_2$W$_3$ binding phase. Vickers microhardness measurements allow to evaluate the fracture toughness of the tungsten, whereas the Ni$_2$W$_3$ counterpart exhibited a ductile behavior. Average value for microhardness was measured to be 5.8±0.6 GPa (HV1), which is comparable with the results obtained for the Ni-W alloys (5.2-5.5 GPa) reported in [37].

4. Conclusions

Ni-W nanocomposite powder was successfully synthesized via co-reduction of metal oxides precursors in combustion mode by reaction’s thermo-kinetic coupling approach. The stepwise mechanism of reduction and phase formation sequences in the NiO-WO$_3$-yMg-xC quaternary system were revealed by using combustion wave quenching technique in the section of bulk copper wedge and XRD analysis of the quenched products. It was demonstrated that the interaction begins with magnesiocarbothermic reduction of NiO and continues with magnesiocarbothermic reduction of WO$_3$. Ni$_2$W$_3$ phase formation occurs in the combustion wave followed by carbothermic reduction of remained oxides. Combination products obtained from the NiO+W$_2$O$_5$+1.8Mg+2.2C mixture at P = 0.5 MPa argon pressure represent target nanocomposite material with an average particle size up to 50 nm. The produced powder was consolidated using spark plasma sintering (SPS) technique. Samples sintered at optimal conditions were characterized by 95% of relative density and Vickers microhardness value of 5.8±0.6 GPa.

References


