



Article Joint Reduction of NiO/WO₃ Pair and NiWO₄ by Mg + C Combined Reducer at High Heating Rates

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Abstract: Functional features of Ni-W composite materials combined with successful performance enabled a breakthrough in their broad application. To disclose the formation pathway of Ni-W composite materials at extreme conditions of combustion synthesis in the NiO-WO₃-Mg-C and NiWO4-Mg-C systems for the optimization of the synthesis procedure, the process was modeled under programmed linear heating conditions by thermal analysis methods. The reduction kinetics of tungsten and nickel oxides mixture and nickel tungstate by Mg + C combined reducer at non-isothermal conditions was studied at high heating rates (100–1200 °C min⁻¹) by high-speed temperature scanner techniques. It was shown that when moving from low heating to high heating rates, the mechanism of both the magnesiothermic and magnesio-carbothermic reductions of the initial mixtures changes; that is, the transition from a solid-solid scheme to a solid-liquid scheme is observed. The strong influence of the heating rate on the reduction degree and kinetic parameters of the systems under study was affirmed. The simultaneous utilization of magnesium and carbon as reducers allowed the lowering of the starting and maximum temperatures of reduction processes, as evidenced by the synergetic effect at the utilization of a combined reducer. The effective values of activation energy (E_a) for the reactions proceeding in the mixtures NiO + WO₃ + 4Mg, $NiO + WO_3 + 2.5Mg + 1.5C$, $NiWO_4 + 4Mg$ and $NiWO_4 + 2Mg + 2C$ were estimated by Kissinger isoconversional method and were 146 ± 10 , 141 ± 10 , 216 ± 15 and 148 ± 15 kJ mol⁻¹, respectively.

Keywords: Ni-W composites; combined reducer; non-isothermal kinetics; high heating rate; activation energy

1. Introduction

Nickel-tungsten composites (Ni-W) are considered useful for a vast number of industrial applications owing to their enhanced mechanical, tribological, magnetic, electrical and corrosion properties [1–3]. Their functional features allow the broad application of Ni-W as substrates for high-temperature superconductors, counter-balance weights, medical radiation shields, kinetic-energy penetrators, barrier layers or capping layers in micro electro mechanical systems (MEMSs) and as catalysts for hydrogen evolution from alkaline solutions [4–6]. These composites are recommended to protect and extend the service life of turbine blades operating at high temperature and high erosion. Electrodeposition (ED) [7], mechanical alloying (MA) [8], hydrogen reduction [9], sintering [10,11] and thermo-mechanical processes [12] are the most common processing routes for nickeltungsten composites, compacts and coatings. Recent trends illustrate the demand for new manufacturing technologies for the in situ production of a more finely dispersed and uniform composite powder for the preparation of compact specimens of improved sinterability operating at high temperature and erosion environments. Energy saving self-propagating high-temperature synthesis (SHS), known also as combustion synthesis



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Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). (CS), provides a technological advance for the synthesis of a great number of materials (metal powders, alloys and nanocomposites) of high purity and allows control over the combustion process parameters, regulation of the powder grain size and maintenance of compositional homogeneity. SHS has already successful performed the reduction of oxides and salts of distinctly different metals at moderate temperature mode using (Mg + C) combined reducer via a reactions' coupling approach [13–16]. In addition, the joint reduction of oxygenous compounds of Ni and W metals is also of significant practical interest in terms of in situ preparation of fine and homogeneous Ni-W composite powder.

However, extreme conditions in the SHS wave (high temperatures and high selfheating rates of substances in the combustion wave) impede the examination of the interaction mechanism of the combustion reaction and optimize synthesis conditions. To tackle this challenge, the process in the NiO-WO₃-Mg-C and NiWO₄-Mg-C systems was preliminary modeled by DTA/TG (Differential Thermal/Thermogravimetric) technique, which is relatively far from the conditions existing in SHS process, but provides primary knowledge about the main stages and intermediates. To reveal the reduction mechanism in the systems under study at conditions closer to heating rates and temperatures in the combustion wave at synthesis of alloys, the process was tuned within the time and the Ni-W formation pathway was explored under programmed linear heating by thermal analysis methods, namely using high-speed temperature scanner (HSTS) [17–19].

The HSTS technique is designed for the kinetic investigation of the powder mixtures to reveal the stepwise nature of complex reactions in multicomponent systems at high heating rates up to 10,000 °C min⁻¹ and up to a temperature of 1300 °C. By varying heating rates of reagents from 100 to 1200 °C min⁻¹, we succeeded in the design of optimum conditions for the preparation of Ni-W composite which contains equal amounts of metals (1:1 molar ratio) and surveyed the underlying reduction mechanism (characterization of phase and microstructure transformations based on SEM and XRD analyses, results of quenched intermediates and calculations of kinetic parameters). We noted that the influence of high heating rates on the salient features of phase formation and mechanisms in the NiO-WO₃-Mg-C and NiWO₄-Mg-C systems has not been investigated to date. By the same token, the understanding of reaction pathways at high heating rates is limited due to insufficient research of phase and structure formation and transformation mechanisms, as well as lack of kinetic studies. The reduction kinetics of tungsten (VI) [20] and nickel (II) oxides [21] by non-metallic reducing agents has garnered interest due to its practical importance. The isothermal reduction and carburization of tungsten and nickel oxides and nickel tungstate over H₂ [22–24], CO [25], CO/CO₂ mixture [26] and carbon [27] have been previously reported. In [28,29], the mechanism and kinetics of the reduction of separate oxides of nickel and tungsten were explored by DTA/TG method at 2.5–20 °C min⁻¹ heating rate region. It was demonstrated that the reduction of nickel (II) oxide with simultaneous utilization of Mg and C is initiated by Mg and followed by concurrent participation of magnesium and carbon. The second stage of the carbothermic reduction starts beyond the magnesiothermic process and leads to the formation of nickel. Using (Mg + C) combined reducer allowed the mitigation of the reduction of the temperature of NiO and to decrease the activation energy, compared to the separate carbothermic and magnesiothermic reduction reactions due to the synergistic action of combined reducers [28]. Magnesium also acts as an initiator of the reduction in the WO₃-Mg-C ternary system [29], followed by stepwise carbothermic reduction of tungsten oxides. The joint reduction of the tungsten and nickel oxides at low heating rates (2.5–20 °C min⁻¹) is initiated by double-stage magnesiothermic reduction (nickel oxide firstly and then tungsten oxide), near the melting point of magnesium, and followed by a carbothermic reduction process [30]. However, MgWO₄ salt formation (by the reaction of unreduced tungsten oxide with the formed magnesium oxide) prevents the complete reduction process. According to the data obtained, the heating rate tends to have dramatic influence on the stepwise nature of the process, phase transformation pathway and conversion rate/degree of the reactants. It should be noted that the joint reduction of two metals with a combined reducing agent at high heating rates is also of significant

practical interest for combustion synthesis of Ni-W composites/alloys with a finer and more homogeneous microstructure. Moreover, the considerable advantages of using nickel tungstate instead of the mixture of metal oxides for the synthesis of W-Ni composite powder has already been reported [22], contributing to enhanced chemical homogeneity of the final product, thanks to the presence of both metals in the same crystal structure. From this point of view, NiWO₄ is of particular interest with an anticipated decrease in the synthesis temperature, production of a more finely dispersed and uniform composite powder. Both of these factors, together with controlled thermal mode of SHS reaction, are of paramount importance for the preparation of compact specimens of reduced porosity.

2. Materials and Methods

Tungsten (VI) oxide (WO₃, Pobedit, Russia, pure, high grade, $\mu < 40 \mu$ m), nickel (II) oxide (NiO, Russia, pure grade, $\mu < 44 \mu$ m), magnesium (MPF-3, Russia, pure grade, 0.15 mm < $\mu < 0.3$ mm) and carbon black (P-803, Russia, $\mu < 0.1 \mu$ m) were used in this study.

A calcination method was utilized for the preparation of nickel tungstate from NiO and WO₃ powders' mixture (1:1 molar ratio) in air at 850 °C for 6.5 h: dark yellow product represents NiWO₄. Figure S1a in the Supplementary Materials represents the XRD pattern of the prepared material. The SEM image of agglomerated NiWO₄ demonstrates well-defined grain boundaries with an average particle size of 5 μ m (Figure S1b).

The HSTS setup was utilized for the kinetic investigations of the NiO-WO₃-Mg-C and NiWO₄-Mg-C precursor mixtures under the programmed linear heating rates, up to 1200 °C min⁻¹ and temperatures up to 1300 °C, which are closer to heating rates and temperatures in the combustion wave at the synthesis of alloys [17–19].

Note that HSTS provides the highest heating rates and involves the widest range of heating rates in existing thermal analysis devices so far. To explore the influence of heating rates and the role of each reducing agent, the mixture of raw materials (20–70 mg) was homogenized in a ceramic mortar (15 min) and placed into the central part of metallic envelope made from nickel foil (thickness of the foil is 0.1 mm), and a chromel-alumel K-type thermocouple, spot-welded directly to the foil in the center of the powder location. Measurements were conducted at 0.1 MPa argon (Ar, 99.8% purity, less than 0.1% O₂) pressure. The heating rate was programmed to be 100, 150, 300, 600 and 1200 °C min⁻¹. The foil heater is heated ($T_{\text{max}} = 1300 \text{ °C}$) directly by the passing of an electric current with the desired temperature-time schedule provided by PC-assisted controller. The inert experiment provides linear temperature time history, which defines the heating rate and coincides with the reactive T profile in the regions when the reaction does not occur. The deviation of the reactive profile from the inert one gives information about exothermic or endothermic reactions. The reaction onset temperature (T_0) , the maximum peak temperature observed during self-heating (T_{max}) and the temperature prescribed by linear heating, where the maximum exothermic effect is observed (T^*) , are determined from the heating curves. The HSTS setup allows the interruption of the process by automatically switching off the electric current at different characteristic stages, but also the continuous registration of the cooling curve by the thermocouple placed in the sample. At that point, extremely fast cooling (up to 12,000 $^{\circ}$ C min⁻¹) takes place, which practically excludes further interaction during the cooling process.

The phase composition of the intermediates and final products was examined by XRD equipment (XRD; D5005, Bruker, Billerica, MA, USA) using CuK α 1 radiation (λ = 1.5406 Å) with a step of 0.02° (2 θ) and a count time of 0.4 s. To identify the products from the XRD spectra, the data were processed using the JCPDS-ICDD database. Morphologies and microstructures of the samples were examined by Prisma E scanning electron microscope (SEM, Thermo Fisher Scientific, Hillsboro, OR, USA) at an accelerating voltage of 10 kV.

Kissinger's isoconversional method [31] was used to calculate the effective activation energies for the systems under study, based on the principle of temperature shift corre-

sponding to the maximum advance in the heating curve at a constant heating rate. The acquired expression for the determination of the activation energy has the following form:

$$\ln\left(\frac{\beta}{\left(T^*\right)^2}\right) = \ln A - \frac{E}{R}\left(\frac{1}{T^*}\right) \tag{1}$$

where *A* is a is the pre-exponential factor, *E* is the effective activation energy of the process, (kJ mol⁻¹), β is the heating rate (K min⁻¹), *T*^{*} is the reduction temperature on the inert temperature profile corresponding to the maximum advance in the reactive heating curve (K) and *R* is the universal gas constant (8.31 J mol⁻¹ K⁻¹).

Gibbs free energies of the reactions under study were calculated by using the HSC-5 software package (Version 5, Pori, Finland).

3. Results and Discussion

The interaction mechanism was primarily investigated in the ternary (NiO-WO₃-Mg, NiO-WO₃-C) and binary (NiWO₄-Mg, NiWO₄-C) systems, then in a complex quaternary (NiO-WO₃-Mg-C) and ternary (NiWO₄-Mg-C) systems, under identical heating conditions. The research data on the previously implemented systems (WO₃-Mg, WO₃-C, WO₃-Mg-C, NiO-Mg, NiO-C, NiO-Mg-C) were also considered [32,33].

To ensure the complete reduction of reactant compounds, the stoichiometric compositions of the initial binary and ternary mixtures were selected (NiO + WO₃ + 4Mg, NiWO₄ + 4Mg, NiO + WO₃ + 4C, NiWO₄ + 4C) according to the following trivial reactions:

$$NiO + WO_3 + 4Mg = Ni-W + 4MgO (\Delta G^0 = -1303.59 \text{ kJ mol}^{-1})$$
(2)

$$NiWO_4 + 4Mg = Ni-W + 4MgO (\Delta G^0 = -919.78 \text{ kJ mol}^{-1})$$
(3)

$$NiO + WO_3 + 4C = Ni-W + 4CO^{\uparrow} (\Delta G^0 = 402.98 \text{ kJ mol}^{-1})$$
(4)

$$NiWO_4 + 4C = Ni-W + 4CO^{\uparrow} (\Delta G^0 = 320.42 \text{ kJ mol}^{-1})$$
(5)

In (NiO-WO₃-Mg-C) and (NiWO₄-Mg-C) systems, the reducers' ratio was chosen based on the preliminary experimental results, considering that high amounts of magnesium induces an explosive reaction, whereas a high amount of carbon makes the interaction self-inhibited [13,15,30]. Based on the foregoing observations, NiO + WO₃ + 2.5Mg + 1.5C and NiWO₄ + 2Mg + 2C compositions were selected, respectively. Note, the preliminary HSTS experiments demonstrated the thermal stability of pure nickel tungstate at the temperature intervals studied.

3.1. NiO-WO₃-Mg and NiWO₄-Mg Systems

There are weak endothermic (characteristic for melting magnesium) and strongly expressed exothermic (typical for magnesiothermic reduction) stages on the heating curves of the both NiO + WO₃ + 4Mg (Figure 1a) and NiWO₄ + 4Mg (Figure 1b) mixtures depicted in Figure 1.



Figure 1. Heating curves of the NiO + WO₃ + 4Mg ((**a**) A—700 °C, B—880 °C, C—1000 °C, D—1300 °C) and NiWO₄ + 4Mg ((**b**) A—600 °C, B—850 °C, C—1000 °C) mixtures, β = 300 °C min⁻¹.

Moreover, for both systems the exothermic interactions (at heating rate 300 °C min⁻¹) are initiated after the magnesium melting (650 °C) by a solid + liquid mechanism ($T_{\rm m}$ (WO₃) = 1473 °C, $T_{\rm b}$ (WO₃) = 1700 °C, $T_{\rm m}$ (NiO) = 1955 °C, $T_{\rm m}$ (NiWO₄) = 1420 °C). The maximum temperature deviations occurring at 734 °C and 759 °C correspond to the single-stage magnesiothermic reduction of oxides and NiWO₄, respectively.

The processes in these mixtures were interrupted at different characteristic temperatures (Figure 1a,b) and the phase composition of the quenched samples was analyzed. The intermediates were identified, the sequence of reactions was found out with the aim to disclose the reduction mechanism. The possibility of simultaneous reduction of nickel and tungsten oxides (Figure S2a) and the decomposition of nickel tungstate during/before the reduction processes (Figure S2b) were examined. No interaction was observed before and during the Mg melting (A point, 700 °C, Figure 1a), while the sample quenched after the exothermic peak (B point, 880 °C, Figure 1a) contained a reduced tungsten, an intermetallic compound of Ni₁₇W₃ composition, as well as MgO along with initial oxides. This circumstance shows that the simultaneous reduction of both oxides emerged in one exothermic peak. The sample cooled at 1000 °C (C point, 1000 °C, Figure 1a) contained partially reduced W (WO_{2.7}), which was completely reduced at 1300 °C (D point, 1300 °C, Figure 1a).

On the other hand, XRD analysis results showed that complete magnesiothermic reduction of NiWO₄ already takes place at 850 °C (B point, 850 °C, Figure S2b), with the formation of tungsten and Ni₁₇W₃ at about 450 °C below the reduction temperature of the mixture (NiO + WO₃). It can be assumed that, in the case of NiWO₄, W and Ni are in more favorable conditions for joint reduction, being in the same crystal structure. However, in both cases, the reduced material was tungsten and intermetallic compound of Ni₁₇W₃ composition. It is worthy to note also, that the thermal decomposition of nickel tungsate into oxides was not observed before the magnesiothermic reduction.

It has been reported [30], that at low heating rates (DTA/TG studies, $\beta = 2.5-20$ °C min⁻¹) the joint reduction of the both oxides by magnesium began with the NiO + Mg reaction before the magnesium melting, with a solid + solid interaction scheme, and afterwards the reduction of tungsten oxide took place followed by the formation of magnesium tungstate. However, it was not possible to achieve complete joint reduction of either oxides or NiWO₄ salt at low heating rates and at a temperature below 1000 °C.

On the other hand, according to [33], only a partial reduction of nickel oxide by Mg was possible at temperatures up to 1200 °C at heating rate $\beta = 300$ °C min⁻¹. Therefore, the complete magnesiothermic reduction of the both metals at 1300 °C becomes possible due to the combined processing of nickel and tungsten oxides.

3.2. NiO-WO₃-C and NiWO₄-C Systems

The heating curves for the NiO + WO₃ + 4C (Figure 2a) and NiWO₄ + 4C (Figure 2b) mixtures (Figure 2) demonstrated that, unlike the magnesiothermic reduction, strongly expressed peaks are absent during carbothermic processes, but there are weak endothermic domains corresponding to the reduction of both the mixture of oxides (1080–1300 °C) and the NiWO₄ (1100–1260 °C).



Figure 2. Heating curves of the NiO + WO₃ + 4 C ((**a**) A—850 °C, B—1000 °C, C—1080 °C, D—1150 °C and E—1300 °C) and NiWO₄ + 4 C ((**b**) A—1050 °C, B—1100 °C, C—1200 °C and D—1260 °C) mixtures, *β* = 300 °C min⁻¹.

XRD examinations of quenched intermediates were performed at characteristic temperatures (Figure S3a,b). The carbothermic reduction process of nickel and tungsten oxides mixture was interrupted at the temperatures of A—850 °C, B—1000 °C, C—1080 °C, D—1150 °C and E—1300 °C. According to the XRD analysis results, the reduction begins at 1000 °C before the endothermic domain starts (Figure 2a). Interruptions for the carbothermic reduction of NiWO₄ were performed at A—1050 °C, B—1100 °C, C—1200 °C and D—1260 °C, demonstrating direct reduction onset of NiWO₄ at 1100 °C (by 100 °C higher compared to the reduction of the oxides mixture) without thermal decomposition (Figure 2b). Note that in contrast to the mixture (NiO + WO₃), the reduction of NiWO₄ proceeded completely. In contrast to the magnesiothermic reduction of the NiO + WO₃ mixture, the carbothermic reduction proceeded partially at the studied temperature interval (up to 1300 °C): carbon reduced NiO up to Ni, while WO₃ was endothermically reduced over WO_{2.7} up to WO₂ (Figure 2).

According to recent research carried out by our research group [33], the carbothermic reduction of nickel oxide began at 950 °C, and by 1030 °C a complete reduction had already been achieved ($\beta = 300 \text{ °C min}^{-1}$). At low heating rate region ($\beta = 2.5-20 \text{ °C min}^{-1}$), the carbothermic reduction of nickel oxide occurs with two sequential endothermic stages noticeable from the DTA, TG and DTG (Derivative Thermogravimetric) curves at 780–900 and 905–985 °C temperature ranges [30]. Therefore, with the increase of the heating rate, the conversion degree of NiO increases. However, the complete reduction was not detected in the studied temperature range (up to 1000 °C). According to [29], the carbothermic reduction of WO₃ starts at 500 °C, but complete reduction was not registered at the given temperature ($T_{\text{max}} = 1000 \text{ °C}$) under identical conditions. At low heating rates in the ternary NiO + WO₃ + 4 C mixture, the reduction process started with NiO and continued with WO₃ reduction leading to NiWO₄ formation at higher temperatures (960 °C) [29].

3.3. NiO-WO₃-Mg-C and NiWO₄-Mg-C Systems

The heating curves for the reduction processes of the mixture (NiO + WO₃) and (Figure 3a) NiWO₄ (Figure 3b) by combined (Mg + C) reducer at β = 300 °C min⁻¹ are

depicted in Figure 3. Strongly peaked exothermic stages correspond to the magnesiothermic reduction of nickel and tungsten oxides (Figure 3a) and nickel tungstate (Figure 3b). The maximum shifts for the mixture of oxides and salt were observed at very close temperatures, 712 °C (Figure 3a) and 728 °C (Figure 3b), respectively.



Figure 3. Heating curves of the NiO + WO₃ + 2.5Mg + 1.5C ((**a**) A—725 °C, B—800 °C, C—1060 °C and D—1300 °C) and NiWO₄ + 2Mg + 2C ((**b**) A—720 °C, B—830 °C and C—1000 °C) mixtures, $\beta = 300$ °C min⁻¹.

To clarify the sequence of oxides' reduction and the role of reducers in each stage, the process was interrupted at different characteristic temperatures (NiO + WO₃ + 2.5Mg + 1.5C; A—725 °C, B—800 °C, C—1060 °C and D—1300 °C / NiWO₄ + 2Mg + 2C; A—720 °C, B—830 °C and C—1000 °C) and cooled samples were examined by XRD analysis (Figure 4). It was revealed that complete reduction of NiWO₄ had already taken place at 1000 °C, while in the case of oxides mixture, the complete reduction of WO₃ was not achieved at the studied temperature range (1300 °C) (Figures 3 and 4) at 300 °C min⁻¹. Note that the sample quenched immediately after the exothermic peak contained tungsten carbide (W₂C). The latter was not observed at the solely carbothermic reduction of (Mg + C) combined reducer, is the reduction of NiWO₄ after decomposition (B point, 830 °C, Figures 3b and 4), in contrast to the separate utilization of Mg or C reducers.



Figure 4. XRD patterns of the NiO + WO₃ + 2.5Mg + 1.5C ((**a**) 725 °C, 800 °C and 1300 °C) and NiWO₄ + 2Mg + 2C ((**b**) 720 °C, 830 °C and 1000 °C) mixtures, β = 300 °C min⁻¹.

By combining the results obtained for the mixture of oxides and NiWO₄, it can be assumed that the reduction reactions of NiWO₄ by Mg and (Mg + C) combined reducer started earlier and that the complete reduction was achieved at comparatively lower temperatures. In addition, the magnesio-carbothermic reduction reactions of nickel and tungsten oxides and nickel tungstate began by ~20 and 30 °C earlier than magnesiothermic ones, and about ~300 and 370 °C earlier than carbothermic processes, evidencing the synergetic effect at utilization of combined reducer in the ternary and quaternary mixtures.

At low heating rates ($\beta = 20 \text{ °C min}^{-1}$, DTA/TG studies), the reduction process in the NiO + WO₃ + Mg + 2C mixture started by Mg reduction of nickel oxide ($T_{\text{max}} = 615 \text{ °C}$; solid + solid mechanism), at first, and then of tungsten oxide ($T_{\text{max}} = 660 \text{ °C}$; solid + liquid mechanism). Later, the reduction process was continued by carbon ($DTG_{\text{min}} = 927 \text{ °C}$). Note that at higher temperatures (T > 927 °C) the MgWO₄ formation took place by the interaction of remaining (non-reacted) WO₃ and obtained MgO [30].

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 + 2.5Mg + 1.5C mixture treated at 100 °C min⁻¹ and higher (300–1200 °C min⁻¹) heating rates revealed that, at 100 °C min⁻¹, the reaction proceeded completely up to W, Ni₁₇W₃ and MgO formation, while higher heating rates (>300 °C min⁻¹) hinder the complete reduction; partially reduced WO₂ remained.

Microstructural images of the initial mixture, intermediate and final products of the NiWO₄ + 2Mg + 2C (Figure 5) reaction cooled down at different temperatures (A—initial mixture, B—720 °C, C—830 °C and D—1000 °C) are presented in Figure 5.



Figure 5. SEM images of the NiWO₄ + 2Mg + 2C mixtures cooled down at different temperatures: (**a**)—initial mixture, (**b**)—720 °C, (**c**)—830 °C and (**d**)—1000 °C.

According to the results obtained, agglomerated NiWO₄ with an average particle size of 5 μ m along with black carbon and magnesium powder with well-defined grain boundaries were present in the initial mixture, without significant microstructural changes, up to 720 °C (Figure 5a,b). During the exothermic reduction process (quenched at 830 °C), the newly formed submicron particles of partially reduced product (NiO, WO₂, W, etc.) underwent partial sintering and crystallization (Figure 5c). Further increases in temperature up to 1000 °C did not cause a change in particle size, but contributed to the homogenization of the final product, comprising submicron sized particles of completely reduced W, Ni₁₇W₃ and MgO mixture (Figure 5d).

3.4. Calculation of Activation Energy

To reveal the influence of the heating rate on the kinetic features of NiO + WO₃ + 4Mg (1), NiO + WO₃ + 2.5Mg + 1.5C (2), NiWO₄ + 4Mg (3) and NiWO₄ + 2Mg + 2C (4) mixtures, the HSTS studies were performed in a wide range of heating rates: from 100 up to 1200 °C min⁻¹. As can be seen from Figure 6, with the increase in the heating rate the exothermic peaks of magnesiothermic reduction of (NiO + WO₃) mixture (Figure 6a) and NiWO₄ (Figure 6b) were shifted to the higher temperature area.



Figure 6. Heating curves of the NiO + WO₃ + 2.5Mg + 1.5C (a) and NiWO₄ + 2Mg + 2C (b) mixtures for various heating rates.

Using the data of the temperatures of the exothermic peaks' maximum deviation at different heating rates (T^*), the values of the effective activation energies for magnesiothermic reduction stages were calculated by Kissinger's isoconversional method [31] according to Equation (1).

Thus, the effective activation energy value for the NiO + WO₃ + 4Mg reaction is calculated to be $146 \pm 10 \text{ kJ} \text{ mol}^{-1}$. The addition of carbon to the mixture (NiO + WO₃ + 2.5Mg + 1.5C) had no notable influence on the effective activation energy value, as it was derived for the magnesiothermic stage of the process ($141 \pm 10 \text{ kJ} \text{ mol}^{-1}$). In comparison with NiO + WO₃ + 4Mg reaction, the activation energy value for the magnesiothermic reduction of nickel tungstate (NiWO₄ + 4Mg) is higher: $216 \pm 15 \text{ kJ} \text{ mol}^{-1}$, and when carbon is added to this mixture (NiWO₄ + 2Mg + 2C), the activation energy of the magnesiothermic reduction stage of the reaction decreases almost 1.5 times, reaching $148 \pm 10 \text{ kJ} \text{ mol}^{-1}$ (Figure 7, Table 1).



Figure 7. Linear fitting of the $-\ln(\beta(1/T^*)^2)-1/T^*\cdot 10^3$ plots to extract effective activation energy of the reactions in the NiO + WO₃ + 4Mg (1), NiO + WO₃ + 2.5Mg + 1.5C (2) (**a**) and NiWO₄ + 4Mg (3), NiWO₄ + 2Mg + 2C (4) (**b**) mixtures.

Reaction	Temperature Interval (°C)	Heating Rate (°C min ⁻¹)	Activation Energy Value (kJ mol ⁻¹)	References
$WO_3 + 3Mg$	520-590	2.5-20	153	[29]
$WO_3 + 0.5Mg + 2C$	560-630	2.5-20	177	[29]
CuO + 0.5Mg	700–748	100-1200	424 ± 25	[32]
$WO_3 + 3Mg$	637-803	100-1200	106 ± 6	[32]
CuO + 0.5Mg + 0.25C	720-803	100-2600	320 ± 19	[32]
$WO_3 + 1.5Mg + C$	658–931	100-2600	92 ± 5	[32]
$CuO + WO_3 + 4Mg$ (I stage)	672–703	100-300	248 ± 15	[32]
$CuO + WO_3 + 4Mg$ (I stage)	809–953	100-300	64 ± 4	[32]
$CuO + WO_3 + 4Mg$ (joint)	810–907	390-5200	260 ± 16	[32]
$NiO + WO_3 + 4Mg$	575-662	2.5-20	152	[30]
$NiO + WO_3 + Mg + 2C$	605–662	2.5-20	149	[30]
NiO + Mg	661–750	100-1200	185 ± 15	[33]
2NiO + Mg + C	663–760	100-1200	185 ± 15	[33]
$NiO + WO_3 + 4Mg$	687–815	100-1200	146 ± 10	[this work]
$NiO + WO_3 + 2.5Mg + 1.5C$	660–790	100-1200	141 ± 10	[this work]
$NiWO_4 + 4Mg$	726-821	100-1200	216 ± 15	[this work]
$NiWO_4 + 2Mg + 2C$	688–812	100-1200	148 ± 10	[this work]

Table 1. Comparison of the activation energy values with reference data calculated by Kissinger method.

Note that at low heating rates (2.5–20 °C min⁻¹) in the 575–662 °C temperature interval, the E_a value for the NiO + WO₃ + 4Mg reaction was determined to be 152 kJ mol⁻¹; for the magnesiothermic stage of the NiO + WO₃ + Mg + 2C reaction, in the 605–662 $^{\circ}$ C temperature interval, to be 149 kJ mol $^{-1}$ [31]. Despite the fact that the reduction process in the NiO-WO₃-Mg-C system at low heating rates started before Mg melting, no notable difference was observed in Ea values. The behaviour of NiWO4-Mg-C and NiO-WO3-Mg-C systems are quite similar according to E_a values, whereas the complete conversion was observed only in the first system. The reduction of the WO_3 and WO_3 + NiO mixture by combined reducers started at the same temperature (~660 $^{\circ}$ C). However, the *E*_a value of the first process was significantly lower, indicating a difference in product composition (W, MgO vs Ni₁₇W₃, W, MgO). Interesting phenomena were observed in the comparative overview of the NiWO₄-Mg and NiWO₄-Mg-C systems, where solely magnesiothermic reduction starts at higher temperature and is characterized by an approximately 70 kJ mol⁻¹ higher E_a value, clearly demonstrating the beneficial influence of combined reducers on the reduction process of nickel tungstate. Comparing both reduction reactions of NiO + WO₃ mixture and NiWO₄ by combined reducers, the insignificant difference in T_s and E_a values

might be attributed to the complete reduction of salt, in contrast to the oxides mixture. On the other hand, the separate reduction of nickel and tungsten oxides by combined reducer illustrated the same starting temperature (conditioned by the fact that both processes started after Mg melting), while having double the E_a values.

In Table 1 the activation energy values obtained in this work and compared with similar thermite type mixtures obtained earlier [29,32,33]. It can be deduced that the influence of the heating rate is mainly notable on T_s but not on the E_a values. In particular, for the NiO-WO₃-Mg system, despite the change from solid-solid mechanism to solid-liquid, E_a values are practically the same, attributed to the conversion degree and phase composition, i.e., to the formation of Ni₁₇W₃, W and MgO.

4. Conclusions

The stepwise nature of complex reactions in the multicomponent NiO-WO₃-Mg, NiO-WO₃-C, NiO-WO₃-Mg-C, NiWO₄-Mg, NiWO₄-C and NiWO₄-Mg-C systems was successfully examined by HSTS technique to reveal the phase and microstructure transformations at high heating rates (up to 1200 °C min⁻¹) and determine the effective activation energy values.

The results showed that:

- simultaneous utilization of magnesium and carbon as reducers allowed the reduction
 of the starting and maximum temperatures of reduction processes, evidencing the
 synergetic effect of the utilization of combined reducers;
- complete magnesiothermic reduction of NiWO₄ had already taken place at 850 °C, which is about 450 °C below the magnesiothermic reduction temperature of the mixture (NiO + WO₃);
- complete magnesio-carbothermic reduction of NiWO₄ took place at 1000 °C, while the reduction of oxide mixtures by (Mg + C) combined reducer at the same conditions proceeded partially;
- unlike the magnesiothermic and carbothermic reduction, magnesio-carbothermic reduction of nickel tungstate proceeded through thermal decomposition of the NiWO₄ into oxides. The effective (apparent) activation energies reported in this work characterize macroscopic kinetics of the exothermic interaction in heterogeneous mixtures taking place by solid + solid or solid + liquid mechanisms.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/ 10.3390/met11091351/s1, Figure S1: XRD pattern (a) and SEM image (b) of the nickel tungstate obtained by calcination method. Figure S2: XRD patterns of the NiO + WO₃ + 4Mg (a; 700 °C, 880 °C, 1300 °C) and NiWO₄ + 4Mg (b; 600 °C, 850 °C) mixtures, $\beta = 300$ °C min⁻¹. Figure S3: XRD patterns of the NiO + WO₃ + 4C (a; 850 °C, 1000 °C, 1300 °C) and NiWO₄ + 4C (b; 1050 °C, 1200 °C, 1260 °C) mixtures, $\beta = 300$ °C min⁻¹.

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