



Article Reduction Behavior and Characteristics of Metal Oxides in the Nanoscale

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Abstract: The development of nanomaterials and nanotechnology enables the production of nanosized metallic alloys with advanced characteristics from their oxides via a thermal reduction technique. The aim of the present work was to produce metallic iron, nickel, and tungsten through the gaseous reduction of nanosized metal oxide powders as a preliminary step towards the fabrication of nanosized heavy tungsten alloys with unique properties. Nanosized NiO, Fe₂O₃, and WO₃ were isothermally and non-isothermally reduced with H₂, and the oxygen weight loss was continuously recorded as a function of time. The Thermogravimetric TG-DTA technique was applied in the non-isothermal reduction up to 1000 °C. The reduction extents were calculated from the TG curve, whereas the accompanying heat of the reaction was measured from the DTA curve. The results revealed that NiO was reduced at <420 °C, Fe₂O₃ was reduced at <600 °C, and WO₃ was reduced at >950 °C. In the isothermal process, metal oxides were reduced with H₂ at 700–1000 $^{\circ}$ C; a micro-force balance was used and the O₂ weight loss was continuously recorded. At a given temperature, the rate of reduction increased in the order NiO > Fe_2O_3 > WO₃. The nano-oxide powders and the reduced products were physically and chemically characterized. The activation energy (Ea) values were computed from the isothermal reduction in the initial and later stages to elucidate the corresponding reduction mechanism. The Ea values indicated that the reduction of metal oxides was controlled by the gas diffusion mechanism at both the initial and later stages of reduction. The results of the present study determined the optimal operation parameters at which the thermal gaseous reduction technique could be applied for preparing metallic alloys from nanosized metal oxides.

Keywords: gaseous reduction; nanostructures; kinetics and mechanism; iron oxides; nickel oxides; tungsten oxide; metallic alloys; thermal technique; activation energy; TG-DTA

1. Introduction

The thermal gaseous reduction technique for metal oxides is considered a promising technology for preparing metallic alloys as it is simple and economical [1–3]. Recently, the fabrication of metallic alloy materials has been considered an important issue for both scientific and industrial applications. These alloys are widely applied in many engineering industries. One of these alloys is heavy tungsten alloy, which has great importance in the engineering and mining industries as well as military and medical applications because of its stability at high temperatures, high strength, and very dense structure [4–10]. However, the present work develops a new technology for the fabrication of metallic materials in the nanoscale by using powder technology instead of traditional powder metallurgy. Nanosized Fe, Ni, and/or W materials can be prepared via the process of gaseous reduction of nanosized metal oxides which mainly depends on the reduction with eco-friendly reducing gas at relatively low temperatures. The understanding of the reduction characteristics of nanosized metal oxides of iron, nickel, and tungsten enables us to determine the optimal



Citation: Halim, K.S.A.; El-Geassy, A.A.; Ramadan, M.; Nasr, M.I.; Hussein, A.; Fathy, N.; Alghamdi, A.S. Reduction Behavior and Characteristics of Metal Oxides in the Nanoscale. *Metals* 2022, *12*, 2182. https://doi.org/10.3390/ met12122182

Academic Editor: Cătălin-Daniel Constantinescu

Received: 17 November 2022 Accepted: 14 December 2022 Published: 18 December 2022

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Copyright: © 2022 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/). conditions for the fabrication of metallic alloys from nanosized materials. The investigation of the reduction phenomena of these metal oxides is considered a preliminary step towards the fabrication of nanosized heavy tungsten alloys.

The gaseous reduction of Fe_2O_3 , NiO, and/or WO₃ by hydrogen gas takes place in more than one step via the formation of intermediate metal oxides. In heterogeneous gas–solid reactions, the structure of the intermediate solid products plays a significant role in the reaction kinetics [11]. The rate of removal of O₂ from solids in the reduction reactions is a function of the partial pressure of gases in the surrounding atmosphere and the activity of O₂ on the oxide surface [12,13]. The magnitude of the dependence of the rate on the partial pressure is important for determining the order of reaction in the absence of intergranular gas diffusion in the porous product layer [11–14].

The reduction of Fe_2O_3 by gases is a complex reaction process due to the formation of lower oxides prior to the formation of metallic iron ($Fe_2O_3 \rightarrow Fe_3O_4 \rightarrow FeO \rightarrow Fe$). Extensive studies were carried out on the reduction of pure Fe_2O_3 and Fe_2O_3 containing impurities [15,16]. Moreover, the reduction behavior of iron oxides with carbon-bearing materials was also studied, and the reaction kinetics and mechanism under different reduction conditions were given and discussed [17–20].

The reduction of NiO by hydrogen consists of two simultaneous reactions: first, a reaction between NiO and hydrogen gas adsorbed on NiO, and second, a reaction at the boundary between the two solid phases NiO and Ni with hydrogen adsorbed on nickel [21]. In general, the reduction rates of nickel oxides have been established as a function of temperature and pressure. Another study [22] showed that at relatively low reduction temperatures (543–773 K), the kinetic curves of NiO have a sigmoidal shape and the reactions are incomplete at long induction times (up to 2000 s). This is due to the formation of a complex polycrystalline Ni/NiO porous structure with characteristic pore size on the order of 100 nm. However, the reduction reactions become complete under high-temperature conditions (1173–1593 K). The reduction of NiO to Ni is achieved within seconds. As mentioned previously, in iron oxide reduction, such a mechanism might be explained in terms of microstructure changes. An extremely fine porous metal structure, with a pore size under 10 nm, forms during high-temperature reductions.

Regarding the process of gaseous reduction of tungsten oxides, it is considered one of the most important methods for tungsten powder production [23–26]. The reduction reactions take place in a streaming hydrogen atmosphere (WO₃ + 3H₂ \rightarrow W + 3H₂O) at relatively high temperatures in many steps. All stable tungsten oxides can be formed (WO₃, WO_{2.9}, WO_{2.72}, WO₂). In addition, the chemical conversion of WO₃ to W metal via gaseous reduction is always associated with the chemical vapor transport of tungsten which determines the characteristics of the produced tungsten to a great extent [23]. Thermodynamically, the reduction system (W-O-H) and phase relations were investigated in many studies [27–30]. In all studies, the reduction mechanisms of WO₃ were demonstrated by the morphological changes accompanying the reduction processes, and in general, two different mechanisms were postulated: The first is solid-state diffusion in which oxygen is removed directly from WO₃. The second mechanism is chemical vapor transport in which the reduction reactions are combined with a chemical vapor transport of tungsten via the formation of volatile WO₂(OH)₂.

On the other hand, the development of nanomaterials and nanotechnology in the last few decades enables the rethinking of the correlation between the structure and properties of a material. Nanostructure materials exhibit amazing properties because of their high surface activity due to their small particle size and enormous surface area.

The present work investigates the reduction behavior and characteristics of three nanosized metal oxides (Fe_2O_3 , NiO, and WO_3). A fundamental study on the reduction kinetics and mechanism of nanosized metal oxides was carried out isothermally and non-isothermally to investigate the conditions for the efficient use of nanomaterials in the conversion processes of oxides to metallic materials. The determination of optimal conditions for the fabrication of metallic materials from nanosized metal oxides via the

thermal reduction technique will enable us to develop a new technology for utilizing nanosized metal oxides in the fabrication of heavy tungsten alloys.

2. Experimental Procedure

2.1. Materials

Analytical grade (>99.8%) nanosized powders (AR) of iron Fe₂O₃ (grain size = 20 nm), NiO (grain size = 20 nm), and WO₃ (grain size = 50 nm) were obtained from Guangzhou Hongwu Material Technology Co., Ltd. (Tangdong East Road, Guangzhou, Guangdong, China)). The chemical purity of metal oxides was analyzed using X-ray fluorescence (Axios Advanced WDXRF, PAN Analytical Empyrean, Eindhoven, the Netherlands). The different phases in the nanosized metal oxides and in the reduced products were identified by X-ray diffraction technique (XRD, PAN Analytical Empyrean, Eindhoven, the Netherlands) using CuK α radiation at an accelerating voltage of 40 kV and a current of 35 mA at a wavelength of λ = 1.54045 Å. The crystallite sizes were also measured. The morphology and grain structures were examined using a reflected light microscope (Zeiss Axio-scope A1, Carl Zeiss AG, Oberkochen, Germany), a scanning electron microscope (HRTEM, JEM2100, JEOL, Tokyo, Japan) operated at an acceleration voltage of 200 kV.

2.2. Reduction Techniques

Nanosized metal oxides were subjected to both non-isothermal and isothermal reduction using different techniques. The non-isothermal reduction behavior of NiO, Fe₂O₃, and WO₃ nanopowder was investigated by thermogravimetric analysis techniques, namely DTA-TGA (STA-504, BÄHR-Thermoanalyse GmbH, Hüllhorst, Germany). The reduction setup and gas purification system were previously described and given elsewhere [18]. For a given reduction experiment, 100 mg of powder of certain metal oxide was inserted in the alumina crucible (d = 6 mm, h = 8 mm) of the DTA-TGA system, and the reference crucible was filled with 100 g Al₂O₃. The furnace was first flushed with Ar gas for 5 min, and then H₂ gas (30 mL/min) was introduced instead of Ar gas flow. The furnace was heated at a heating rate of 10 °C/min to 1000 °C. The weight loss (TG) and the heat of the reaction (DTA) were recorded continuously. At the end of the experiments, Ar was introduced and replaced the flow of H₂, and the sample was cooled to room temperature. The reduced products were kept dry in a desiccator for subsequent measurements.

For isothermal reduction experiments, the nanosized metal oxide powders were pressed to produce compacts with equal sizes and shapes. Compacts (d = 7 mm, h = 10 mm) were made by pressing about 1.0 g of metal oxide powder in a stainlesssteel mold at 5 kN/cm² using a hydraulic press (Sealey hydraulic Press, 4 tonne, bench type, Suffolk, UK). Dry compacts were isothermally reduced at 700–1000 °C in a purified H₂ gas flow at a 1.0 L/min flow rate. This flow rate efficiently overcomes the gas boundary layer effects. The course of reduction was followed by measuring the weight loss as a function of time under controlled conditions of reduction temperature. For each reduction experiment, the furnace was heated to the predetermined temperature in a continuous flow of purified argon gas (1.0 L/min), and then the furnace temperature was kept constant for 10 min to ensure its stability. The metal oxide compact placed in a platinum wire basket was slowly inserted in the furnace and positioned in the middle of the hot zone and kept steady for a while. Under this condition, Ar was turned off and H_2 gas (1.0 L/min) was introduced to start the reduction reactions. The O_2 weight loss resulting during the experiment was measured using a micro-force balance (Sartorius Corporate Administration GmbH, Göttingen, Germany), and the data were continuously recorded as a function of time. At the end of the experiment, the reduced sample was cooled in purified Ar by removing it from the hot zone until it reached <200 °C. The basket with the sample was quickly removed and quenched in pure acetone to prevent reoxidation reactions from occurring. The reduced products were kept dry in a desiccator for further characterization.

3. Results

3.1. Characterization of Nanosized Metal Oxides

The metal oxide powders of NiO, Fe_2O_3 , and WO_3 were elementally analyzed using the XRF technique in order to measure the purity of the materials. The elemental analysis indicated that the purity of metal oxides was $\geq 99.5\%$ and the balance was very minor percentages of Si, Ca, Mg, etc. XRD diffraction was used to identify phases and measure the crystallite sizes. Figure 1a–c present the typical XRD patterns of NiO, Fe_2O_3 , and WO_3 , respectively. The XRD patterns show that these materials are composed of a well-crystalline form of metal oxides, as indicated by well-defined sharp peaks. The measured crystallite sizes of NiO, Fe_2O_3 , and WO_3 were 109–123, 216–347, and 92–180 Å, respectively. The morphology and grain structure of the nanosized metal oxides were investigated. The SEM-TEM images for NiO, Fe_2O_3 , and WO_3 are given in Figure 2. Most of the particles showed a spherical shape in a homogeneous matrix with a particle size of less than 50 nm. Micro- and macropores can be detected in all oxide samples.



Figure 1. XRD phase analysis of nanosized metal oxides: (a) NiO; (b) Fe₂O₃; (c) WO₃.



Figure 2. SEM (a) and TEM (b) images of nanosized metal oxides.

3.2. Reduction Behavior of Metal Oxides

The gaseous reduction of nanosized metal oxide powder of NiO, Fe_2O_3 , and WO_3 was applied to obtain high-purity metals from the corresponding oxides. Two reduction techniques were applied in the present investigation, namely non-isothermal and isothermal processes. A TG-DTA system was used in the non-isothermal experiments and a micro-force balance was used in the isothermal experiments. In both experiments, the reduction was carried out in a continuous flow of H₂ gas. In the non-isothermal reduction experiments, the TG curve was used to follow the reduction reactions, and the corresponding heat of the reaction (DTA) was measured at different reduction steps. In the isothermal experiments, the O₂ weight loss was used to measure the reduction. The investigation of the reduction behavior of nanosized metal oxides using both techniques is important for elucidating the reduction kinetics and mechanism. In addition, it will determine the optimal reduction temperature at which metallic materials can be formed. Furthermore, DTA curves might be used to confirm the stepwise manner of the reduction behavior of metal oxides.

3.2.1. Non-Isothermal Reduction of Nanosized Metal Oxide Powder

The ease of reducibility of nanosized metal oxides plays an important role in the fabrication of metallic materials from their oxides. The kind of metal oxide, purity, and reduction temperature are the main parameters controlling the reducibility of metal oxides. The reduction of nanosized metal oxides by hydrogen was investigated using TG-DTA. This technique was applied to measure accurately both weight loss and the corresponding changes in the heat of the reaction of nanosized metal oxides. The reduction tests were carried out from room temperature up to 1000 °C at a constant heating rate of 10 °C/min. in a 30 mL/min H_2 gas flow. Figure 3a–c show the typical non-isothermal reduction behavior of nanosized NiO, Fe_2O_3 , and WO_3 , respectively. The non-isothermal reduction behavior of NiO given in Figure 3a shows that 2.8 wt.% loss was recorded at 130 °C due to the removal of moisture from the sample as indicated by the TG curve. This is followed by a considerable mass loss which accounts for 21.5 wt % at 285–430 $^\circ$ C. This mass loss resulted from the reduction reaction of NiO (NiO + H_2 = Ni + H_2O), after which no more weight loss could be detected. The DTA curve given in Figure 3a shows the presence of an endothermic peak corresponding to the removal of moisture content followed by an exothermic peak at 400 °C which resulted from the reduction reaction of NiO to Ni. Figure 3b depicts the nonisothermal reduction behavior of Fe₂O₃. The TG curve illustrates that the first reduction step of Fe₂O₃ to metallic iron starts at 375 °C and continues until 460 °C, corresponding to the Fe_2O_3 -to- Fe_3O_4 phase transformation. The second step of the reaction (Fe_3O_4 to wűstite) is very fast and begins at 580 °C; it is followed by the third reaction step (wűstite to iron), which is completed at 830 °C. The total measured weight loss of the Fe_2O_3 to Fe is 30.5 wt %, corresponding to the total O_2 weight loss of Fe_2O_3 to Fe. The DTA curve in Figure 3b indicates the presence of an endothermic peak at 130–150 $^{\circ}$ C as a result of the removal of moisture. The exothermic peak that appears at 350 °C is due to the Fe₂O₃-Fe₃O₄ transformation step. The presence of an endothermic peak at 580 °C is accompanied by the reduction of Fe₃O₄ to wűstite followed by a well-defined endothermic peak at 830 $^{\circ}$ C which results from the reduction of wűstite to metallic iron [11–13]. Figure 3c shows the TG-DTA curves obtained from the reduction of WO₃ to W. The TG reaction behavior reveals no measurable weight loss up to 550 °C, beyond which a small weight loss was observed up to 657 $^{\circ}$ C, which could be related to the partial reduction of WO₃ to lower tungsten oxides [23]. This step is followed by a considerable weight loss of 7.5 wt % at 750 °C which is related to another reduction step producing WO. The final weight loss of 14 wt % was detected at 900–960 °C and resulted from the WO-to-W transformation step. The DTA in Figure 3c shows the presence of an endothermic peak at 130 °C due to moisture removal followed by a broad exothermic peak up to 850 °C. The presence of a sharp endothermic peak at 960 °C is attributed to the last reduction step of WO to W. It can be noticed from the TG of the three metal oxides (Figure 3a–c) that the reduction of NiO is relatively very fast compared with Fe₂O₃-Fe and WO₃-W. This is due to the fact that the reduction reactions of



 Fe_2O_3 and WO_3 proceeded through intermediate reaction steps as was indicated by the presence of different peaks in the DTA curves [12–15].

Figure 3. Non-isothermal reduction of nanosized metal oxides reduced with H₂: (**a**) NiO; (**b**) Fe₂O₃; (**c**) WO₃.

3.2.2. Isothermal Reduction of Metal Oxide Compacts

Figure 4a–c show the isothermal reduction behavior of nanosized NiO, Fe₂O₃, and WO₃, respectively. Reduction tests were undertaken at different temperatures ranging from 700 to 1000 $^{\circ}$ C in a H₂ atmosphere. The extent of reduction was calculated as a function of time, and the reduction curves were plotted. The obtained curves reflect the influence of temperature on the reduction behavior of nanosized metal oxides. For each reduction curve, the rate of reduction was highest at the early stages and gradually decreased with time until the end of the reduction reaction. The reduction behavior of NiO given in Figure 4a shows that the rate of reduction directly increased with the rise in temperature, showing no slowing down in later stages. This indicates that the reduction reaction (NiO to Ni) proceeded very fast and was completed at all temperatures applied as a result of the one-step reduction process. The reduction behavior of Fe₂O₃ given in Figure 4b indicates that there is a delay in the reduction rate in later stages at lower temperatures as a result of the relatively lower reduction rate for the wűstite-iron transformation step. This step is considered the slowest step in the whole reduction process of Fe₂O₃ to Fe; therefore, it controls the overall reduction of Fe_2O_3 to $Fe_1(2,31)$. Figure 4c represents the reduction behavior of WO₃. It can be noticed that the reduction reaction of WO₃ to W could not be completed at <1000 °C. This behavior was previously discussed in the description of the non-isothermal reduction (Figure 3c) in which the reaction was completed at >930 °C. The maximum reduction extents obtained at 700, 800, and 900 °C were 35.25%, 52.53%, and 95.24%, respectively. These results show that the higher the reduction temperature, the higher the extent at which the reaction stopped. The slower reduction rate of WO_3 can be explained in terms of morphological changes accompanying the reduction processes which will be discussed in detail in the next section.



Figure 4. Isothermal reduction behavior of nanosized metal oxides reduced with H₂ at 700–1000 °C: (a) NiO; (b) Fe₂O₃; (c) WO₃.

For a better understanding of the influence of reduction temperature on the behavior of nanosized metal oxides, the typical reduction curves obtained at 700, 800, 900, and 1000 °C for NiO, Fe₂O₃, and WO₃ were plotted together as given in Figure 5a–d, respectively. It can be noticed that the reduction behaviors of NiO and Fe₂O₃ at 700–900 °C are relatively close to each other and far from the reduction behavior of WO₃ and that the difference increased with the increase in the reduction extent. This indicates that each nanosized metal oxide used has its own reduction behavior, particularly at lower reduction temperatures (700–900 °C). The discrepancy in reduction rates of these metal oxides might be due to the difference in the morphologies of the metal oxides and their microstructures.

The morphology and phase analysis of the reduced samples were investigated to explain the variation in the reducibility of nanosized metal oxides and obtain more information about reduction kinetics and mechanisms. Figure 6a–c show the XRD phase analysis of the reduced NiO, Fe₂O₃, and WO₃, respectively. The XRD phase analysis revealed the formation of a well-crystalline metallic phase as a result of the reduction of metal oxides at 1000 °C in a H₂ atmosphere.



Figure 5. Reduction behavior of nanosized NiO, Fe_2O_3 , and WO₃ during the isothermal reduction with H₂ at (a) 700 °C, (b) 800 °C, (c) 900 °C, and (d) 1000 °C.

The reduced products were also examined by optical microscopy and SEM-EDAX. The internal structure and morphology of NiO, Fe₂O₃, and WO₃ samples reduced at 800 and 1000 °C were examined with an optical microscope (RLM). The RLM photomicrographs recorded at 800 °C are given in Figure 7a–c, and those recorded at 1000 °C are given in Figure 7d–f. To a great extent, these images reflect the effect of reduction temperature on the microstructure changes accompanying the reduction reactions. Increasing the reduction temperature from 800 °C to 1000 °C leads to the densification of the freshly reduced metal nuclei. In the case of NiO, the predominant sintering started early and continued until the end of reduction, and special consideration is given to the relatively lower softening and melting point of Ni. The grains in the case of reduction of Fe_2O_3 and WO_3 are less dense. This behavior is expected due to the incomplete reduction of both oxides at relatively lower reduction temperatures. For Fe₂O₃, the reduction is completed at <800 °C, resulting in less chance for sintering at 800 °C (Figure 7c) and a greater sintering effect at 1000 °C (Figure 7d). On the other hand, the reduction of WO₃ to WO (grey nanoparticles) at 800 °C proceeded, showing no sintering effect (as shown in Figure 7e). With a further rise in temperature up to 1000 °C, where metallic tungsten is formed, the micro-grains of W became relatively larger and less dense, as depicted in Figure 7f. In conclusion, the sintering effect has a weak effect on the reduction of Fe_2O_3 and WO_3 due to the formation of lower oxides prior to the formation of iron and tungsten metals which was recorded at 850 and 960 °C, respectively.



Figure 6. XRD phase analysis of nanosized metal oxides reduced with H₂ at 1000 °C: (a) NiO; (b) Fe_2O_3 ; (c) WO_3 .

The SEM images with EDX analysis of the nanosized metal oxides reduced at 1000 °C are shown in Figure 8. The reduced Fe₂O₃ shown in Figure 8b shows that the grains are still affected by sintering and almost have the same structure with well-defined boundaries. This resulted from the step reduction process where the formation of metallic iron was not completed at temperatures of up to 850 °C, and the reduced metallic iron that was heated to 1000 °C for 15 min showed less effect of sintering compared to Ni metal. Figure 8c shows the grain structure in the WO₃ reduced to W at 1000 °C. The WO₃ was completely reduced to W at >930 °C, and the time left for sintering was about 7 min, which shows no measurable effect on the morphology of the grains compared to others.



Figure 7. RLM photomicrographs of nanosized metal oxides reduced with H₂ at 800 and 1000 °C: (**a**,**b**) NiO; (**c**,**d**) Fe₂O₃; (**e**,**f**) WO₃.



Figure 8. SEM-EDAX images of nanosized metal oxides reduced with H_2 at 1000 °C: (a) NiO; (b) Fe₂O₃; (c) WO₃.

3.3. Reduction Kinetics and Mechanism

Studying the kinetics and mechanism of gaseous reduction of metal oxides by hydrogen is important for testing the possibility of fabrication of metallic materials from metal oxides via powder technology. There are many mathematical equations applied to test and predict the rate-controlling mechanism of reduction reactions in different stages. The calculation of the apparent activation energy (*Ea*) values is one of the common techniques for identifying the reduction mechanism. The apparent activation energy (*Ea*) values were calculated by applying the Arrhenius equation:

$$K_r = K_0 e^{-Ea/RT}$$

where K_r is the reduction rate constant, Ko is the frequency factor, R is the gas constant, and T is the absolute temperature. The relationships between the logarithm of the rate of reduction (dr/dt) of NiO, Fe₂O₃, and WO₃ and the reciprocal of the absolute temperature 1/T were plotted in initial stages (5–10% extent) and in later stages (80–85% extent) as given in Figure 9a,b, respectively. From the Arrhenius plots, the apparent activation energy (*Ea*) values in early and later stages were computed (Table 1) and tabulated together with the *Ea* value range corresponding to the different rate-controlling steps [32,33].



Figure 9. Arrhenius plots for the reduction of nanosized NiO, Fe_2O_3 , and WO_3 with H_2 at 700–1000 °C: (a) initial stages; (b) later stages.

<i>Ea</i> Values (kJ/mol) and the Corresponding Rate-Controlling Step		Oxide	Ea Initial	Ea Initial
Ea Values	Rate-Controlling Step		(KJ/IIIOI)	(KJ/1101)
8–16	Gas diffusion	NiO	9.6	13.24
29–42	Combined gas diffusion and interfacial chemical reaction	Fe ₂ O ₃	12.43	21.65
>90	Solid-state diffusion	WO ₃	23.68	-

Table 1. Apparent activation energy (Ea) values for the reduction of nanosized metal oxides.

In the present study, nanosized metal oxides were reduced with H₂ at 700–1000 $^{\circ}$ C, and the computed *Ea* values given in Table 1 indicate the following:

• In the initial stages (5–10% extent), the *Ea* values obtained from the reduction of NiO and Fe₂O₃ are 9.6 and 12.43 kJ/mole, indicating that the reduction is controlled by a gaseous diffusion mechanism. The *Ea* value for WO₃ is relatively high (23.68 kJ/mole) but is still in the range of the gas diffusion mechanism. The considerable difference in the *Ea* values between NiO, Fe₂O₃, and WO₃ is in accordance with the slower reduction rate of WO₃ compared to other oxides, as was previously shown in Figure 4a–c. This finding is in agreement with the principles of gas–solid reactions in which the rate-determining step is considered the slowest step in the whole reactions [11–15]. In the present study, nanosized metal oxides were reduced in a H₂ atmosphere, and the

chemical reaction easily proceeded at the grain surface. The produced metallic phase at this stage could not be able to surround the whole oxide grain surface. Under these conditions, the gas diffusion inside the oxide grains is relatively the slowest process in the gas–solid reaction and is considered the determining step.

In the later stages (80–85 % extent), the *Ea* values for the reduction of NiO and Fe₂O₃ are 13.24 and 21.65 kJ/mole, indicating that the reduction reactions are still also controlled by the gaseous diffusion mechanism. On the other hand, the *Ea* value for the reduction of WO₃ could not be calculated due to the stopping of reduction at 700–900 °C at lower extents depending on the applied reduction temperature, and the reduction is completed only at 1000 °C.

Based on the above results, it can be reported that the thermal gaseous reduction technique is a promising route for the fabrication of metallic materials from nanosized metal oxides. The nanosized powders of NiO, Fe₂O₃, and WO₃ can be reduced completely in pure hydrogen at a temperature greater than 900 °C. As the reduction rates of the three nanosized metal oxides vary in the following sequence NiO > Fe₂O₃ > WO₃, the presence of NiO is very important for enhancing the overall rate of the reduction. It is expected that the presence of NiO and/or Fe₂O₃ will accelerate the rate of reduction of WO₃ during the synthesis of heavy tungsten alloys from a nanosized composite material (WO₃-Fe₂O₃-NiO).

4. Conclusions

The nanosized powders of NiO, Fe₂O₃, and WO₃ were physically and chemically characterized by XRD, RLM, SEM-EDAX, and TEM. These metal oxides were non-isothermally and isothermally reduced in H₂ gas flow, and the weights were continuously recorded. The TG-DTA technique was applied for the non-isotheral reduction at 1000 °C, while a microforce balance was used in the isothermal reduction tests at 700–1000 °C. In non-isothermal tests, it was found that the reduction of NiO proceeds at 375 to 430 °C, showing an exothermic peak at 400 °C. The reduction of Fe₂O₃ to metallic iron proceeded in a stepwise manner through magnetite and wűstite phases, showing an exothermic peak at 460 °C (Fe₂O₃ to Fe₃O₄), an endothermic peak at 580 °C (Fe₃O₄ to wűstite), and an endothermic peak at 830 °C corresponding to the last reaction step from wűstite to metallic iron. The reduction of WO₃ also proceeded in a stepwise manner through intermediate lower oxides. A broad endothermic peak resulting from intermediate reaction steps was observed at 550–850 °C and was followed by a sharp endothermic peak at 960 °C corresponding to the last step of reduction to metallic tungsten.

In isothermal reduction tests, the rate of reduction of metal oxides at 700–1000 °C increased in the order NiO > Fe₂O₃ > WO₃. The reduction of WO₃ was only completed at 1000 °C, while at lower temperatures it was stopped at different extents depending on the applied temperature. The computed values of activation energy (*Ea*) indicated the reduction of metal oxides was controlled by gaseous diffusion in the initial stages, which is still valid in the later stages for only NiO and Fe₂O₃. The *Ea* value for WO₃ could not be determined due to the reduction stopping before completion at 700–900 °C.

The morphology and structure of the reduced metal oxides revealed that Ni grains are enlarged due to the sintering effect, so their size was greater than that in the case of Fe_2O_3 and WO_3 . This is attributed to the reduction of NiO to Ni which was completed at <450 °C leading to the sintering of the freshly reduced metal, giving larger grain sizes. The sintering effect is weaker in the reduction of Fe_2O_3 and WO_3 due to the formation of lower oxides prior to the formation of iron and tungsten metals which was recorded at 850 and 960 °C, respectively.

The present work confirms the possibility of using a reduction technique for nanopowder metal oxides in the synthesis of metallic alloys instead of traditional powder metallurgy. The understanding of the kinetics and mechanism of reduction reactions enables us to determine the optimal conditions for the fabrication of metallic alloys from nanosized materials. Accordingly, future work will focus on the synthesis of heavy tungsten alloys from blended nanosized metal oxides. Author Contributions: Conceptualization, K.S.A.H. and A.A.E.-G.; methodology, K.S.A.H., M.R, A.H., and A.A.E.-G.; software, M.I.N. and N.F.; validation, K.S.A.H., A.S.A., M.R. and A.A.E.-G.; formal analysis, M.I.N., K.S.A.H.; investigation, A.A.E.-G., A.S.A.; resources, N.F., M.R.; data curation, K.S.A.H. and A.A.E.-G.; writing—original draft preparation, K.S.A.H., A.A.E.-G., M.I.N.; writing—review and editing, M.I.N. and A.A.E.-G.; visualization, M.R.; supervision, A.S.A.; project administration, K.S.A.H.; funding acquisition, A.S.A. All authors have read and agreed to the published version of the manuscript.

Funding: This research has been funded by the Scientific Research Deanship at the University of Ha'il, Saudi Arabia, through project number RG-22 028.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest.

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