

CARBOTHERMIC REDUCTION OF MECHANICALLY ACTIVATED NiO-CARBON MIXTURE: NON-ISOTHERMAL KINETICS

S. Bakhshandeh, N. Setoudeh*, M. Ali Askari Zamani, A. Mohassel

Yasouj University, Materials Engineering Department, Yasouj, Iran

(Received 23 March 2018; accepted 10 December 2018)

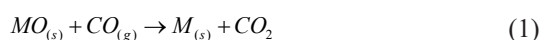
Abstract

The effect of mechanical activation on the carbothermic reduction of nickel oxide was investigated. Mixtures of nickel oxide and activated carbon (99% carbon) were milled for different periods of time in a planetary ball mill. The unmilled mixture and milled samples were subjected to thermogravimetric analysis (TGA) under an argon atmosphere and their solid products of the reduction reaction were studied using XRD experiments. TGA showed that the reduction of NiO started at ~800°C and ~720°C in un-milled and one-hour milled samples respectively whilst after 25h of milling it decreased to about 430°C. The kinetics parameters of carbothermic reduction were determined using non-isothermal method (Coats-Redfern Method) for un-milled and milled samples. The activation energy was determined to be about 222 kJ mol⁻¹ for un-milled mixture whilst it was decreased to about 148 kJ mol⁻¹ in 25-h milled sample. The decrease in the particle size/crystallite size of the milled samples resulted in a significant drop in the reaction temperature.

Keywords: Ball milling; Carbothermic reduction; Nickel oxide; Non-isothermal kinetics; Thermo-gravimetric analysis (TGA).

1. Introduction

There have been many investigations on the carbothermic reduction of metal oxide in the literature and the mechanism of this reaction has been the subject of intense research [1-5]. Recently, the use of solar energy for production of metals from their oxides with carbothermal process has been a subject of the study to optimize the carbothermal reduction of MgO using concentrated solar energy in low vacuum conditions [6]. Several mechanisms have been proposed to explain the carbothermic reduction between two solid reactants (such as oxide and carbon) and the formation of solid metal. The oldest and most widespread mechanism in this regard is the oxide reduction through gaseous intermediate CO_(g) and CO₂ in accordance with the following reactions [7]:



The carbothermic reduction of nickel oxide and reduction of NiO with CO_(g) have been studied under different conditions by many researchers [8-15]. It has been reported that the reduction of NiO is attributed to the special class of solid-state reactions where the

solid product catalyzes the reaction rate [11].

It has been shown that mechanical activation by milling reactants together with extended periods of time can intensify the reactions [16-19]. During mechanical activation and ball milling processes, the reactant materials are intimately mixed at the nanoscale. Previous works have indicated the rate of carbothermic reduction reactions can be greatly increased by pre-milling the mineral and carbon together compared to with powders milled separately and then mixed [16-19]. The effect of mechanical activation and extended milling on the carbothermic reduction of manganese ore [18], ilmenite [20], hematite [21], titanium oxides [22] celestite [19, 23], and carbonitridation of zircon [24] have been studied recently. The results show that, generally, the longer the samples are milled together the greater the extent of reaction at lower temperatures is [24]. Reduction of nickel oxide by graphite during ball milling at both ambient and elevated temperatures has been studied by Yang and McCormick [25]. Their results showed that milling significantly reduced the critical reaction temperature for reduction [25].

There are many research works about the carbothermic reduction of nickel oxide. However, the kinetics of reduction reaction between NiO and carbon has been studied under an isothermal condition

*Corresponding author: nsetoudeh@yu.ac.ir

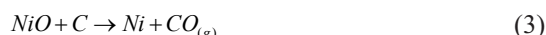


in the previous works [8, 11-14]. Reduction of nickel oxide with carbon, polyethylene, and polystyrene has been investigated under non-isothermal conditions in the temperature range 20-1000°C. The authors indicated that at heating rates of 5-20 K/min, both carbon and polyethylene reduce nickel oxide. Moreover, they determined that the effective activation energies of NiO reduction with carbon are about 284 kJ mol⁻¹ (68 kcal mol⁻¹) [15].

The present work was conducted in order to study the effects of mechanical activation on the carbothermic reduction of nickel oxide with activated carbon. The aim of this work is to investigate the kinetics of carbothermic reduction of nickel oxide under non-isothermal conditions for un-milled mixture and milled samples. The kinetics parameters for both un-milled and milled samples are determined using Coats-Redfern method. Moreover, the fundamental characteristics of both un-milled mixture and milled samples are examined using TGA, XRD, and SEM analyses.

2. Experimental

The characteristics of starting materials (nickel oxide and carbon active with purity of 99%) are listed in Table 1. The amount of ash for carbon active was less than 1%. Stoichiometric mixtures of NiO-Carbon (86.148 wt.% of NiO and 13.852 wt.% of carbon active) were prepared based on reaction (3).



Thermodynamic calculations indicate the value of ΔG^0 for reaction (3) is negative at a temperature above ~440°C at standard conditions [26,27].

Table 1. The characteristics of starting materials.

Characteristic of materials	Nickel oxide (NiO)	Carbon active
Colour	black	black
Structure	Cubic (JCPDS-71-1179)	amorphous
Size analyses (µm)	d(0.1) = 0.86	d(0.1) = 4.961
	d(0.5) = 6.153	d(0.5) = 18.806
	d(0.9) = 24.805	d(0.9) = 58.392

The stoichiometric mixtures were mechanically milled in a closed chamber using a planetary ball mill (Farapazhouhesh, FP2 model) for different milling times. The milling conditions for all runs were: a rotation speed of 600 rpm, high-chromium steel balls (20 mm diameter), high-chromium steel milling chamber, and the ball-to-powder weight ratio of 40:1. Thermogravimetric analysis (TGA) was carried out on the NiO-carbon mixtures at the heating rate of 10 C/min up to 1,200°C under the flow of argon (99%purity, flow rate of 5 mL/min) using a

thermogravimetric analyzer (BAHR thermoanalyzer-STA503-GmbH). Physical mixtures of raw materials (NiO-Carbon active) was prepared in accordance with the stoichiometric mixture given by reaction (3) in order to study the carbothermic reduction in the un-milled samples,

All solid products were analyzed using X-ray diffraction (XRD, Philips Analytical, Co-K α radiation, 40 kV, 40 mA, X'Pert APD) over a 2 θ range of 20-100° and 2 sec count time for every 0.05° step. The microstructures of the as-milled and the heated samples were studied using a scanning electron microscope (TESCAN-VEGA3). The crystallite size of solid products in the as-milled samples was determined using the well-known Scherrer equation.

3. Results and discussion

3.1 Characterization of mixtures

Fig. 1 illustrates the XRD patterns of the as-milled samples for different milling times. The major peaks of NiO (JCPDS card file No. 71-1179) were clearly observed in the 25h as-milled sample. Therefore, based on the XRD results in Fig. 1, reduction of nickel oxide by carbon active cannot occur after 25h milling. Thermodynamic calculations [26-27] indicate that reaction (3) is endothermic and feasible at temperatures above of 440°C. Therefore, the signs of NiO in the XRD patterns of as-milled samples (Fig.1) clearly show that the temperature of solid mixtures in the milling vial can never reach 440°C after 25 hours of milling. The broadening of the main peak of NiO at $2\theta \approx 50.7^\circ$ ($d=2.08794\text{\AA}$, 200) with increasing milling time (Fig. 1) may be related to the reduction of mean crystallite size. It is worth noting that reduction of mean crystallite size of particles and amorphization, a well-known phenomenon during high-energy ball milling, results in not only decreased peak intensity but broadening of the peak width as well [28-29]. Table 2 lists the mean crystallite sizes of the nickel oxide for different milling times. The crystallite size of nickel phase was determined using Scherrer equation based on its main peak (i.e., $2\theta=50.705$). The results in Table 2 show that with increasing milling time, the crystallite size of nickel oxide decreases and reaches about 20 nm in 25h milled sample.

Table 2. The values of crystallite size of nickel oxide and percent of iron contamination in the as-milled samples with increasing milling times.

Milling time (hr.)	Crystallite size (nm)	Amount of Iron (in ppm)
1	38.76	6.61
5	28.91	12.41
10	25.56	11.54
15	25.78	13.92
25	19.84	14.72



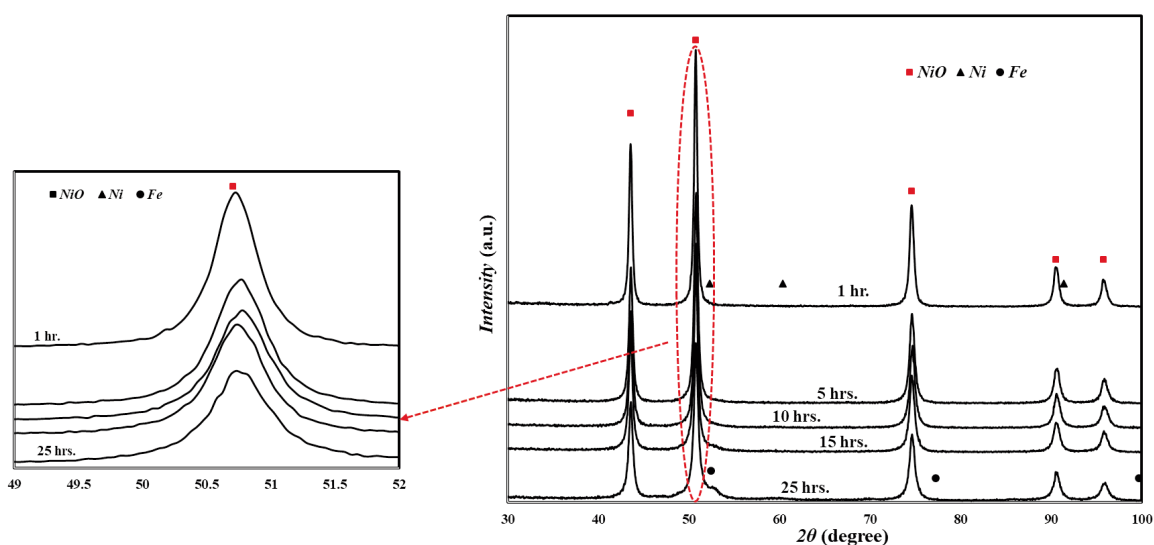


Figure 1. XRD patterns of the as-milled samples in different milling times.

A weak sign is observed at about 52° in the 25h milled sample. Although elemental nickel has a peak at $2\theta \approx 52^\circ$, however thermodynamic calculations [26-27] indicate that carbothermic reduction of nickel oxide cannot occur at a temperature below 440°C . The trace of a new peak at $2\theta \approx 52^\circ$ disappeared after acid washing of the 25h as-milled sample with dilute hydrochloric acid (1 N). The acid washing was done in order to remove any iron contamination in the milled powders due to abrasion milling media and ball collisions events during milling operations. The percentage of the iron content in the milled powders is listed in Table 2. Clearly, the content of iron contamination increases with milling time. Therefore, the trace of a new peak at about 52° may be attributed to iron contamination during milling operations.

Fig. 2 presents SEM micrographs of raw mixtures and milled powders. It is clear from Fig.2a that the particle sizes of carbon content in the raw mixture are much larger than those of agglomerated nickel oxide particles. A decrease in the size of particles with milling time was observed in the SEM micrographs of milled mixtures (Figs. 2b to 2d). The XRD results (Fig. 1) show that reduction reaction of nickel oxide to metallic nickel cannot occur during mechanical activation of NiO-Carbon mixture. However, milling significantly reduces the particle/crystallite size and microstructural refinement is observed in the milled samples (Fig. 2).

Considering the XRD patterns in Fig. 1 and the values in Table 2, 1h and 25h milled samples were prepared for TGA under argon atmosphere. To compare the results of milled samples with the un-milled mixture, TGA was also done on the un-milled stoichiometric mixture of NiO-Carbon under an argon atmosphere flow.

Fig. 3 shows the TGA traces of un-milled and milled stoichiometric mixtures of NiO-Carbon under pure argon atmosphere. The mass loss up to $\sim 430^\circ\text{C}$ in the 25h milled sample is likely due to desorption of gas from activated carbon. An increase in gas sorption onto activated carbon after milling alone and with harder phases has been demonstrated previously [24, 30-32]. The main mass loss starts in un-milled and one-hour milled samples at 800°C and 720°C , respectively; however, it begins in 25h milled sample at a lower temperature ($\sim 430^\circ\text{C}$). According to reaction (3), the complete reduction of nickel oxide with carbon should cause a weight loss of 32.3%. This event is observed in TGA curve for un-milled and 1h milled mixtures at $\sim 1000^\circ\text{C}$ and at $\sim 630^\circ\text{C}$ for 25h milled sample. The total mass losses of samples in the TGA analyses (Fig. 3) are consistent with the theoretical value of 32.3% calculated from reaction (3). Therefore, TGA results indicate that the reaction between NiO and carbon active is completed in both un-milled mixture and 1h milled samples after heating in argon atmosphere up to $\sim 1000^\circ\text{C}$. The results of TGA graphs also show that milling significantly reduces the critical reaction temperatures from 800°C in the un-milled sample to $\sim 430^\circ\text{C}$ for the 25h milled sample. Table (2) indicates that with increasing milling time, the crystallite size of NiO decreases to ~ 20 nm in the 25-h milled sample. According to Fig.2, the particle refinement also observes in the SEM micrographs of milled samples. Therefore, the microstructural refinement due to milling operations results in significant reduction in the critical temperature of TGA analyses. The previous study on the reduction of NiO with graphite revealed that the decreasing in particle size during milling causes a significant reduction in reaction temperature during subsequent heating [25].

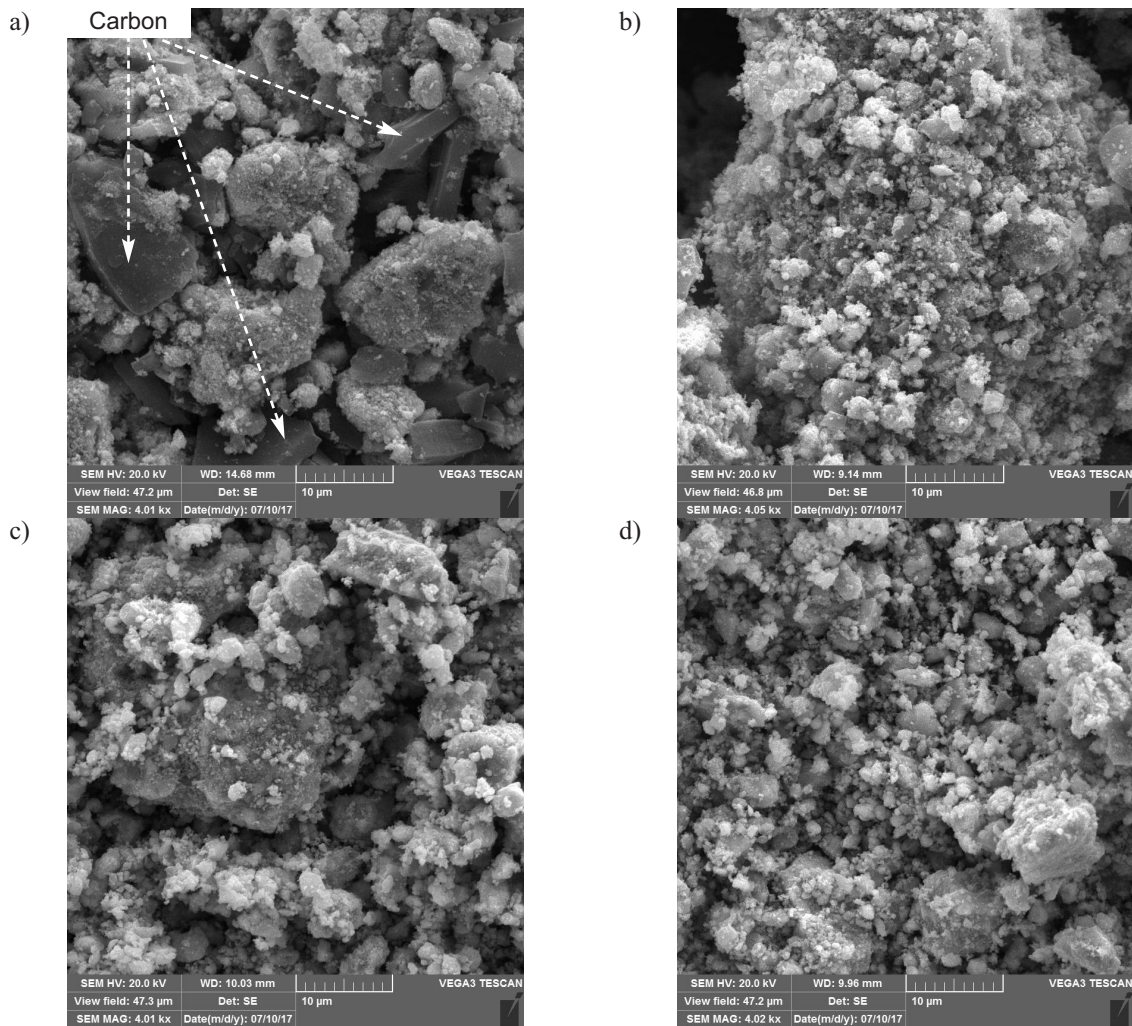


Figure 2. SEM micrographs of raw mixture and as-milled powders: (a) raw mixture; (b) 1 hour milled sample; (c) 15 hours milled sample; (d) 25 hours milled sample.

Fig.3 shows a mass gain takes place in the 25h milled samples after heating above $\sim 630^{\circ}\text{C}$ and continues up to 1100°C . It seems that a reaction to being occurred in the temperature range of $630\text{--}1100^{\circ}\text{C}$ under argon atmosphere for 25h milled sample. It may be presumed that the reduced metallic nickel phase (the solid product of reaction 3) reacts with an impurity of argon atmosphere (oxygen). This scenario confirms the presence of traces of nickel oxide peak in the XRD analysis of the solid residual sample of TGA analysis under argon atmosphere in 25h milled sample.

Other mixtures of NiO-Carbon were prepared to give NiO:Carbon molar ratio of 1:1.5 (50% excess of stoichiometry according to reaction 3). These new mixtures were also milled in a planetary ball mill for 25h under milling conditions same as stoichiometric NiO-Carbon mixtures. Fig 4 indicates the TGA graphs for 25h milled samples with stoichiometric mixture and NiO-Carbon mixture with a molar ratio of 1:1.5 under argon atmosphere. It is clear from Fig.4 that the

25h milled samples have three stages of mass loss. Those traces of mass losses are same for both samples up to $\sim 500^{\circ}\text{C}$. Heating beyond 500°C results in continuing mass loss in the 1:1.5 ratios (NiO:Carbon molar ratio of 1:1.5) and reaching about 38% at 800°C . Traces of nickel oxide are not observed for 1:1.5 sample in the XRD pattern of the solid residuals of the TGA analysis. Although few mass gains are observed beyond heating 800°C in the 1:1.5 molar ratios, however the results of Fig.4 show that the addition of carbon more than stoichiometric ratio is effective and plays a significant role in the carbothermic reaction of nickel oxide.

Fig. 5 presents the rates of mass losses (dTGA) for un-milled mixture and milled samples. Those traces were driven from Fig. 1 by differentiating the curves mathematically. The curves demonstrate the reaction regions in the un-milled mixture and milled samples. The dTGA graphs (Fig. 5) indicate that there is only one single continuously smooth peak evident in all

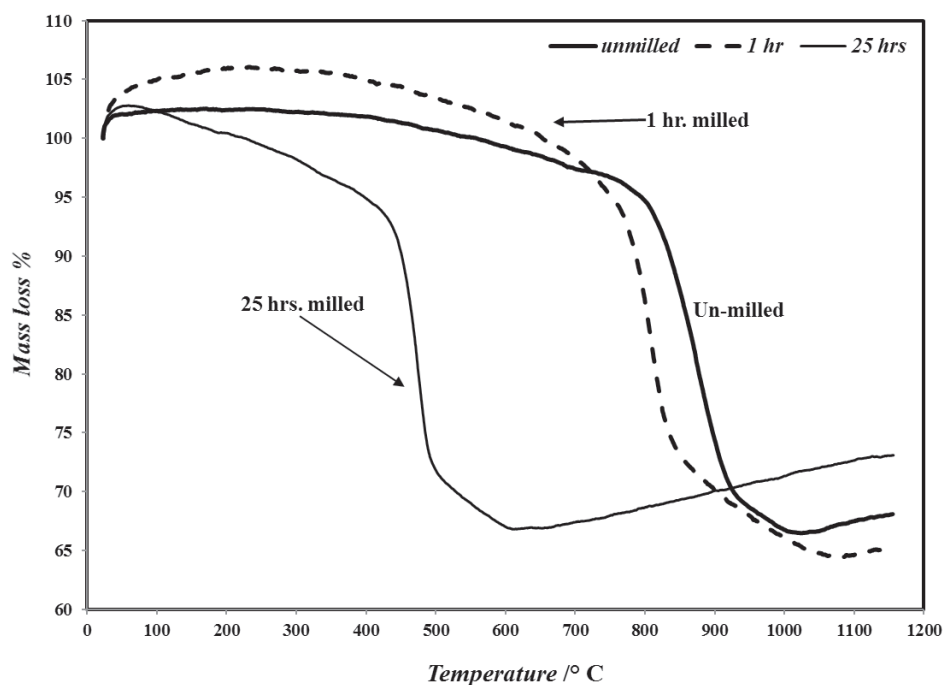


Figure 3. TGA traces of un-milled mixture and milled sample of NiO-Carbon with stoichiometric ratio under pure argon atmosphere.

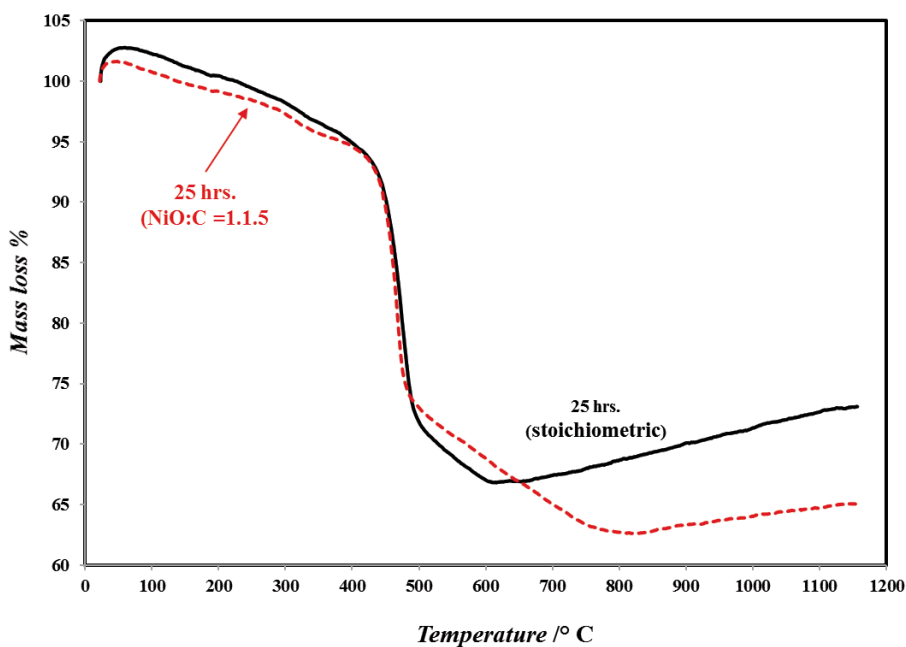


Figure 4. TGA graphs for 25 hours milled mixture of NiO-Carbon with stoichiometric ratio and 25 hours milled mixture of NiO-Carbon with molar ratio of 1:1.5 under argon atmosphere.

samples (un-milled and milled samples), confirming the presence of a single reaction. In the case of multiple sequential reactions in the reduction of nickel oxide by carbon, the peak is expected to be discontinuous with shoulders or other peaks becoming evident. Fig. 5 show that the temperatures of those

single peaks in dTGA graphs decrease with increasing milling time. The peak temperature is about 870°C in the un-milled mixture and, finally, is reduces to ~470°C in the 25h milled sample. Therefore, Fig. 5 shows that an increase in milling time is accompanied by a decrease in the critical reduction temperature.

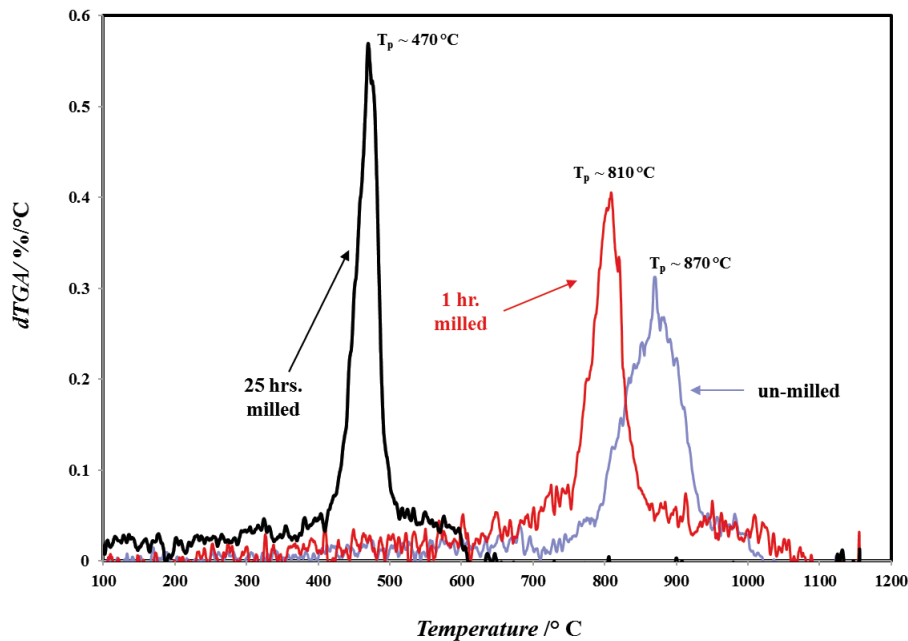


Figure 5. The rates of mass losses ($dTGA$) for un-milled mixture and milled samples driven from figure 3. The peak temperature (T_p) of each sample has been indicated at $dTGA$ graph.

3.2 Non-isothermal kinetics study

The kinetics of carbothermic reduction of nickel oxide in the un-milled and 1h and 25h milled samples were studied by TGA under non-isothermal conditions. The kinetics parameters can be obtained from non-isothermal rate laws by both model-fitting and isoconversional (model-free) methods [3, 33-34]. Model-fitting methods involve fitting different models to extent of reaction (α) versus temperature curves (α -temperature) and simultaneously determining the activation energy (E) and frequency factor (A) [3]. There are several non-isothermal model-fitting methods, with the Coats-Redfern method being among the most popular ones [3, 34]. By plotting the left-hand side of equation (4), which includes the integral reaction model versus (temperature in Kelvin), the activation energy (E_a) and frequency factor (A) can be obtained from the slope and intercept of the curve, respectively [3].

$$\ln \left[\frac{g(\alpha)}{T^2} \right] = \ln \left[\frac{AR}{\beta E_a} \left(1 - \frac{2R\bar{T}}{E_a} \right) \right] - \frac{E_a}{RT} \quad (4)$$

where R , β , and \bar{T} in equation (4) are gas constant ($8.314 \text{ J.mol}^{-1}\text{K}^{-1}$), heating rate (k min^{-1}), and mean experimental temperature, respectively. Several reaction models including differential reaction model, $f(\alpha)$, and integral reaction model are listed in Table 3. The extent of reaction (α) for all samples can be calculated using the thermogravimetric data (Fig. 3) by the following equation [3]:

$$\alpha = \frac{(w_0 - w_t)}{(Bw_0)} \quad (5)$$

where w_0 and w_t are masses of the sample initially and at the time (t) respectively and B is the fraction of mass loss for complete reduction reaction of NiO to nickel. These data can be obtained from TGA graphs (Fig.3) for each sample. Fig. 6 illustrates the variations of the extent of reaction (α) versus temperature using equation (5) for the un-milled mixture and 1h and 25h milled samples. Fig. 6 shows that the required temperatures for starting the carbothermic reaction of NiO decrease with an increase in milling time. The reaction temperatures in Fig. 6 are in reasonable agreement with results of Table 2 and Figs. 2 and 3. Therefore, the results demonstrate the significant role of a decrease in crystallite/particle sizes of NiO caused by milling on the carbothermic reaction kinetics.

By inserting various integral reaction models, $g(\alpha)$ in Table 3 into equation (4), Arrhenius parameters are determined for all samples from plotting $\ln \left[\frac{g(\alpha)}{T^2} \right]$ versus $\frac{1}{T}$. The temperature ranges for all samples are selected using TGA and $dTGA$ graphs (Figs. 3 and 5). The integral reaction models in Table 3 are inserted in equation (4) and the model that gives the best linear fit is selected as the optimum one. Meanwhile, it is proved that the theoretical values of pre-exponential factors for solid-state reactions are in the range of $10^6 - 10^{18} \text{ s}^{-1}$ [3].

Using variations of extents of reaction (Fig. 6) and by plotting $\ln \left[\frac{g(\alpha)}{T^2} \right]$ versus $\frac{1}{T}$ curves for all models in Table 3, the first order model (Mampel) resulted in the best linear fit.

Table 3. The common reaction rate models in the solid-state reactions [3, 34].

Reaction model	$f(\alpha)$	$g(\alpha)$
Nucleation Models		
Power law	$4\alpha^{3/4}$	$\alpha^{1/4}$
Power law	$3\alpha^{2/3}$	$\alpha^{1/3}$
Power law	$2\alpha^{1/2}$	$\alpha^{1/2}$
Avrami-Erofeev	$4(1-\alpha)[- \ln(1-\alpha)]^{3/4}$	$[- \ln(1-\alpha)]^{1/4}$
Avrami-Erofeev	$3(1-\alpha)[- \ln(1-\alpha)]^{2/3}$	$[- \ln(1-\alpha)]^{1/3}$
Avrami-Erofeev	$2(1-\alpha)[- \ln(1-\alpha)]^{1/2}$	$[- \ln(1-\alpha)]^{1/2}$
Diffusion Models		
One dimensional diffusion	$\frac{1}{2}\alpha^{-1}$	α^2
Diffusion control (Jander)	$2(1-\alpha)^{2/3}[1-(1-\alpha)^{1/3}]-1$	$[1-(1-\alpha)^{1/3}]^2$
Diffusion control (Crank)	$\frac{3}{2}[(1-\alpha)^{-1/3}-1]^{-1}$	$1-\frac{2}{3}\alpha-(1-\alpha)^{2/3}$
Reaction order and geometrical contraction models		
Mampel (first order)	$1-\alpha$	$-\ln(1-\alpha)$
Second order	$(1-\alpha)^2$	$(1-\alpha)^{-1}-1$
Contracting cylinder	$2(1-\alpha)^{1/2}$	$1-(1-\alpha)^{1/2}$
Contracting sphere	$3(1-\alpha)^{2/3}$	$1-(1-\alpha)^{1/3}$

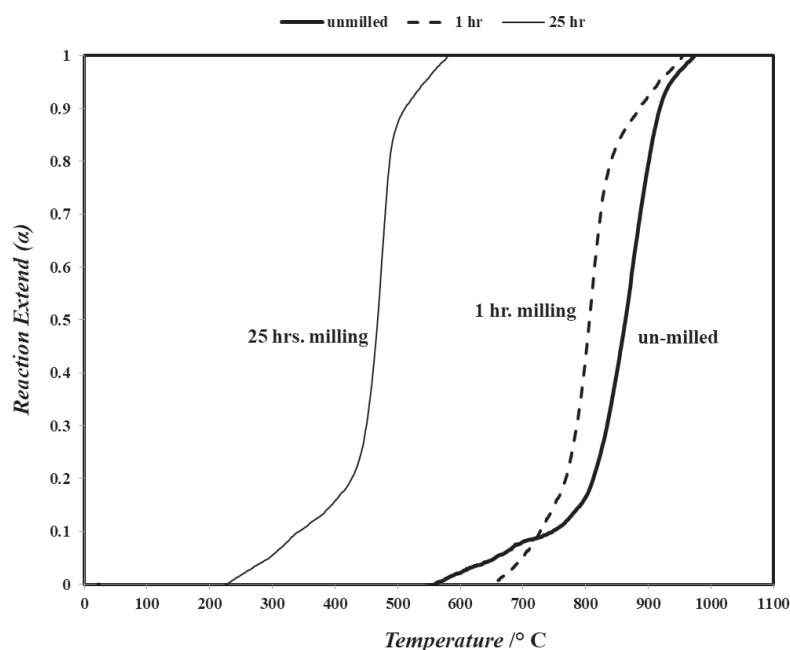
**Figure 6.** The variations of extend of reaction (α) versus temperature using equation (5) for un-milled mixture, 1 hour and 25 hours milled samples.

Fig. 7 presents the corresponding plots of the first-order model for the un-milled mixture and 1h and 25h milled samples. The first order model (Mampel) in Table 3 shows the chemically-

controlled mechanism for carbothermic reduction of nickel oxide. The set of Arrhenius parameters for the un-milled mixture and 1h and 25h milled samples is presented in Table 4.

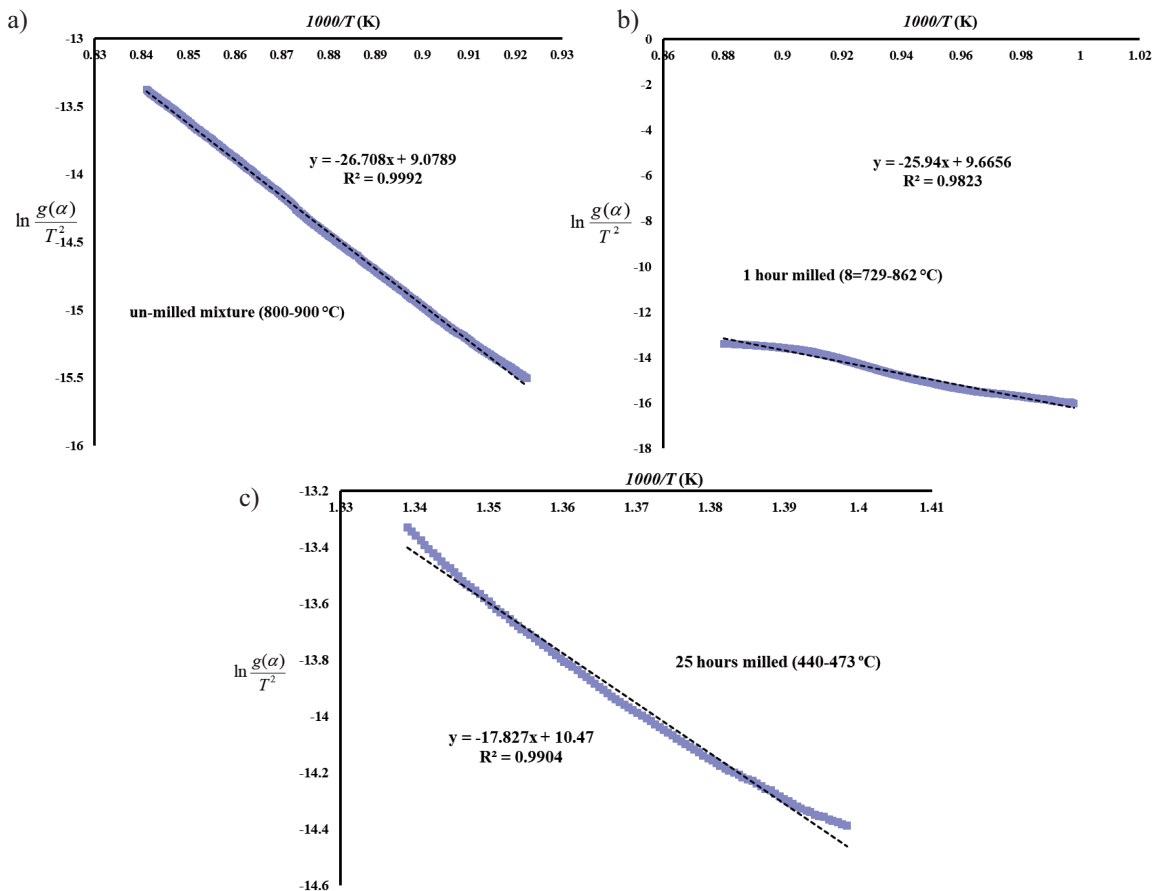


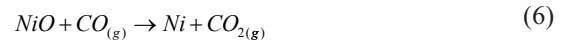
Figure 7. The plots of $\ln\left[\frac{g(\alpha)}{T^2}\right]$ versus $\frac{1}{T}$ for first-order model (Mampel) of:
a) un-milled mixture; b) 1 hour and c) 25 hours milled samples.

Table 4. Arrhenium parameters for non-isothermal carbothermic reduction of nickel oxide according to first order (Mampel) model.

Sample	un-milled	1 hr milled	25 hrs. milled
Activation energy E (kJ mol ⁻¹)	222	215	148
Pre-exponential constant A	2.34×10 ⁹	4.09×10 ⁹	6.28×10 ⁹

3.3 Reaction kinetics parameters

The previous investigations about the carbothermic reduction of metal oxide indicate that a direct reaction between the solid oxide and solid carbon is important only when the gaseous products of the reaction, CO and CO₂, are immediately released from the reaction system [1]. The direct reaction can only proceed at the contact points between the two solid reactants (metal oxide and carbon) [1]. Therefore, the carbothermic reduction of NiO takes place in accordance with reaction (6) and Boudouard reaction (reaction 2).



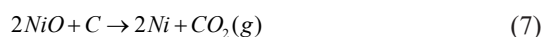
If the nickel oxide particles cannot be in contact with carbon particles, it is expected that the major reducing role in the carbothermic reaction of nickel oxide is that of CO_(g), which is formed according to Boudouard reaction (reaction 2). It has been reported that the reaction between NiO and CO_(g) is fast compared to Boudouard reaction [11]. In other words, the rate of carbothermic reduction of NiO is controlled by the rate of CO_(g) supplying using Boudouard reaction. The autocatalytic nature of the reduced nickel metal phase is also known and the reduced nickel metal phases catalyze the Boudouard reaction in progressing reduction reaction [11]. Nickel is also known to be one of the active catalysts for gasification of activated carbons and less valuable coals at low temperature [35]. Therefore, it is concluded that Boudouard reaction plays a significant role in the carbothermic reduction of nickel oxide.

The standard free energy (ΔG^0) of Boudouard reaction is negative at above 700°C at the standard atmospheric pressure. Thermodynamic assessments

also show that the lowest temperature for carbothermic reduction of NiO by carbon (reaction 3) is about $\sim 440^\circ\text{C}$ under the standard atmospheric pressure [26-27]. The onset temperature of carbothermic for un-milled mixture and 1hour milled sample are $\sim 800^\circ\text{C}$ and $\sim 770^\circ\text{C}$, respectively (Figs. 3 and 5). Figs. 3 and 5, however, indicate that the onset temperature of 25h milled sample reduces to $\sim 400^\circ\text{C}$.

Many researchers have reported different values of activation energy for carbothermic reduction of NiO under isothermal conditions [8, 10, 11, 14, 15]. Sharma et al. [12-14] studied the reduction of NiO with natural graphite in vacuum and reported an activation energy of 313 kJmol^{-1} (75 kcal mol^{-1}) using the first-order plots. The activation energy value for reduction of NiO by active charcoal powder was reported to be about 207 kJmol^{-1} ($49.47\text{ kcal mol}^{-1}$) for the non-catalytic carbothermic case [11]. Krasuk et al. [8] observed the first-order reduction reaction of NiO by $\text{CO}_{(g)}$ and reported an activation energy of 196 kJmol^{-1} (47 kcal mol^{-1}) over the temperature range of 566 to 682°C . The activation energy of the Boudouard reaction has been reported to be 200 - 250 kJmol^{-1} [1]. The present work showed that the activation energy values for un-milled mixture and 1h milled sample (Table 4) are in good agreement with those reported by Krasuk [8] and Satish [11]. The results in Table 4 also show that the values of activation energy for un-milled mixture and 1h milled samples are in good agreement with the activation energy of Boudouard reaction. Therefore, the results of present work reveal that the overall carbothermic reduction of NiO in the un-milled mixture and one-hour milled sample can take place by solid-gas reactions (reactions 6 and 2) which are carried out at the same time.

Table 4 shows that the activation energy for carbothermic reduction of the 25h milled sample is about 148 kJmol^{-1} . This value is much lower than the activation energy of Boudouard reaction. Therefore, the kinetics parameters of Table 4 show that Boudouard reaction cannot be the rate-controlling reaction in the 25h milled sample. It appears, therefore, that the reaction between NiO and carbon in the 25h milled sample occurs through the following reaction:



Thermodynamic assessments show the value of ΔG^0 for reaction (7) is negative at a temperature above of 180°C [26-27]. Meanwhile, according to reaction (7), the complete reduction of NiO with carbon must cause a mass loss of 27%, which is close to the amount of mass loss of 25h milled sample at 500°C . Fig. 3 shows that the percentage of the mass loss of 25h milled sample reaches about 30% at a temperature of 500°C .

Previous results show that the rate of reduction

of NiO depends upon the rate at which carbon atoms reach Ni/NiO interface as well as the extent of reduction of NiO [14]. The rate at which carbon atoms reach NiO/Ni interface should depend upon the concentration of active sites in the carbon surface and contact area between the active sites in the carbon surface and the Ni surface [14]. It is clear that mechanical milling increases the interfacial area and reduces the diffusion distances of reactants powders. Decreasing in particle/crystallite size of reactants (Table 2 and Fig. 2) during milling operations causes a significant reduction in the reaction temperature of carbothermic reduction of NiO. Hence, a decrease in onset carbothermic reduction temperature can be attributed to the microstructural refinement observed in the 25h milled sample.

4. Conclusions

The results of TGA graphs and the XRD analyses of the samples showed that the carbothermic reduction of nickel oxide could be improved by extended milling. The mass losses are initiated at a lower temperature in 1h and 25h milled samples than in the un-milled sample. The kinetics parameters of carbothermic reduction of nickel oxide were determined using non-isothermal method (Coats-Redfern method) for un-milled mixture and milled samples. The kinetics results of the un-milled and milled samples revealed that the rate of carbothermic reduction of NiO could be described by the first-order model (Mampel model). The kinetics results revealed that Boudouard reaction (reaction 2) is the predominant reaction in the carbothermic reduction of NiO. Therefore, the overall reduction reaction of nickel oxide occurred by reactions (6) and (2) for un-milled and 1h milled samples. The activation energy values of the carbothermic reduction of nickel oxide were 222 kJmol^{-1} for un-milled mixture and 148 kJmol^{-1} for the 25h milled sample, respectively. Therefore, mechanical activation intensified carbothermic reduction of NiO by decreasing particle/crystallite sizes of reactants and by inducing increase thorough mixing of the reactants (NiO-Carbon).

Acknowledgements

This work has formed a part of research master plan of the corresponding author (Nader Setoudeh) and has been supported by Yasouj University. The authors gratefully acknowledge Deputy of Research and Technology of Yasouj University for financial support of the research project.



References

- [1] L. Hong, H.Y. Sohn, M. Sano, Scand. J. Metallurgy, 32 (2003) 171-176.
- [2] B. Su Kim, J-Min Yoo, J-Tae Park, J-Chum Lee, Mater Trans., 47 (2006) 2421-2426.
- [3] R. Ebrahimi-Kahrizsangi, E. Amini-Kahrizsangi, Inter. J. Refractory Metals & Hard Mater., 27 (2009) 637-641.
- [4] D. Guzman, J. Fernansez, S. Ordonez, C.Aguilar, P.A. Rojas, D.Serafini, Inter. J. Miner. Process., 102-103 (2012) 124-129.
- [5] Y-Jun Li, Y-Sheng Sun, Y-Xin Han, and G. Peng, Trans. Nonferrous Met. Soc. China, 23 (2013) 3428-3433.
- [6] J. Puig, M. Balat-Pichelin, J. Min. Metall. Sect. B-Metallurgy, 54(1) B (2018) 39-50.
- [7] B.V. L'VOV, Thermochim. Acta, 360 (2000) 109-120.
- [8] J.H. KrasukK, J.M. Smith, AIChE Journal, 18 (1972) 506-512.
- [9] J. Szekely, C.I. Lin, Metall. Trans. B, 7B (1976) 493-495.
- [10] C.I. Lin, Metall. Trans. B, 19B (1988) 685-686.
- [11] B.J. Satish, B.K. Bharat, N.G and Ashok, Metall. Trans. B, 23B (1992) 93-95.
- [12] S.K. Sharma, F.J. Vastola, P.L. Walker Jr, Carbon, 34 (1996) 1407-1412.
- [13] S.K. Sharma, F.J. Vastola, P.L. Walker Jr, Carbon, 35 (1997) 529-533.
- [14] S.K. Sharma, F.J. Vastola, P.L. Walker Jr, Carbon, 35 (1997) 535-541.
- [15] E.G. Grigoryan, O.M. Niazyan, S.L. Kharatyan, Kinet. and Catalysis, 48 (2007) 773-777.
- [16] N.J. Welham, Mater. Sci. Eng. A., 248A (1998) 230-237.
- [17] N.J. Welham, Metall. Mater. Trans. A., 31A (2000) 283-289.
- [18] N.J. Welham, Int. J. Miner. Process., 67 (2002) 187-198.
- [19] N. Setoudeh, M. Ali Askari Zamani, N.J. Welham, World Academy of Science Engineering and Technology, 74 (2011) 531-534.
- [20] M. Chen, A-Tao Tang, X. Xiao, Trans. Nonferrous Met. Soc. China, 25 (2015) 4201-4206.
- [21] S. Raygan, J.V. Khaki, M.R. Aboutalebi, J. Mater. Synth. Process., 10 (2002) 113-120.
- [22] N. Setoudeh, A. Saidi, N.J. Welham, J. Alloys and Compd., 390 (2005) 138-143.
- [23] M. Erdemuglu, Int. J. Miner. Process. 92 (2009) 144-152.
- [24] N. Setoudeh, N.J. Welham, J. Alloys and Compd., 586 (2014) 730-735.
- [25] H. Yang and P.G. McCormick, Metall. Mater. Trans. B, 29B (1998) 449-455.
- [26] HSC Chemistry for Windows, version 5.1. 1994, Outokumpu, Oy.
- [27] D.R. Gaskell, Introduction to the thermodynamics of materials. Fifth edition, Taylor & Francis Books, Inc.
- [28] C. Suryanarayana, Prog. Mater. Sci., 46 (2000) 1-184.
- [29] N. Setoudeh, N.J. Welham, J. Mater. Sci., 52 (2017) 6388-6400.
- [30] N.J. Welham, N. Setoudeh, Carbon, 43 (2005) 892-894.
- [31] N.J. Welham, V. Berbenni, P.G. Chapmen, J. Alloys and Compd., 349 (2003) 255-263.
- [32] N.J. Welham, V. Berbenni, P.G. Chapmen, Carbon, 40 (2002) 2307-2315.
- [33] A. Khawam, D.R. Flangan, Thermochim. Acta, 436 (2005) 101-112.
- [34] B. Jankovic, B. Adnadevic, S. Mentus, Thermochim. Acta, 456 (2007) 48-55.
- [35] T. Osaki and T. Mori, React. Kinet. Catalysis Lett., 89 (2006) 333-339.

KARBOTERMIČKA REDUKCIJA MEHANIČKI AKTIVIRANE SMEŠE NiO-UGLJENIK: KINETIKA U NEIZOTERMALNIM USLOVIMA

S. Bakhshandeh, N. Setoudeh*, M. Ali Askari Zamani, A. Mohassel

Univerzitet u Jasudžu, Odsek za nauku o materijalima, Jasudž, Iran

Abstract

U ovom radu je ispitivan uticaj mehaničke aktivacije na karbotermičku redukciju nikl oksida. Smeša nikl oksida i aktivnog uglja (99% ugljenik) je usitnjena u planetarnom kugličnom mlinu tokom različitih vremenskih perioda. Neusitnjena smeša i usitnjeni uzorci su podvrgnuti termogravimetrijskoj analizi (TGA) u argonskoj atmosferi, a zatim su čvrsti produkti nastali redukcijom ispitani putem rentgenske difrakcije (XRD). Termogravimetrijska analiza je pokazala da je redukcija NiO počela na ~800°C kod neusitnjenih uzoraka i na ~720°C kod uzoraka koji su usitnjavani 1h, dok se kod uzoraka koji su usitnjavani 25h temperatura smanjila na 430°C. Kinetički parametri karbotermičke redukcije su određeni putem neizotermalne metode (Koats-Redfernova metoda) za neusitnjene i usitnjene uzorke. Aktivaciona energija za neusitnjenu smešu je iznosila oko 222 kJ mol⁻¹, dok je za uzorak koji je usitnjavan 25h iznosila oko 148 kJ mol⁻¹. Smanjenje veličine čestice/ kristalita kod usitnjenih uzoraka uzrokovala je značajno smanjenje reakcijske temperature.

Ključne reči: Sitnjenje u kugličnom mlinu; Karbotermička redukcija; Nikl oksid; Kinetika u neizotermalnim uslovima; Termogravimetrijska analiza (TGA).

