

AN EVOLVED GAS ANALYSIS STUDY OF THE REDUCTION OF NICKEL OXIDE BY HYDROGEN*

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The reduction of NiO by H₂ was followed by conventional thermogravimetry and a new evolved gas analysis approach which follows the course of the reaction by measuring the H₂O content of the gas stream. Excellent correspondence is observed between the two techniques for simultaneous measurements. Heating rates between 0.5 and 10° min⁻¹ shift the temperature of the reaction as does changing the surface area of the NiO. These shifts are discussed in terms of the Neel temperature (T_N) of NiO and the thermal history of the sample. No correlation between reaction rate and T_N is observed under dynamic conditions. Preheating the sample in vacuum at 130° has a marked effect on shape of the DTG and EGA curves.

The chemical, metallurgical, and magnetic uses of the transition metals, iron, cobalt, nickel, and their alloys are enormous. Recently fabricated powdered metal shapes have been prepared from these materials by the in-situ reduction of the preformed oxides by H₂ [1]. Catalysts of these finely divided metals supported on an inert refractory material are also prepared by H₂ reduction of oxides and salts of these metals [2]. Consequently, methods for controlling the rates, mechanisms, and resulting morphologies of such reductions are of considerable technological importance.

In recent years there have been studies that suggest an applied magnetic field will influence the rate of such reductions [3–6] and even more complicated behavior has been reported for the effects of a magnetic field on the direct formation of Ni(CO)₄ [7–9]. Other reports suggest no influence of external magnetic fields on these and related reactions [10–12]. The effects of an intrinsic magnetic moment have also been noted by observations of anomalies, at the magnetic transition, in the reaction rates of reductions [13–17], oxidations [18–21], and other reactions [22] of these metals and oxides.

Studies of the reduction of metal oxides by H₂ in the presence of an external magnetic field have been performed using gravimetric techniques [4, 5]. Such investigations have been hampered by the strong influence of the magnetic field upon the mass of the reactant, product or both. Evaluating the extent of the reaction by changes in weight therefore is tentative. Variations of the magnetic influence would

* Presented at the 11th Annual NATAS Meeting, New Orleans, LA, Oct. 19–21, 1981.

also occur due to changes in temperature as well as crystallite size, morphology, and rearrangement or movement. For these reasons an evolved gas analysis (EGA) technique was developed whereby the moisture in the gas stream formed by the hydrogen reduction was measured as a function of time or temperature [23, 24]. Excellent agreement has been achieved between thermogravimetry (TG) and this EGA technique using the dehydration and decomposition of $\text{Ba}(\text{OH})_2 \cdot \text{H}_2\text{O}$ [23, 24].

The reduction of NiO by H_2 (eq. 1)



was selected as the starting point for the application of this technique to magnetic studies for two reasons. Firstly, this reaction has been extensively studied and information exists that indicates magnetic factors play a role since anomalies occur at the magnetic transition of NiO during the reduction [13–17] and at that of Ni during oxidation [18, 19]. Secondly, of the three elements of interest (Fe, Co, and Ni) Ni has the least tendency towards variable oxidation states and hence less possibility of forming complicating intermediates.

This work specifically reports the use of EGA to study the reduction of NiO by H_2 at various heating rates using samples having much different surface areas. It then compares these results taken in the absence of a magnetic field with results obtained from conventional TG under similar conditions. Having demonstrated the validity of this EGA method for studying reductions by H_2 in this paper it is then applied in a subsequent paper [25] to comparing the reduction of NiO, Co_3O_4 , and Fe_2O_3 with and without an external magnetic field.

Experimental procedures and results

Samples of NiO having markedly different surface areas were prepared by calcination of NiCO_3 (Fisher Scientific Co.). The sample heated at 460° for 1 hr in air had a surface area of $57 \text{ m}^2\text{g}^{-1}$ while that heated at 1000° for 16 hr in air had an area of $1.0 \text{ m}^2\text{g}^{-1}$. Surface areas were measured by the BET technique with N_2 adsorption using a Micromeritics Digesorb 2500 apparatus.

The aluminium EGA cell has been described elsewhere [24]. Since a range of heating rates was used, it was decided to compare the temperature output from the Perkin-Elmer System 4 furnace controller with the actual sample temperature. The System 4 was calibrated in accordance with the manufacturers instructions using a standard gas flow, 300 ml min^{-1} of H_2 (STP), and a dummy sample of Al_2O_3 . A thermocouple was then inserted into this sample through a fitting in the top of the cell. A comparison of the sample thermocouple with the control temperature between the extremes of the heating rates employed, 0.5 and $10^\circ \text{ min}^{-1}$, indicated no difference at room temperature and a maximum difference of $+2^\circ$ at 600° for $0.5^\circ \text{ min}^{-1}$ and $+11^\circ$ at 600° for $10^\circ \text{ min}^{-1}$. The non-control thermocouple

was removed and the System 4 temperature output was used thereafter. Samples were placed in a fused quartz crucible which rested on the control thermocouple. Samples were weighed before and after each run to determine the percentage of weight loss.

The TG/EGA experiments utilized a CSI Model TGA-5B thermobalance to which a Panametrics Model 700 moisture detector had been added at the exit of the gas stream. A flow of H_2 at 400 ml min^{-1} (STP) was maintained. The sample

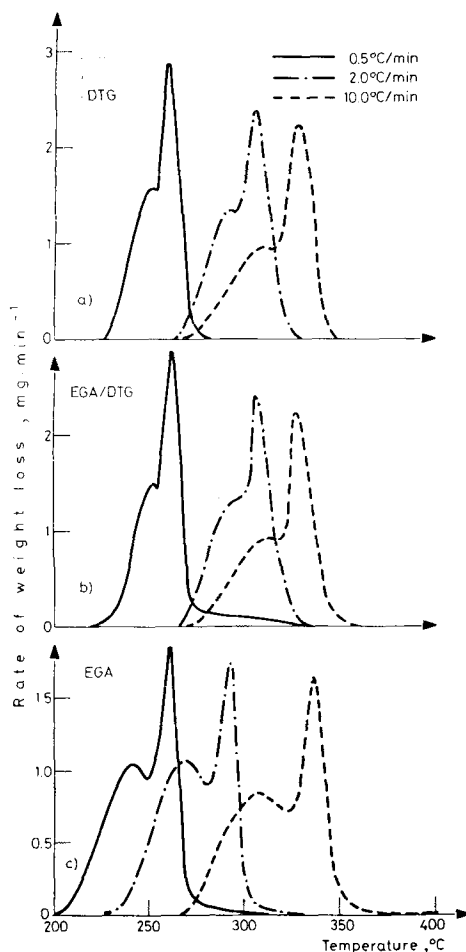


Fig. 1. Thermoanalytical results on the reduction of NiO ($1.0 \text{ m}^2\text{g}^{-1}$) by H_2 . a) DTG curves. $0.5^\circ \text{ min}^{-1}$, 24.64 mg of NiO, 21.1 wt % loss, ($\times 20$); $2.0^\circ \text{ min}^{-1}$, 27.08 mg of NiO, 21.3 wt % loss, ($\times 5$); $10^\circ \text{ min}^{-1}$, 26.12 mg of NiO, 21.4 wt % loss, ($\times 1$). b) Simultaneous EGA curves of the samples in a), c) EGA analysis using the apparatus designed for experiments in a magnetic field. $0.5^\circ \text{ min}^{-1}$, 24.20 mg of NiO, 21.2 wt % loss, ($\times 20$); $2.0^\circ \text{ min}^{-1}$, 24.69 mg of NiO, 21.4 wt % loss, ($\times 5$); $10^\circ \text{ min}^{-1}$, 24.73 mg of NiO, 21.3 wt % loss, ($\times 1$)

temperature was measured by a Fluke Model 2190A digital thermometer using a type S thermocouple whose junction was about 1 mm below the fused quartz sample holder. Outputs of the balance, digital thermometer and moisture detector were transcribed onto magnetic tape for subsequent computer processing [26].

Reduction experiments were performed at 0.5, 2.0, and 10° min⁻¹ in both the EGA and TG/EGA instruments using both samples of NiO. Results of these 12

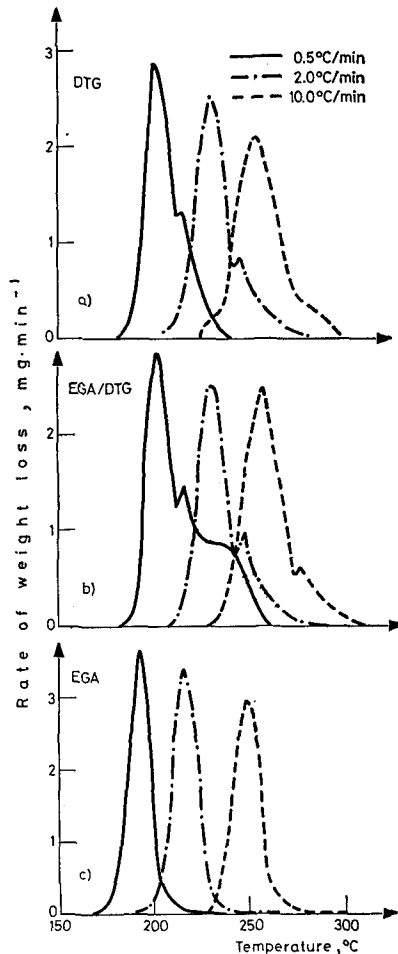


Fig. 2. Thermoanalytical results on the reduction of NiO ($57 \text{ m}^2\text{g}^{-1}$) by H_2 . a) DTG curves. $0.5^\circ \text{ min}^{-1}$, 25.70 mg of NiO, 22.1 wt % loss, ($\times 20$); $2.0^\circ \text{ min}^{-1}$, 24.04 mg of NiO, 22.4 wt % loss, ($\times 5$); $10^\circ \text{ min}^{-1}$, 23.50 mg of NiO, 22.5 wt % loss, ($\times 1$); b) Simultaneous EGA curves of the samples in a). c) EGA analysis using the apparatus designed for experiments in a magnetic field. $0.5^\circ \text{ min}^{-1}$, 24.65 mg of NiO, 23.0 wt % loss, ($\times 20$); $2.0^\circ \text{ min}^{-1}$, 26.20 mg of NiO, 22.7 wt % loss, ($\times 5$); $10^\circ \text{ min}^{-1}$, 25.54 mg of NiO, 22.7 wt % loss, ($\times 1$)

experiments are summarized in Figs 1 and 2. The background in the EGA curves has been subtracted as described earlier [23].

The output of the moisture analyzer was the dew point ($^{\circ}\text{C}$) of the gas stream which was converted to the partial pressure of water by use of Eq. 2.

$$\begin{aligned} \log(\text{Torr}_{\text{H}_2\text{O}}) = & 0.6531236 + 3.372986 \times 10^{-2}(\text{^{\circ}\text{C}}) - 2.258758 \times 10^{-4}(\text{^{\circ}\text{C}})^2 - \\ & - 1.765107 \times 10^{-7}(\text{^{\circ}\text{C}})^3 + 3.309650 \times 10^{-8}(\text{^{\circ}\text{C}})^4 + 6.831686 \times 10^{-10}(\text{^{\circ}\text{C}})^5 + \\ & + 3.371173 \times 10^{-12}(\text{^{\circ}\text{C}})^6 \end{aligned} \quad (2)$$

This equation was derived by a least squares fit of available tabulated data [27] (at 10° intervals from -90 to $+30^{\circ}$) to a sixth order polynomial. The standard error of the resulting estimate in $\log(P_{\text{H}_2\text{O}})$ is ± 0.0044 . Values of the rate of water loss were then calculated from Eq. 3.

$$\text{mg/min} = [P_{\text{H}_2\text{O}}/760] [(L/\text{min}) (1 \times P_{\text{H}_2\text{O}}/760)] [18000/22.4] \quad (3)$$

Equation 3 is derived from multiplication of the fraction of water, corrected flow rate in L min^{-1} , and the weight of pure water vapor in mg L^{-1} . This is an estimate based upon STP conditions at the moisture sensor. Since the values calculated are per unit time but plotted versus temperature, the curves have been normalized by multiplying by the heating rate in $^{\circ}\text{C min}^{-1}$ divided by 10 so that the ordinate scale is correct, only for the most rapid heating rate.

Selected EGA experiments were performed using samples dried for several days at 130° in a vacuum and an additional TG/EGA experiment was done after having dried the sample at 130° overnight in situ on the balance in flowing H_2 . These experiments are summarized in Fig. 3.

Because it was felt that the magnetic transition in NiO may affect the reduction, the Neel temperature of the coarse sample ($1 \text{ m}^2\text{g}^{-1}$) was determined by DTA using a CSI model JP-202 DTA apparatus and platinum ring thermocouples. The heating rate was $10^{\circ} \text{min}^{-1}$ in N_2 at 50 ml min^{-1} . Figure 4 shows the experimental result which suggests that the T_{N} is 248° , or somewhat less due to the dynamic nature of the experiment.

Discussion

Besides demonstrating the suitability of the EGA technique and its close correspondence with more conventional methods, it was also hoped that the dynamic techniques would reveal irregularities in the reduction curve at the T_{N} of NiO as described in the introduction. Coincidentally the initial experiments which used NiO ($1.0 \text{ m}^2\text{g}^{-1}$) at a heating rate of $0.5^{\circ} \text{min}^{-1}$, see Fig. 1, did indeed show a marked decrease in the rate of the reduction around 250° . This was in very close agreement with the observed T_{N} as indicated in Fig. 4. The comparison amongst the three different methods of analysis under these conditions was good and suggested that the

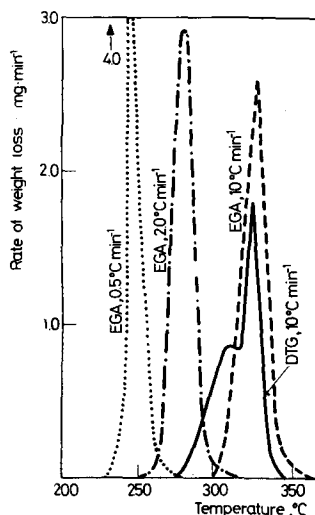


Fig. 3. Thermoanalytical results on the reduction of predried NiO ($1.0 \text{ m}^2\text{g}^{-1}$) by H_2 , DTG, $10^\circ \text{ min}^{-1}$, 19.52 mg NiO, 21.4 wt % loss, ($\times 1$); EGA, $10^\circ \text{ min}^{-1}$, 25.56 mg NiO, 21.4 wt % loss, ($\times 1$); EGA, $2.0^\circ \text{ min}^{-1}$, 25.38 mg NiO, 21.4 wt % loss, ($\times 5$); EGA, $0.5^\circ \text{ min}^{-1}$, 25.17 mg NiO, 21.5 wt % loss ($\times 20$)

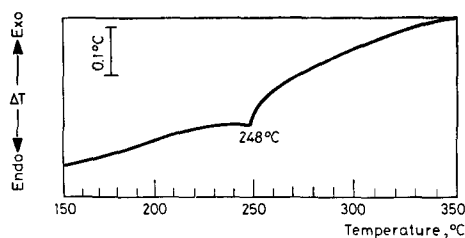


Fig. 4. Differential thermal analysis of NiO ($1.0 \text{ m}^2\text{g}^{-1}$) in N_2 at $10^\circ \text{ min}^{-1}$, 23.11 mg

separate EGA technique had greater sensitivity and resolution. Agreement for the simultaneous TG/EGA measurements was excellent.

The change in rate of reaction at T_N , although it strongly resembled results of other dynamic experiments on this system [2], was much greater than anticipated. Consequently, further experiments were designed to determine if this dramatic decrease in rate was really associated with the T_N of NiO. Shifting the zone of reaction to other temperatures should reveal whether this effect occurs at the same temperature or whether it is more closely associated with other parameters such as fraction reacted, α . The shift in reaction temperature was achieved by changes in both the heating rate and surface area of the sample.

It is immediately obvious from inspection of Figs 1 and 2 that a faster heating rate displaces the reaction to higher temperatures and spreads the reaction over a

wider range of temperature as would be expected. The shape of the curve, however, is well preserved and it is evident, therefore, that the decrease in the rate of the reaction is not associated with T_N of NiO. As expected, increasing the surface area of the NiO has shifted the reaction to lower temperatures. The shoulder on the curves seem related to α , however, the value of α at which the saddle occurs in the curves is quite different between the samples of different surface area.

The correspondence between the two instruments does not appear as good for the high surface area material (Fig. 2) since the shoulder is absent in the EGA curves. This apparent discrepancy, however, was induced by changes in the pre-treatment of the sample rather than differences in the equipment or technique. In order to minimize the background corrections due to the water content of the H_2 and, much more importantly, the outgassing of the system; a practice was instituted of vacuum drying the samples of the higher surface area material at 130° overnight prior to inserting into the EGA cell. This preheating step made no difference in the overall weight loss of the reduction, however it markedly influenced the nature of the reduction.

This effect was substantiated by repeating the EGA experiments using the low surface material and the preheating step. The results again clearly show that the shoulder in the EGA curve, see Fig. 3, is eliminated similar to the effect observed in Fig. 2. The temperature of maximum reaction, however, is not changed significantly by preheating. The attempt to duplicate the preheating condition on the thermobalance was not effective, as seen for the DTG curve in Fig. 3, implying that the vacuum was a more effective than flowing H_2 . However, if the surface was changed during preheating at 130° in vacuum, it was not accompanied by a significant change in weight.

Conclusions

1. The EGA technique being developed for studying the reduction of oxides by H_2 gives results in good agreement with conventional thermogravimetry (TG/DTG).

2. The shape of the DTG and EGA curves indicate a complex (multi-step) process when samples have not been thoroughly outgassed. This process is not related to the magnetic transition in NiO. The change in rate appears to occur at approximately the same fraction reacted regardless of the heating rate but that this fraction reacted varies for different materials. The fact that these pronounced changes in the rate observed herein are not related to the magnetic transition within the product or reactant phase does not mean that more subtle changes do not take place at those temperatures.

3. The complex shape of the DTG and EGA curves disappears upon outgassing the NiO in vacuum overnight at 130° . This outgassing does not result in a significant weight change (<0.1 wt %).

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The authors are grateful to Mr. F. Schrey for measurements of the surface area.

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ZUSAMMENFASSUNG — Die Reduktion von NiO durch H₂ wurde durch konventionelle Thermogravimetrie und eine neue Analyse des entwickelten Gases untersucht, welche den Reaktionsablauf durch Messung des H₂O-Gehalts des Gasstromes verfolgt. Eine ausgezeichnete Übereinstimmung beider Techniken wird bei simultanen Messungen beobachtet. Aufheizgeschwindigkeiten zwischen 0.5 und 10° min⁻¹ verschieben die Temperatur der Reaktion und verändern die Oberfläche des NiO. Diese Verschiebungen werden auf Grund der Neel-Temperatur (T_N) des NiO und der thermischen Vergangenheit der Probe erörtert. Unter dynamischen Bedingungen wird keine Korrelation zwischen der Reaktionsgeschwindigkeit und T_N beobachtet. Das Vorwärmen der Probe im Vakuum bei 130° zeigt einen deutlichen Einfluß auf die Form der DTG und EGA Kurven.

Резюме — Исследование реакции восстановления окиси никеля водородом с помощью методов термогравиметрии (ДТГ) и анализа выделяющегося газа (АВГ), позволило проследить ход реакции путем измерения содержания Н₂О в газовом потоке. Хорошее совпадение наблюдается между этими двумя совмещенными методами. Используемые скорости нагрева между 0.5 и 10° в минуту сдвигают температуру реакции, поскольку происходит изменение площади поверхности окиси никеля. Установленные сдвиги обсуждены на основе температуры Нееля (T_N) и термического происхождения образца. В динамических условиях не установлено корреляции между скоростью нагрева и T_N. Предварительный нагрев окиси никеля в вакууме при 130° оказывает заметное влияние на форму ДТГ- и АВГ-кривых.