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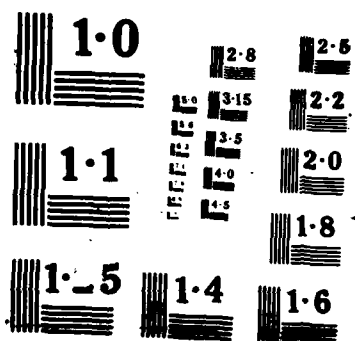
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TECHNICAL REPORT NO. 4

AN EXAMINATION OF THE RELATIVE STABILITIES OF

$Mg_xNi_{1-x}O$ AND NiO ON SPHEROCARB

by

Michael Schwartz, Robert Kershaw, Kirby Dwight and Aaron Wold

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in

MATERIALS RESEARCH BULLETIN

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AN EXAMINATION OF THE RELATIVE STABILITIES OF
 $Mg_xNi_{1-x}O$ AND NiO ON SPHEROCARB

by

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ABSTRACT

The H_2 reductions of $Mg_xNi_{1-x}O$ and NiO dispersed on Sphero carb Carbon were studied using a combined magnetic-thermogravimetric technique. It was found that the NiO was greatly stabilized by solid solution formation with MgO, but the carbon support did not stabilize the NiO towards H_2 reduction.

MATERIALS INDEX: $Mg_xNi_{1-x}O$, NiO/Sphero carb, Thermomagnetic, Thermogravimetric

Introduction

It has been shown (1) that stabilization of hexagonal iron oxide on rutile TiO_2 only occurs if ternary phases such as Fe_2TiO_4 or $FeTiO_3$ are formed under a reducing atmosphere. The stabilization of a transition metal oxide can also be achieved by the formation of a solid solution without a change of crystal structure. A simple example of such solid solution formation is the system $Mg_xNi_{1-x}O$ where all of the members crystallize with the rock salt structure.

The system $Mg_xNi_{1-x}O$ was chosen for this study because of the ease of reduction of Ni(II) to metallic nickel in a hydrogen atmosphere. Furthermore, the Curie point of nickel, $358^\circ C$, makes it convenient to study the magnetic properties as the reduction proceeds as a function of temperature. In addition, the solid solution $Mg_xNi_{1-x}O$ is an ideal system to study for several reasons. First, MgO is not reduced by hydrogen up to $2500^\circ C$ (2), and therefore any weight changes can be attributed solely to the reduction of NiO. Second, the magnetic properties of NiO-MgO solid solutions are readily understood. They have been reported to be paramagnetic at low nickel oxide concentrations (3) and antiferromagnetic at higher nickel oxide concentrations (4). Finally, there have been no reports of other nickel-magnesium oxides which would interfere with the interpretation of the experimental results.

A recent paper by Gallagher et al. concerns a study of the H_2 reduction of NiO using thermogravimetric and evolved gas analyses (5). For NiO with low surface areas, $1.0 m^2/g$, and using pure H_2 as the reductant, they found that initial reduction began at approximately $250^\circ C$, depending upon the rate of heating. Their results were consistent with other reports and presented a clear picture of the temperature dependence of the reduction of NiO. A second relevant paper described the effect that doping small amounts of MgO into NiO

had upon the rate of H_2 reduction of NiO (6). Small amounts of MgO, 1.5% and 7.1%, greatly decreased the rate of reduction at constant high temperatures. However, the study did not correlate the magnetic properties of the phases formed on reduction with the increased stabilization of the NiO.

It was the purpose of this study to investigate this correlation and to compare the stabilization of nickel oxide in a solid solution containing MgO with a sample of NiO dispersed on Sphero carb Carbon where there appear to be no interactions present (7).

Experimental

The starting materials were $Mg(NO_3)_2 \cdot 6H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$ (Fisher Certified Reagents) and Sphero carb particles (Analab, GCA-012). $Mg_xNi_{1-x}O$ solid solutions were prepared by the codecomposition of the nitrates. Typically, the appropriate amount of the metal nitrates were dissolved in distilled H_2O , 2 ml of H_2O per gram of starting material. This solution was then dried 12 hr at $150^\circ C$. The resulting solid was ground and then heated in a porcelain crucible in air for 24 hr at $600^\circ C$. A temperature of $600^\circ C$ was chosen as the preparation temperature in order to ensure complete decomposition of the dried magnesium nitrate precursor. X-ray powder diffraction patterns showed the resulting products to be single phased with the rock salt structure. NiO was also prepared by the same procedure.

The samples of NiO dispersed on Sphero carb were prepared according to the method of Kim et al. (7) using $Ni(NO_3)_2 \cdot 6H_2O$ (Fisher Certified Reagent) as the source of Ni. The dried Ni nitrate/C precursor was heated at $450^\circ C$ in a wet N_2 atmosphere in order to prevent reduction. The resulting product consisted of NiO as determined by x-ray powder diffraction. No Ni metal was detected in the samples by either x-ray powder diffraction or magnetic measurements. A loading of 10 atomic percent of Ni was used.

The thermogravimetric balance used in this study combines magnetic measurements with thermogravimetric analysis. As the reaction proceeds, the weight of the sample can be determined alternately in a magnetic field gradient and without the magnetic field gradient. This allows for the constant monitoring of the appearance and growth of a magnetic phase in conjunction with weight changes associated with the reaction. The new phases can be identified on the basis of their Curie temperatures. Although x-ray powder diffraction can be used to identify new phases, this technique is more useful because it monitors the reaction as it occurs. Magnetic measurements are also much more sensitive than x-ray powder diffraction. Therefore, new information on reactions can be gained using this combined technique.

A schematic diagram of the apparatus used for the combined magnetic and thermogravimetric analyses is shown in Fig. 1. The magnet is mounted on a shaft which is connected to a motor through a crank. The magnet moves from the vertical position (sample out of the field) up to the horizontal position (sample in the field) once a minute. The sample is positioned so that it sits in the maximum field gradient. The weight of the sample was determined using a Cahn electrobalance (model RG). The temperature was measured by a type

S thermocouple which was positioned just below the sample.

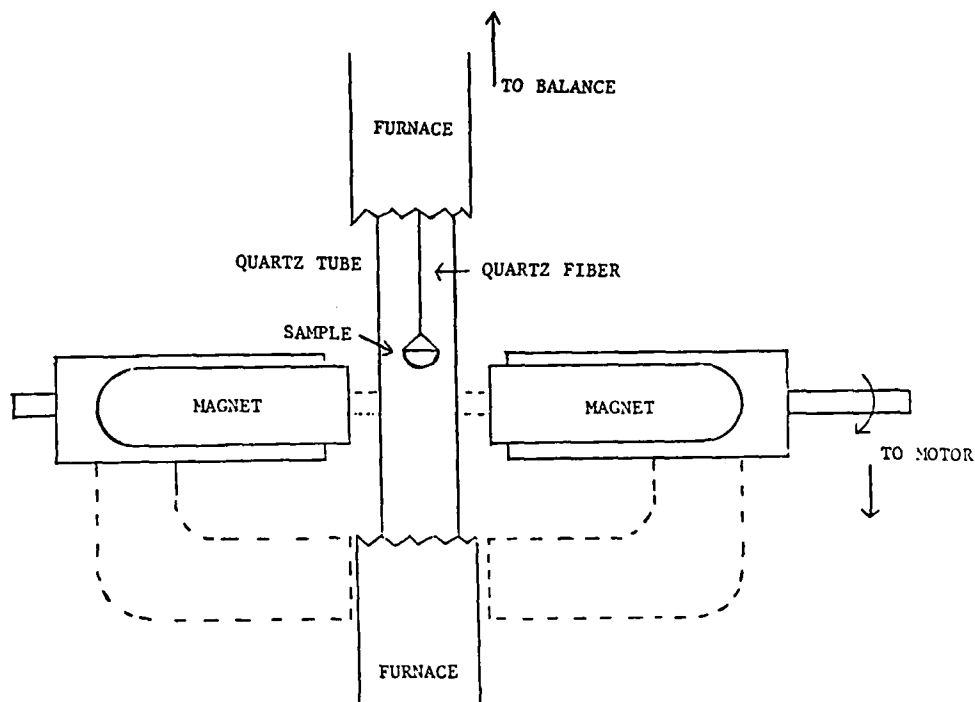


Fig. 1
Schematic Diagram of Magnetic-Thermogravimetric Balance

Typical sample weights were 35-40 mg. 85%Ar/15%H₂ was used for the reductions. The gas was dried by passing through a P₂O₅ column. The flow rate was 30 cm³/min and the samples were heated at 50°C per hour.

X-ray powder diffraction patterns were taken with a Philips diffractometer using copper radiation ($\lambda = 1.5405 \text{ \AA}$) and a single crystal graphite monochromator. The scan rate was 1° 2 θ per minute with a chart speed of 30 in/hr. For cell constant determination, the scan rate was 1/4° 2 θ per minute.

Results and Discussion

Samples having the composition Mg_xNi_{1-x}O ($x = 0.1-0.3$) were prepared by double decomposition of the nitrates. The minimum temperature for complete decomposition of the nitrates was established from TGA data. X-ray analysis indicated that all members of the system crystallized with the rock salt structure. The variation in the cell parameters vs. nickel content is shown in Fig. 2. A comparison of the stability of bulk nickel oxide was made with the compositions in the system Mg_xNi_{1-x}O. The TGA results obtained under an 85%Ar/15%H₂ atmosphere are shown in Fig. 3. In order to avoid discrepancies due to kinetic effects, samples of at least 35-40 mg were used for the stability

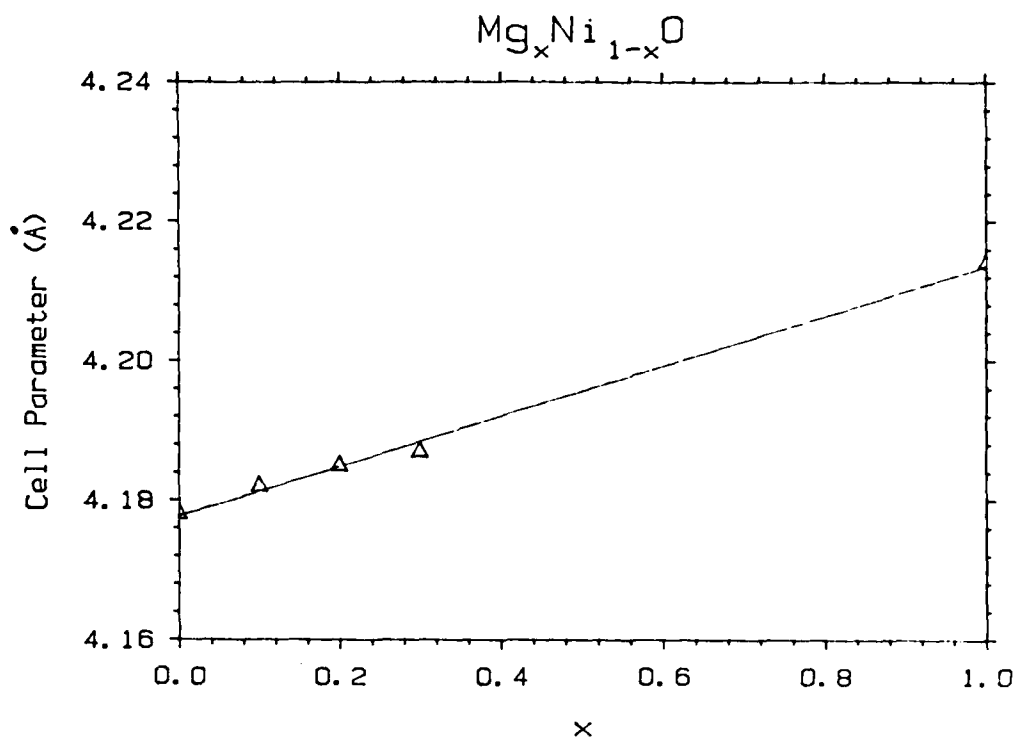


Fig. 2
Plot of Cubic Cell Parameter vs. Composition Parameter x

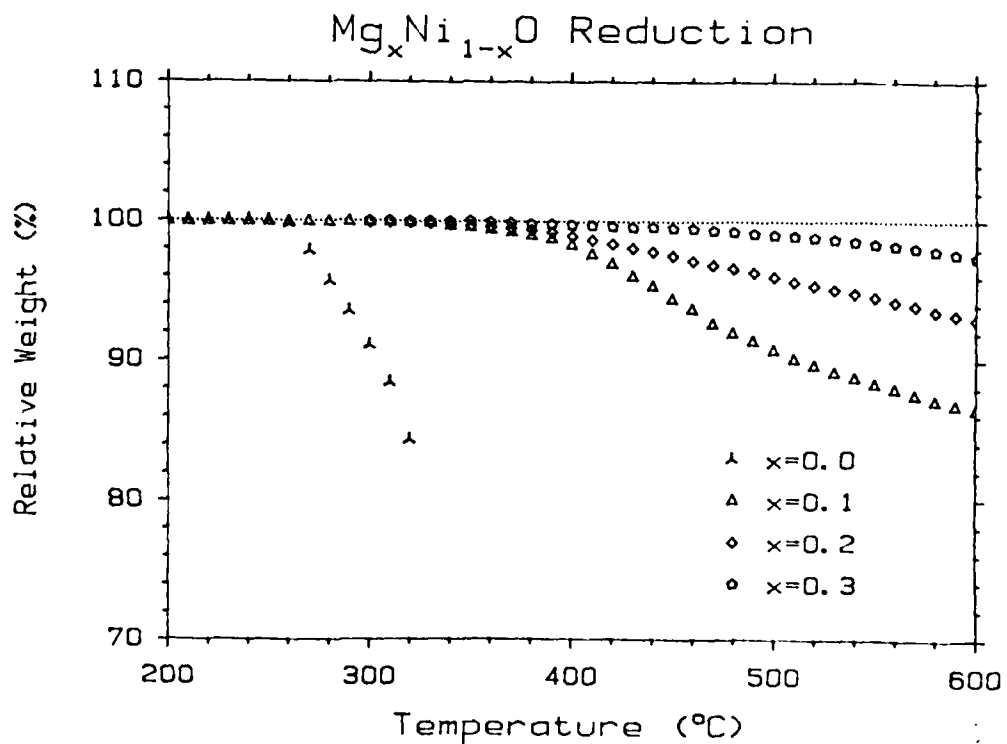


Fig. 3
Thermogravimetric Results for H_2 Reduction of $Mg_xNi_{1-x}O$

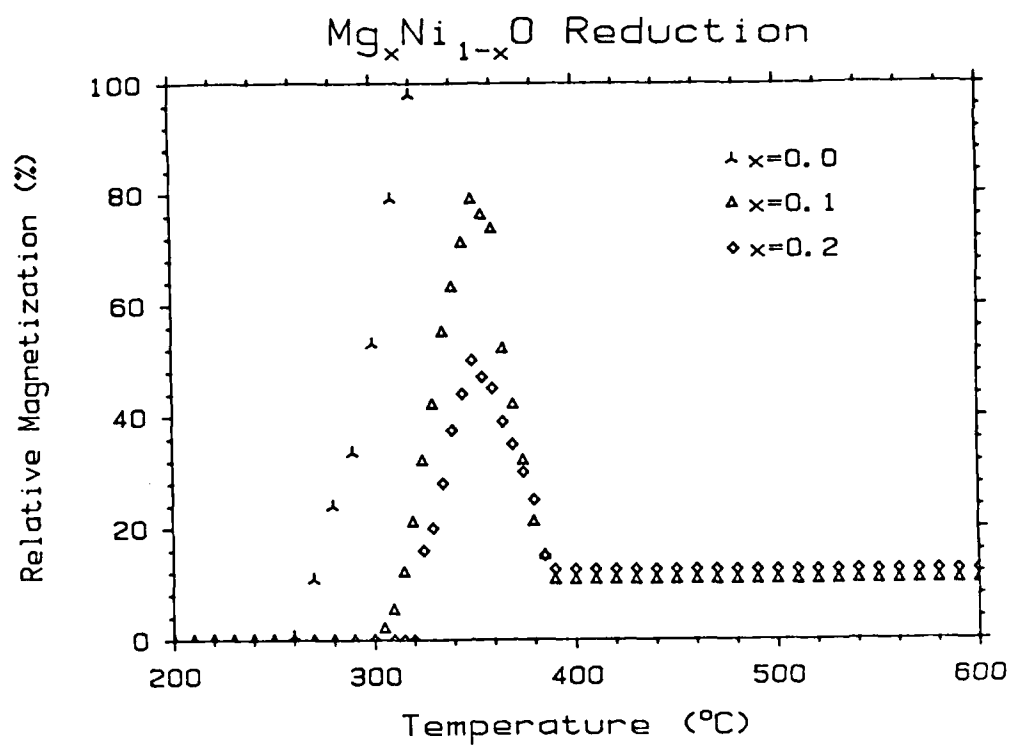


Fig. 4
Thermomagnetic Results for H₂ Reduction of Mg_xNi_{1-x}O

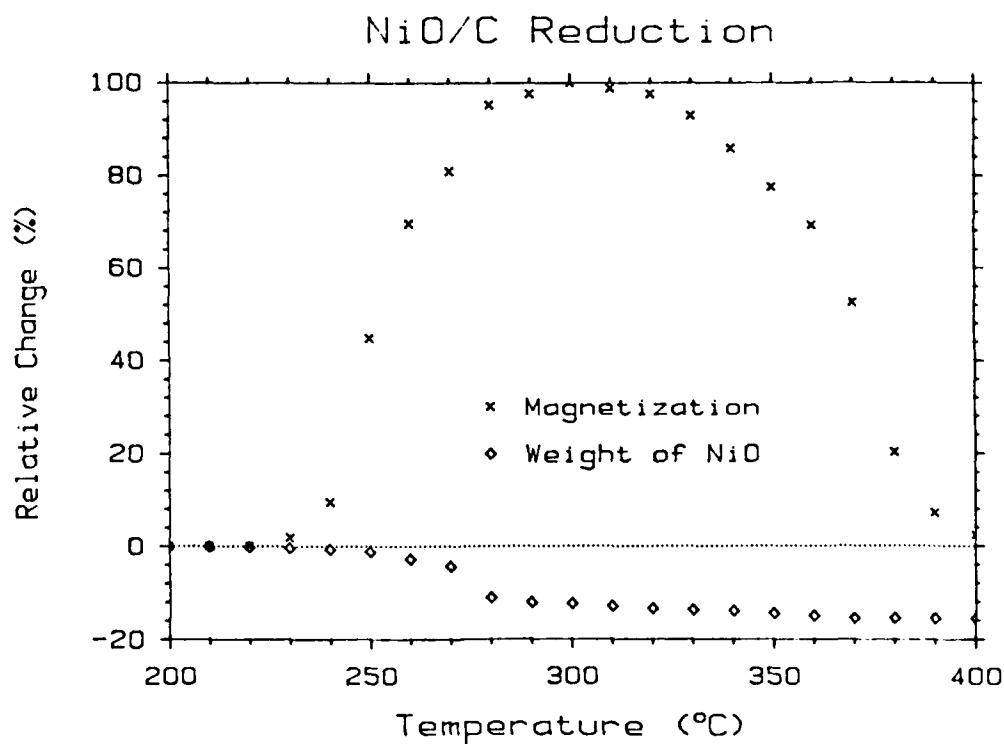


Fig. 5
Thermogravimetric and Thermomagnetic Results for H₂ Reduction of NiO/C

determinations. Whereas bulk NiO begins to reduce at 255°C, samples with the composition $Mg_xNi_{1-x}O$ ($x = 0.1-0.3$) begin to reduce at temperatures between 312 - 365°C. However, the initial weight loss is so small that it is not apparent on the scale of Fig. 3. The rate of temperature increase was 50°C per hour.

Thermomagnetic studies (Fig. 4) were carried out simultaneously with the TGA experiments using the thermomagnetic balance previously described. Reduction of bulk NiO with 85%Ar/15%H₂ resulted in the formation of metallic nickel which was detected at 255°C. This is the same temperature at which TGA results indicate reduction of NiO. For samples containing approximately 30 mg of metallic nickel, the Curie point was found to be 358°C. This agrees with the reported Curie point of metallic nickel. For the compositions $x = 0.1$ and 0.2 , magnetic studies clearly indicate the formation of nickel at temperatures which correspond to those reported above where the barely detectable weight losses began. It is evident that thermomagnetic studies are far more sensitive in determining the onset of reduction. For $x = 0.3$, the temperature required for the formation of nickel is above the Curie temperature. It can be seen that appreciable stabilization of nickel occurs when only a small fraction of magnesium is substituted into the rock salt structure.

The degree of stabilization of nickel towards reduction in the system $Mg_xNi_{1-x}O$ ($x = 0.1-0.3$) was compared to nickel dispersed on Sphero carb carbon where no solid solution occurs. The magnetic TGA results for the reduction in 85%Ar/15%H₂ of NiO dispersed on carbon are shown in Fig. 5. Both the formation of the magnetic phase and weight loss were first detected at 225°C. A comparison of these results with those obtained for reduction of bulk nickel oxide and nickel-magnesium oxides indicate that there is a lowering of the reduction temperature of nickel oxide. Furthermore, it is clear that there is no stabilization of NiO when it is supported on Sphero carb.

Conclusion

MgO, which interacts with NiO through solid solution formation, greatly stabilizes the NiO. When NiO is dispersed on C, no stabilization is observed.

These results also show the utility of the combined magnetic-TGA experiment. Moreover, the barely detectable weight loss is coincident with the pronounced appearance of a magnetic phase.

Acknowledgments

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References

1. J. Yu, R. Kershaw, K. Dwight and A. Wold. Submitted for publication in *J. Sol. State Chem.*
2. E. Newberry and J. N. Pring, *Proc. Royal Soc. London* A92, 276 (1916).
3. A. Cimino, M. LoJacono, P. Porta and M. Valigi, *Z. Phys. Chem. (Weisbaden)* 55, 14 (1967).
4. O. Evrard, J. Francois and J. M. Lecuine, *Rev. Chim. Miner.* 9, 463 (1972).
5. P. K. Gallagher, E. M. Gyorgy and W. R. Jones, *J. Thermal Anal.* 23, 185 (1982).
6. M. H. Tikkanen, B. O. Rosell and W. Wiberg, *Acta Chem. Scand.* 17, 513 (1963).
7. K. Kim, R. Kershaw, K. Dwight, A. Wold and K. Colle, *Mat. Res. Bull.* 17, 591 (1982).

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