Oxidation of Nickel in the Vicinity of Its Curie Temperature

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The oxidation rate of nickel has been measured in the vicinity of its Curie temperature. The results reveal a large difference in the oxidation kinetics, manifested as a change in activation energy of ~1 eV/atom, between the paramagnetic and ferromagnetic phases of nickel. The observed modifications of the kinetics are qualitatively consistent with recent theoretical predictions by Suhl.

In this Letter, we report measurements of the oxidation of nickel in the vicinity of its Curie temperature ($\theta_C = 631$ K) by means of a gravimetric technique. The purpose of the experiment was to determine the effect of the paramagnetic-ferromagnetic phase transition on the kinetics of nickel oxidation. The results reported here show a large difference in the oxidation kinetics, manifested as a change in activation energy of ~1 eV/atom, between the paramagnetic and ferromagnetic phases of nickel. The observed modifications of the kinetics are qualitatively consistent with recent theoretical predictions by Suhl.[1,2]

The nickel powder used was obtained by reducing small particles (60–125 μm) of NiO (Atomergic; 99.999% pure) in flowing dry hydrogen at 673 K, and then presintering the powder at 823 K for 90 h. For the nickel oxidation data presented here, the sample investigated weighed 85 mg and had a surface area of 75 ± 2 cm^2. The surface area of the presintered nickel powder was determined by comparing the high-temperature oxidation isotherms of the powdered sample with those obtained from a 0.025-mm-thick nickel foil with a geometric surface area of 16.8 cm^2 (assuming a surface roughness of 1 for the foil). The measurements were made in flowing oxygen at 1 atm pressure using a Cahn RG microbalance. After each isotherm was recorded, the sample was reduced in flowing H_2 at 563 K for 15 min. When the isotherms were taken in this manner, the reproducibility was within ±2%.

The temperature was monitored with a Chromel-Alumel thermocouple placed directly below the sample, and stabilized to better than ±0.5 K with a simple feedback circuit. The actual temperature of the nickel was determined by measuring the bulk ferromagnetic transition temperature *in situ* by placing a small bar magnet outside the oven which produced a sufficient magnetic field and magnetic-field gradient to give an apparent weight change of about 20 μg as the nickel was slowly warmed or cooled through θ_C.

Several typical Ni oxidation isotherms taken at various temperatures between 587 and 648 K are shown in Fig. 1. The solid line shown for each isotherm was drawn through 120 data points taken at 15-sec intervals, and the width of the line is representative of the scatter in the data. We attempted to fit the isotherms to various analytic expressions derived in the literature, but found that the best overall description of the data was given by a simple power law

$$x = At^{\alpha}, \tag{1}$$

where x is the average oxide thickness in ang-

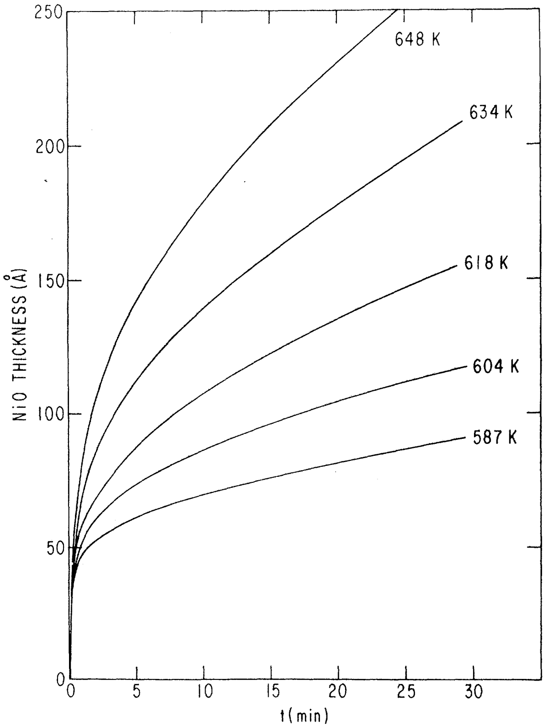

FIG. 1. Typical thickness x vs time t isotherms for Ni oxidation for 1 min $\leq t \leq 30$ min at various temperatures between 587 and 648 K.

stroms, t is the time in minutes, and both A and α depend on temperature. For t between 1 and 30 min, each isotherm was fitted by the method of least squares to a line of the form:

$$\ln x = \ln A + \alpha \ln t. \qquad (2)$$

For most of the isotherms taken, the statistical correlation coefficient, R, was better than 0.999. The temperature dependence of A and α are shown in Figs. 2(a) and 2(b), respectively. The parameter $A(T)$ can be described by the relation

$$A(T) = A_0 \exp(-\Delta/T), \qquad (3)$$

where $A_0 = 2.1\times10^5$ Å and $\Delta = 5.1\times10^3$ K, and apparently represents an activated process. The exponent α increases monotonically with temperature from 0.17 at 570 K to 0.44 at 700 K and can be described well by the function

$$\alpha(T) = \tfrac{1}{2}[1 - (T_0/T)^9], \qquad (4)$$

where $T_0 = 555$ K, although we are unable to attach any physical significance to the form of Eq. (4) at this time. Presumably, α cannot exceed the diffusion value of $\frac{1}{2}$ at high temperatures, but unfortunately, it was not possible to determine α at temperatures much greater than 673 K because of problems associated with sintering.

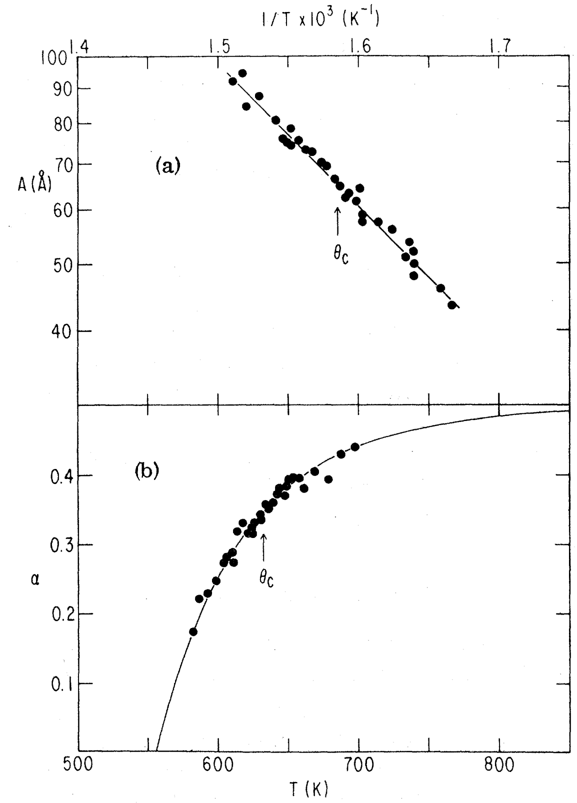

FIG. 2. (a) The factor A vs inverse absolute temperature. The solid line represents the function $A(T) = A_0 \exp(-\Delta/T)$ where $A = 2.1\times10^5$ Å and $\Delta = 5.1\times10^3$ K. (b) The exponent α vs absolute temperature. The solid line represents the function $\alpha(T) = \frac{1}{2}[1-(T_0/T)^9]$ where $T_0 = 555$ K.

Originally, we hoped to study the rate of formation of the first one or two monolayers of NiO, since in this regime the physical properties of the nickel should have the largest effect on the oxidation rate. However, we found that the initial rate was limited not by surface kinetics, but rather by the rate at which oxygen could be delivered to the sample; i.e., at a given temperature, the initial oxidation rate was found to be roughly proportional to the oxygen flow rate. In addition, the initial few monolayers of NiO appear to be formed via an unactivated process, a result consistent with earlier work.[3] From room temperature to 500 K, the oxidation isotherms are essentially step functions with the initial "jump" in average oxide thickness, Δx, changing from about four monolayers at room temperature to eight monolayers at 500 K. Expressed in the form of an Eyring plot $[\ln(\Delta x/T) \text{ vs } 1/T]$, these data yield an activation energy of 0.4 ± 0.2 kcal/mole, so that the initial oxidation is essentially unactivated. A possible mechanism for this unactivated initial oxidation has recently been advanced by Fehlner and Mott.[3]

Because of the very fast initial oxidation regime, the smallest oxide thickness at which we could accurately determine the rate of NiO growth was about 100 Å. The rate r of Ni oxidation is defined as the rate of oxide growth at a fixed oxide thickness x_0. The oxidation rate was obtained from the data by least-squares fitting each isotherm to Eq. (2) to determine A and α, and then differentiating Eq. (1); i.e.,

$$r \equiv \frac{dx}{dt}\bigg|_{x=x_0} = A\alpha t^{\alpha-1}\big|_{x=x_0} = A\alpha\left(\frac{x_0}{A}\right)^{(\alpha-1)/\alpha}, \qquad (5)$$

where $x_0 \cong 100$ Å. Figure 3 shows the logarithm of the rate of oxidation at an average oxide thickness of 115 Å versus inverse absolution temperature in the vicinity of the Curie temperature θ_C of bulk nickel. There is a definite change in slope at a temperature of 631 ± 2 K. The slopes were obtained by a least-squares fitting procedure and for temperatures below 631 K, the activation energy is 61 ± 1 kcal/mole, whereas for temperatures above 631 K, the activation energy is 36.8 ± 1 kcal/mole. The change in activation energy amounts to 24 ± 2 kcal/mole or 1 ± 0.1

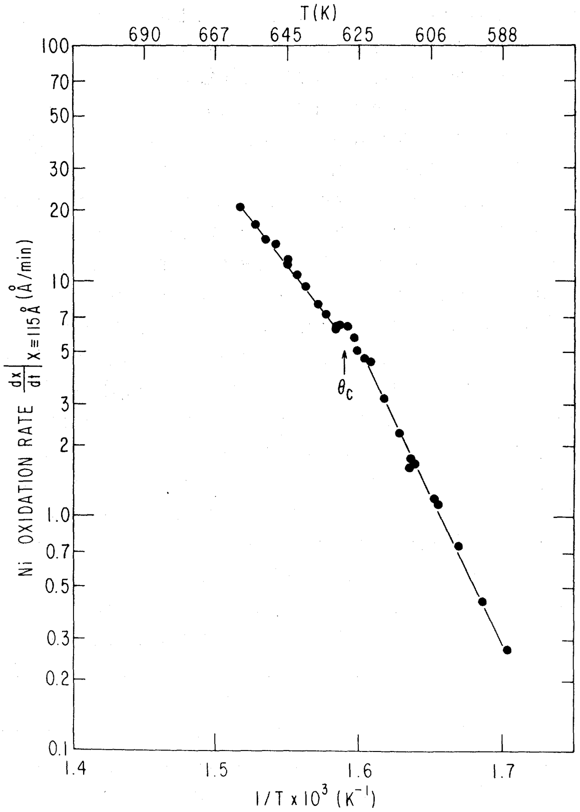

FIG. 3. Logarithm of the Ni oxidation rate dx/dt at $x = 115$ Å vs inverse absolute temperature.

eV/atom. There also appears to be a small cusplike feature at 631 K. Although the experimental uncertainty is not much smaller than this feature, it was present in three separate measurements and is believed to be a real effect. Within an experimental uncertainty of ±2 K, the break in slope shown in Fig. 3 occurs exactly at the ferromagnetic transition temperature of bulk nickel. It was also found that the oxidation rate was more reproducible than either A or α and hence, within the resolution of the present experiment, it was not possible to determine whether primarily A or α changed at θ_C. The experiment was repeated on three different samples under slightly different conditions and virtually the same results were obtained.

There have been many previous studies of the interaction of a nickel substrate with oxygen gas. However, most of the earlier work was restricted to relatively high temperatures of ~700–1000 K and thick NiO layers of ~2000 Å,[4-6] or to low temperatures of ~300 K and the first few monolayers of NiO.[7,8] Thus, it is difficult to compare these earlier results with those presented here.

The low-temperature studies cited above indicate that at an oxide thickness of less than two monolayers, the surface layer is already characteristic of bulk NiO. At temperatures above 473 K, NiO crystallizes in a cubic NaCl structure.[9] Oxides of this type have no larger channels through which the oxygen ions can diffuse, but do have interstitial and cation vacancies through which the smaller metal ions can migrate. Hence for nickel oxidation, the growth is believed to be primarily by cation motion.[3]

If the oxide grows via cation migration, the nickel ion must first migrate from the metal surface to a vacancy in the oxide. To do this, the nickel atom must first overcome a potential-energy barrier of height W, which is related to the energy necessary to break Ni-Ni bonds at the surface. In general, W can be considered to be the energy required to transfer a nickel atom through the metal-oxide interface. Once in the oxide, there will be another potential-energy barrier U for diffusion from one interstitial site to the next, but it is generally believed that U is less than W.[10] Therefore, for thin oxide layers (~10–200 Å), the oxide growth rate will be limited by the time necessary for the surface Ni atom to overcome the first potential-energy barrier W. If there are no other forces present, then the *initial* rate will be approximately given by

$$r \equiv dx/dt = BN\nu \exp(-W/k_BT), \qquad (6)$$

where B is a constant, N is the number of mobile Ni atoms at the surface, ν is the attempt frequency (which will be the order of a phonon frequency), and the Boltzmann factor gives the probability that the nickel atom will succeed at temperature T.

If one includes the possibility of electric fields developing during the oxidation process,[10] then the growth rate for thin oxide layers is approximately given by

$$r \equiv dx/dt = BN\nu \exp\{[-W + eaV(x)/x]/k_BT\}, \qquad (7)$$

where e is the electronic charge, a is the order of the NiO lattice constant (4 Å), and $V(x)$ is the electrostatic potential which develops during the oxidation process. The actual shape of the isotherms is obtained by integrating Eq. (7); however, this can be quite complicated since $V(x)$ must be determined in a self-consistent manner and specific assumptions must be made cation, anion, and electron motion. In this Letter, we make no attempt to determine V but refer the interested reader to the work of Fromhold and co-workers who have investigated this problem in great detail.[11-13]

The experimental data shown in Fig. 3 indicate that the activation energy for temperatures below θ_C is about 1 eV higher than the value for temperatures above θ_C. It is difficult to envisage how a magnetic transition in the substrate could effect the electrostatic potential $V(x)$ shown in Eq. (7). However, the energy necessary to remove a nickel atom from the surface, W, could be affected by the paramagnetic-ferromagnetic transition since in the ferromagnetic state, the nickel atoms are presumably more strongly bonded to the surface by an energy of the order of the exchange energy. The exchange energy, which is believed to be responsible for the ferromagnetism of nickel, has been estimated by Herring[14] to be of the order of 0.4 eV in the bulk.

Additional bonding due to the exchange energy is perhaps the simplest explanation for the change in the activation energy of the oxidation rate at the Curie temperature and is at least the correct order of magnitude. We emphasize, however, that this is only a hypothesis and further experimental in external magnetic fields may help clarify how the oxidation kinetics are modified at the Curie temperature.

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