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Effects of the magnetic transition on the anodic oxidation rate in chromium

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Abstract. The first-order Néel transition in chromium and a change in behaviour between the paramagnetic and the antiferromagnetic phase are observed in its electrochemical properties. The explanation must relate the kinetics of anodic oxide film growth to changes in the electronic structure at the magnetic phase transition.

1. Introduction

The reactivity of solids has been found to be influenced by phase transitions [1,2]. The oxidation of nickel, for example, changes noticeably near the Curie temperature ($T_C = 631$ K) [1], and the decomposition rate of nitrous oxide and carbon dioxide in the presence of nickel catalyst rises significantly above T_C [2,3]. Among the transition metals of group 6B, chromium is the only one that has a magnetic phase transition, being paramagnetic (PM) above the Néel temperature (T_N) of 311 K and antiferromagnetic (AFM) below this temperature [4]. The aspect of the electronic structure relevant to the present work is the gap which opens up at the Fermi surface at T_N , causing a first-order jump in the order parameter. This affects many physical properties of chromium, causing dramatic changes of the Young's modulus, the internal friction coefficient, the thermal expansion coefficient, the electrical resistivity, and thermoelectric power [4].

Another relevant feature of the Néel transition in chromium and some of its alloys is that it occurs at temperatures within the liquid water phase. This allows the use of electrochemical techniques to investigate the influence of the phase transitions on the rate of the anodic oxidation of chromium in aqueous solutions.

2. Experimental details

The working electrode was prepared from a high-purity chromium crystal, pressed into a Teflon® tube, exposing a {110} surface area of 0.28 cm². The auxiliary electrode was a platinum wire, placed in a glass tube separated from the main solution compartment by a porous plate. All potentials were measured with respect to a Hg/Hg₂SO₄, 1 m H₂SO₄ reference electrode.

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The electrolyte was a buffered solution of analytical grade acetic acid and sodium acetate in distillate and deionized water. Using sodium sulphate as a support electrolyte, the solution was maintained at a pH of 4.5. The measuring equipment consisted of a PARC model 173 potentiostat/galvanostat coupled to a PARC model 175 universal programmer and a Bryans model 50 000 x - y recorder.

The surface of the electrode was polished with alumina ($0.3 \mu\text{m}$), degreased with acetone, rinsed with distilled water and dried. Before each new cyclic voltammogram, the electrode was made cathodic at -1.7 V for 10 minutes, in order to remove the chromium oxide film.

Cyclic voltammetry was used to promote the oxidation of chromium, that is, a cyclic triangular sweep potential was applied between the working and the reference electrodes. The rates of increase and decrease of the potential were identical. Before starting the experiment, nitrogen was bubbled through the solution for about 30 minutes. The solution was kept under a nitrogen atmosphere thereafter.

The current between the working electrode and the auxiliary electrode was measured and analysed as a function of potential. A maximum i_p in the anodic current density, i is clearly noticeable at the peak potential, E_p . These two parameters were affected by temperature, T , potential sweep rate, v and other variables which were kept constant in these experiments. Reproducible data were obtained at sweep rates greater than 20 mV s^{-1} , in buffered solutions.

3. Results and discussion

A typical voltammogram, showing the current density $i(E)$ as a function of the potential for an anodic oxide film growing on chromium is illustrated in figure 1. The various parts of this diagram may be interpreted as follows:

(1) the slow current rise in region A is associated with the oxidation of hydrogen absorbed on the metal surface, as the oxide film is being reduced;

(2) the subsequent rapid increase followed by a saturation peak in region B is initially the consequence of Cr(III) formation, which creates a soluble complex, and when the formation rate of Cr(III) becomes equal to the formation rate of insoluble Cr_2O_3 , the current density reaches a maximum;

(3) in region C, the scanning of the potential is reversed and field in the film is reduced, leading to a rapid decrease in the current;

(4) finally, in region D, reduction of Cr_2O_3 takes place before the water is reduced.

As can be seen in figure 2, there is a linear relation between the peak current, i_p , and the square root of the sweep velocity, \sqrt{v} , so that the slope $W = di_p/d\sqrt{v}$ becomes a temperature-dependent parameter. The temperature dependence is shown in figure 3, where W rises slowly with increasing temperature up to T_N , showing an anomaly at T_N and then rises more rapidly at $T > T_N$.

It may be seen in figures 2 and 3 that the parameter W can be determined by electrochemical experiments. It is not possible to resolve the exact physical nature of W at this point. It is clear, however, from the interpretation of figure 1 that the parameter W is associated with the anodic growth processes of chromium oxide. The peak current and the potential at the peak depend on the sweep rate, and it is known that different sweep rates will generate different defect densities on the film. These defects are generated by the excess of Cr(III) or O^{2-} ions in the film. The linear form of $i_p(\sqrt{v})$ shows that the parameter W is not dependent on v and, therefore, also independent of defect concentration.

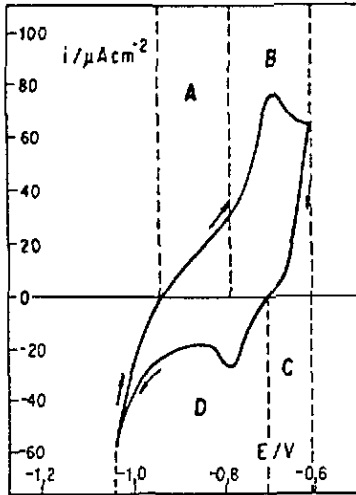


Figure 1. Cyclic voltammogram for anodic oxidation over a chromium electrode in 0.5 M Na_2SO_4 , in a buffer solution of acetic acid and sodium acetate, with the pH adjusted to 4.5, $T = 303$ K and $v = 0.075$ V s^{-1} .

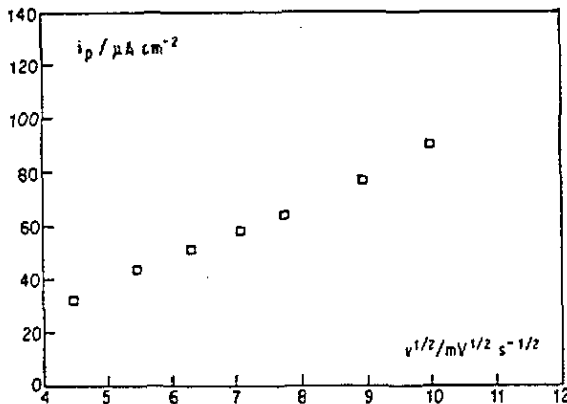


Figure 2. Peak current density, i_p , as a function of the square root of the potential sweep rate, v , for chromium at 310 K.

The temperature variation of the resistivity of chromium $\rho(T)$, near T_N , bears a strong resemblance to $W(T)$ in figure 3. The drop of ρ below T_N is caused largely by the decrease in conduction electrons during the magnetic phase transition, mentioned earlier. One may suggest that the sudden drop in W at T_N shown in figure 3 is associated with the first-order weak Néel transition, which is observed in several physical properties of chromium [4]. The gradual variation of W with temperature in the AFM phase may be attributed to the progressive reduction in the number of conduction electrons with decreasing temperature. The change in slope dW/dT between the AFM and PM phase is believed to be due to this effect.

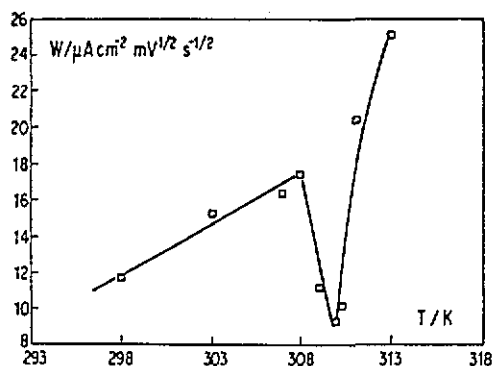


Figure 3. The parameter $W = di_p/d\sqrt{v}$ as a function of temperature, T , for chromium.

4. Conclusions

A new feature of the electrochemical behaviour of chromium near its magnetic phase transition is reported. This result is expected to be relevant for the understanding of the reactivity of solids. While thermal oxidation follows a different physical process than anodic oxidation, it is interesting to note the similarity between the temperature dependence of the thermal oxidation of nickel near the Curie temperature and the present results.

The parameter W which clearly shows the anomaly near T_N is too complex to allow an interpretation in terms of a simple model. The investigation of alloys and of other electrochemical properties are desirable in order to propose a consistent model.

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