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# Investigation of the magnetic phase transition in chromium alloy using electrochemical techniques

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**Abstract.** The magnetic phase transition of chromium–0.2 at.% vanadium alloy was investigated using electrochemical methods. The temperature dependence of the potentiodynamic and open circuit potential data shows an anomalous behaviour close to the Néel temperature. This anomaly closely follows the shift of the Néel temperature due to alloying with vanadium. The transition is suppressed when the alloy is anodically oxidized, therefore the anomalies observed in the electrochemical parameters must be caused by the magnetic phase transition in the alloy itself. Electrochemical parameters, such as peak current density and zero-current potential, also present either distinct temperature dependences above and below the Néel temperature or anomalies around it.

## 1. Introduction

Chromium changes from an antiferromagnetic (AFM) state to a paramagnetic (PM) state when heated above the Néel temperature ( $T_N = 311$  K). This magnetic phase transition is followed by anomalies in electric, magnetic and mechanical properties [1–3]. Recently, the cyclic voltammetry technique [4] has revealed that the magnetic phase transition in a chromium single crystal causes a discontinuous variation in the anodic peak current density near the Néel temperature.

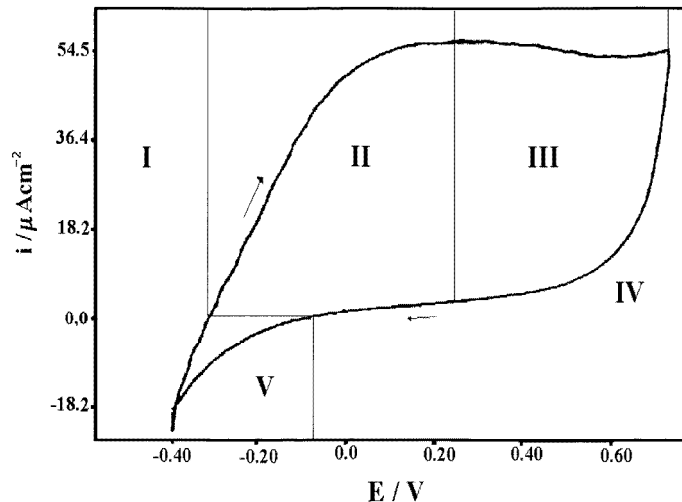
Several properties of chromium AFM alloys can be described by the rigid-band model and the nesting of electrons at the Fermi surface [2].

The decrease in the electrons/atom ratio and in the chemical potential due to alloying with vanadium results in a linear decrease in the transition temperature ( $T_N$ ) at a ratio of 80 K/at.% V [2]. Otherwise, elements like Mn increase the chemical potential, causing an increase in  $T_N$  of about 50 K/at.% Mn. The phase transition is followed by the formation of a band gap in the AFM state [3]. This gap can be described as a function of the Néel temperature as  $\Delta = 5.0 k_B T_N$ , where  $k_B$  is the Boltzmann constant. Residual resistivity data for CrFe and CrSi alloy systems doped with vanadium and manganese show evidence that the Fermi level  $E_F$  can be ‘tuned’, roughly as expected for a rigid-band model, where V decreases  $E_F$  while Mn increases it [2].

Electrochemical measurements are expected to be sensitive to electronic changes related to the magnetic phase transition on the electrodes.

The reactivity of solids may be affected by magnetic phase transitions, as is the case of the so-called ‘Ewald effect’ observed on the thermal oxidation of nickel [5].

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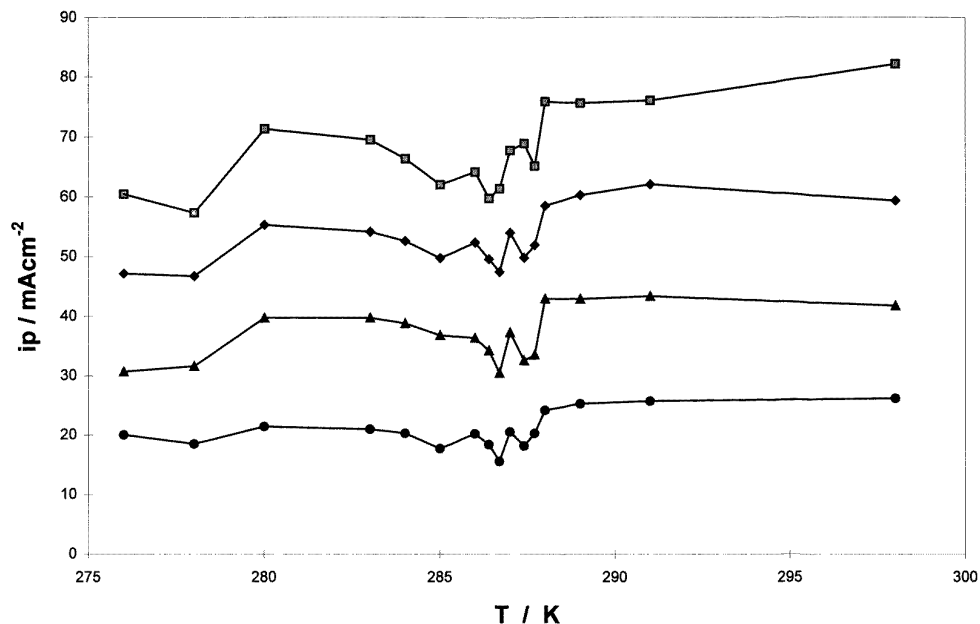
**Figure 1.** Voltammogram for chromium–0.2 at.% vanadium alloy at temperatures higher than  $T_N$  in buffer solution of acetic acid/sodium acetate pH = 3.5,  $I = 0.2$ ,  $T = 25^\circ\text{C}$  and  $v = 15 \text{ mV s}^{-1}$ .

From an electrochemical point of view, the investigation of oxide growth on chromium and its alloys is important since this metal is the basic alloying element for stainless steel.

The oxidation characteristics of any metal are fully dependent on their electronic properties so that a magnetic phase transition leading to changes in electronic structure is expected to correlate with electrochemical properties of Cr–V alloy near  $T_N$ . Following the previous work on pure chromium [4], this report contributes with new results, which are simpler and give stronger support to the idea that the electrochemical approach can be relevant in understanding the correlation between magnetic phase transformations and the reactivity of solids.

## 2. Experiment

Electrochemical measurements were made in a one-compartment, three-electrode cell. The working electrode was prepared with a rod of chromium–0.2 at.% vanadium alloy, embedded with epoxy resin in a glass tube (electrode surface area of  $0.55 \text{ cm}^2$ ). The auxiliary electrode was a platinum wire that was separated from the working solution by a fritted glass plate. The potential measurements were made with a hydrogen electrode prepared galvanostatically using a  $1 \text{ mA}$  current density for  $300 \text{ s}$  in the working solution. The electrolyte used was an acetic acid/sodium acetate buffer solution with pH = 3.5 and ionic strength of 0.2, with sodium sulphate as the supporting electrolyte. All the electrolytic solutions were prepared with water purified by the Milli Q system. The measurements were performed on a potentiostat/galvanostat EG&G PARC model 273 A, connected to an Allen xy register, model 725. To keep the temperature constant, a cryothermostat from PolyScience, model 9000, was used. The temperature of the cell was measured in the solution using a mercury thermometer with  $0.05^\circ\text{C}$  precision. Before each experiment the electrode surface was mechanically polished with 600 grit sand paper, and washed with distilled water to remove the previously formed oxide in order to obtain the same initial surface. Potential sweep rates between  $5$  and  $20 \text{ mV s}^{-1}$  were used within the temperature range of  $276 \text{ K}$  to  $298 \text{ K}$ . The results were reproducible for all the sweep rates.



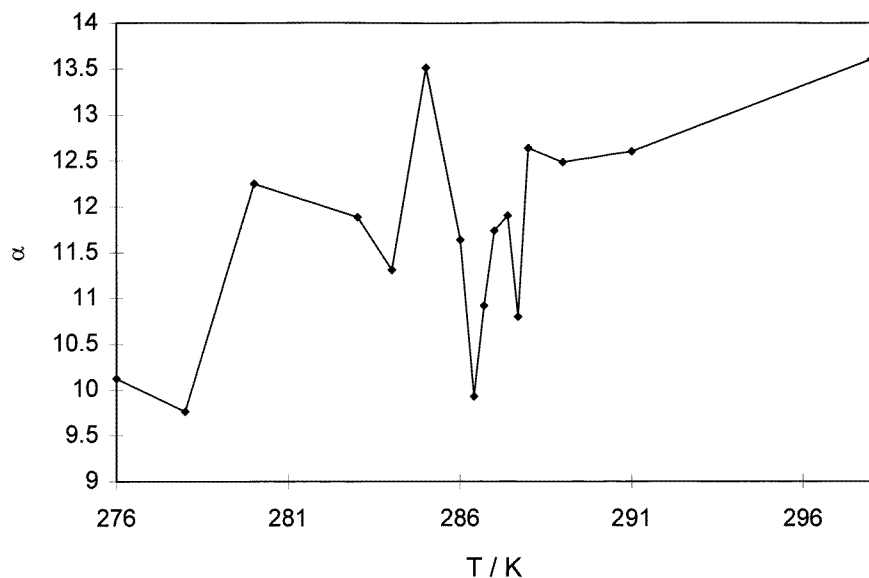
**Figure 2.** Current density as function of temperature for chromium–0.2 at.% vanadium alloy in acetic acid/sodium acetate solution pH = 3.5 and  $I = 0.2$ . Sweep rate: (●)  $5 \text{ mV s}^{-1}$ ; (▲)  $10 \text{ mV s}^{-1}$ ; (◆)  $15 \text{ mV s}^{-1}$  and (■)  $20 \text{ mV s}^{-1}$ .

### 3. Results and discussion

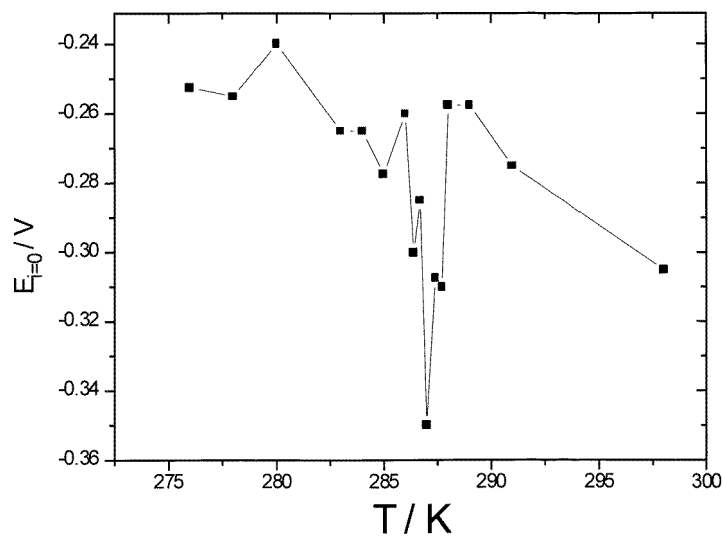
A typical cyclic voltammogram for Cr–V alloy is shown in figure 1 in which five regions are defined. As described in [4], region I refers to reduction reaction of  $\text{H}^+$  ions and of oxides present on the metal surface. Region II corresponds to the oxidation of the alloy and the adsorption of hydrogen. In region III ions are transported through the oxide film, assisted by the high electrical field. The fourth region (IV) is related to the inversion of the potential sweep. Finally, region V corresponds to a region where reduction of  $\text{H}^+$  and oxidation happens.

Several electrochemical techniques have been used in order to determine the dissolution mechanism and the kinetics of film growth. With the coupled gold ring–disc technique it was shown that below  $-0.58 \text{ V}$  ring potential, chromium dissolves into solution as  $\text{Cr}^{2+}$ , while above this voltage a passivating oxide is formed [6]. Heumann and Panesar [7] determined the chromium passive layer composition by comparing the electrochemical behaviour of Cr,  $\text{CrO(OH)}$  and  $\text{Cr}_2\text{O}_3$ . Although  $\text{CrO(OH)}$  is the most accepted passive layer composition on chromium, other authors describe it as  $\text{Cr}_2\text{O}_3$  [8] or hydrated  $\text{Cr}_2\text{O}_3$  [9].

Using the current density peak of the voltammogram at different sweep rates, a discontinuity near the Néel temperature can be observed as depicted in figure 2 where the peak current level is higher and varies in a smoother manner in the PM phase than in the AFM phase. Similarly to what was found for chromium [4], the peak current density is a linear function of the square root of the sweep rate, therefore we can define a new parameter,  $\alpha = di_p/dv^{1/2}$ , which depends only on temperature. This parameter is represented in figure 3, where a strong anomaly is observed close to the Néel temperature. The variation of  $\alpha$  with temperature above  $T_N$  is quite different from that below  $T_N$ . The

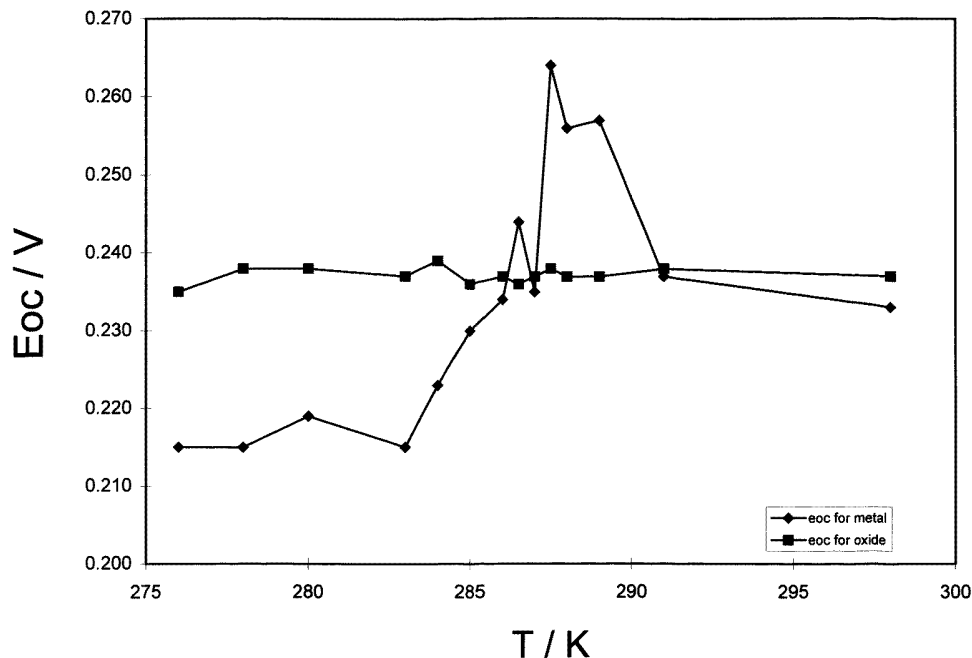


**Figure 3.** Parameter  $\alpha = (di_p/dv^{1/2})$  as function of temperature for chromium–0.2 at.% vanadium alloy.



**Figure 4.** Zero-current potential as a function of temperature for chromium–0.2 at.% vanadium alloy in acetic acid/sodium acetate solution. pH = 3.5;  $I = 0.2$ .

effective slope is larger at the AFM phase due to the existence of the gap at the Fermi surface; also the data are much more scattered due to a poorer definition of the peak in the voltammograms. Figure 4 presents the zero-current potential,  $E_{ZC}$ , as a function of temperature. This potential represents a transient behaviour in which the cathodic current is equal to the anodic one. In this way, the displacement to higher potentials can be associated with a greater difficulty in promoting metal oxidation. This can be concluded without doubt,



**Figure 5.** Open-circuit potential as function of the temperature for polished metal surface (◆) and for the pre-anodized metal surface (■).

since it is known that there is no oxide formation in this potential range. Considering these aspects, the  $E_{ZC}$  is related to the chromium oxidation to the soluble  $\text{Cr}^{2+}$  complex and to the reduction of these ions and of  $\text{H}^+$ . In this way, figure 4 clearly shows that metal oxidation in the AFM phase is more difficult than in the PM phase.

In order to verify whether the anomalous behaviour associated with all the electrochemical parameters investigated is due to the metal itself or to the oxide grown on its surface, open-circuit potential experiments with polished and pre-anodized metal were performed. The choice to measure the open-circuit potential,  $E_{OC}$ , was made because in this case no external perturbation is introduced into the system, therefore just the behaviour of the metal/solution interface is investigated. However, one must consider that the open-circuit potential is a mixed potential and not an actual equilibrium potential, since the reactions in the anodic part (chromium dissolution) and in the cathodic part (proton reduction) are different. Figure 5 presents the  $E_{OC}$  as a function of temperature for freshly polished and pre-anodized surfaces. For the temperature range investigated, the pre-anodized surface is practically unaffected by the magnetic transition. However, for the mechanically polished surface there is a large peak for  $E_{OC}$  near  $T_N$  and significantly smaller values in the AFM phase. The suppression of the magnetic transition effects on  $E_{OC}$  for pre-anodized surface samples is evidence that the observed anomalies are actually due to the phase transformation in the metal itself. The other convincing evidence is the fact that in this work it is clearly shown that the Néel temperature is what actually determines the temperature where the anomalies occur and where the temperature dependence changes. Adding vanadium lowers the temperature where all anomalies are observed, including the electrochemical properties.

#### 4. Conclusions

The electrochemical investigation of pure chromium ( $T_N = 311$  K) and of Cr–V 0.2 at.% alloy ( $T_N = 288$  K) showed anomalous behaviour at the Néel temperature, and distinct qualitative temperature dependence above and below  $T_N$ . The voltammograms showed that in the initial oxidation stage there is a dissolution of chromium ions into the solution and that at higher potentials there is oxide film formation. The voltammogram parameters related to the peak current density,  $i_p$ , have anomalies in the Néel transition temperature region. The zero-current potentials, during a voltammetric sweep, also have a clear discontinuous behaviour in the AFM–PM phase transition. Open-circuit potential measurements with the alloy surface polished showed evidence of the Néel transition, although the same alloy covered with an anodic oxide film is not sensitive to the magnetic phase transformation. Finally, one can say that the electrochemical measurements are undoubtedly proved to be sensitive to the Néel transition in chromium and its AFM alloys.

#### Acknowledgments

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