

PHOTOSTIMULATED EXOELECTRON EMISSION FROM THIN LAYERS OF NICKEL, CHROMIUM AND THEIR OXIDES DURING MAGNETIC PHASE CHANGES

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Electron exoemission into air atmosphere from thin layers of nickel and chromium and their oxides formed on their surface has been studied. An air point counter and an air point counter with quenching vapour above the free liquid surface have been used as detectors. In both cases the occurrence of emission maxima was found at the Néel point for NiO, Cr₂O₃, and pure chromium and at the Curie point pure nickel.

It follows from the above-mentioned investigations that:

- a) the intensity of emission depends on the thickness of the oxide film covering the investigated samples,
- b) the dependence of the position of the maximum corresponding to the Néel point for NiO on oxide thickness is a parabolic one,
- c) the positions of emission maxima from chromium samples correspond to phase transition points both for chromium and its oxides.

1. Introduction

In first attempts of explaining the results of electron exoemission studies (Kramer 1950) an important role was played by the measurements of electron emission accompanying the recrystallization of Wood's alloy. These measurements were the basis of the so-called

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modification theory (Modifikationstheorie) which has been abandoned by now. This theory treated the exoemission of electrons from metal surfaces as electron emission associated with the transition of the metal from the "non-metallic" to "metallic" state.

In later works the emission of electrons was observed many times during the recrystallization of different metals and alloys (Bruna *et al.* 1956; Steiner 1957; Bogachev *et al.* 1967), however, only quite recently attention was drawn to the fact that in many cases the necessary condition for the occurrence of the emission is a simultaneous illumination of the sample surface with UV-light. It has been also found that emission during the recrystallization is connected above all with those metals for which large volume changes occur during the recrystallization, which in turn lead to surface strain in the oxide film covering the sample and its fracture (Sujak *et al.* 1966; Sujak, Całusiński 1968). This fact enormously complicates the description of the mechanism (Całusiński 1967).

During the study of thermostimulated emission from ferrite in the temperature range up to 1000°K Bergstein and Bohun (1957) have found that one of the three maxima observed on the $\frac{N}{t} = f(T)$ curve corresponds to the Curie point of the sample.

Recently we have reported about the occurrence of electron exoemission associated with the transition of NiO from antiferromagnetic to paramagnetic state (Néel point) and with the transition of pure nickel from ferromagnetic into paramagnetic state (Curie point). The present paper gives the results of systematic studies on exoemission of electrons during magnetic phase transitions in the case of this films of nickel and chromium as well as their alloys.

2. Experimental conditions

The block diagram of the measuring apparatus is shown in Fig. 1. Exoelectrons were detected by means of an air point counter with saturated vapour above the free surface of the liquid together with a classical pulse registration circuit (Stepniowski *et al.* 1964; Stepniowski 1966). The cathode diameter of the counter was 1.3 cm and the operation voltage 2240–2260 V depending on atmospheric pressure (Podolak *et al.* 1964). The counter

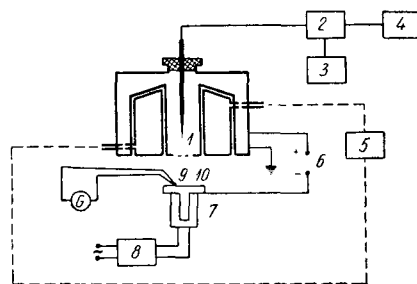


Fig. 1. Block diagram of the apparatus: 1 - counter, 2 - preamplifier, 3 - HV-supplier, 4 - scaler, 5 - Hoeppler's thermostat, 6 - accelerating voltage source, 7 - furnace, 8 - autotransformer, 9 - thermocouple, 10 - investigated sample

with quenching vapour above the free surface of ethyl alcohol was operated at 318°K. The cathode of the counter was earthed.

The investigated nickel samples were deposited electrolytically on flat metal cores. Chromium samples were deposited electrolytically on previously nickel-plated brass cores. The thickness of the films was about 10 μm . The field which accelerated the electrons was produced by applying a voltage of 500 V between the surface of the sample and the counter grid. The potential of the sample was negative whereas the screening grid was earthed.

The temperature of the sample was changed by means of a resistor furnace supplied from an autotransformer. The heating rate was about 10 degrees/min. The cooling rate was similar but gradually decreased in the temperature interval between 350 and 290°K. The copper-isotan thermo-couple permitted temperature measurements with the accuracy of about 5°K.

Before the measurements of the $\frac{N}{t} = f(T)$ curve the samples were not excited. They were only illuminated with UV-light with constant intensity from a Q 400 quartz lamp.

In order to avoid uncontrolled effects of UV-radiation which would bias the results of measurements, several checking measurements have been carried out which showed that the yield of the counter does not depend on the temperature of the furnace. The UV-radiation which stimulates the emission, gives only rise to an insignificant increase in counter background which can be well distinguished from the dependence of emission intensity $\left(\frac{N}{t}\right)$ on

temperature (T): $\frac{N}{t} = f(T)$.

The exoemission of electrons during the heating and cooling of nickel samples was studied by simultaneous measurement of the time dependence. These data were used for the determination of the dependence of the emission intensity on sample temperature.

3. Results of measurements

a) Nickel

It was found that in order to observe exoemission of electrons significantly different from counter background it is necessary to stimulate the surface of the sample with UV-light.

Fig. 2 shows the temperature dependence of the intensity of emission from a virgin nickel sample. There are two maxima on the $\frac{N}{t} = f(T)$ curves both during the heating and during the cooling process. The position of the first maximum changes from about 400°K during the heating to about 460°K during the cooling. The position of the second maximum is almost independent of the direction of temperature change. This maximum occurs at about 630°K which corresponds to the Curie point of pure nickel.

During a repeated heating cycle of the same sample an increased intensity of electron emission is observed as well as a further shift of the first maximum towards higher temperatures whereas the position of the second maximum remains the same (Fig. 3).

In order to elucidate the nature of the processes responsible for the occurrence and shift of the first maximum the nickel sample was subjected to a cycle of heating to about 570°K and subsequent cooling to room temperature. Simultaneously the emission intensity was measured as a function of the temperature. Fig. 4 shows the dependence of the temperature

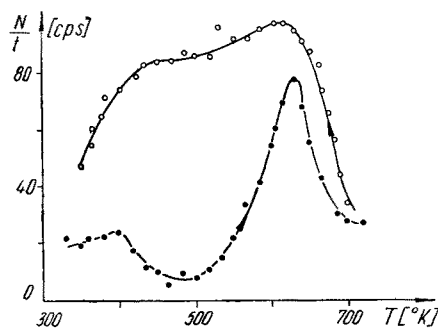


Fig. 2. Dependence of emission intensity on temperature $\frac{N}{t} = f(T)$ for a virgin nickel sample. Arrows drawn on the curves indicate the direction of the temperature change

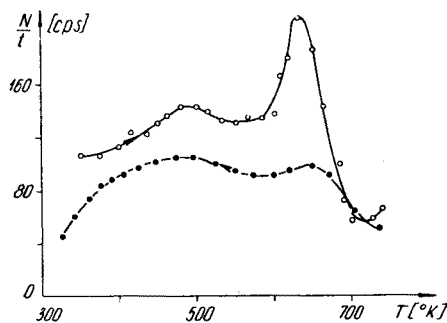


Fig. 3. Dependence of emission intensity on temperature $\frac{N}{t} = f(T)$ for a nickel sample subjected to repeated heating and cooling. Arrows indicate the direction of temperature change

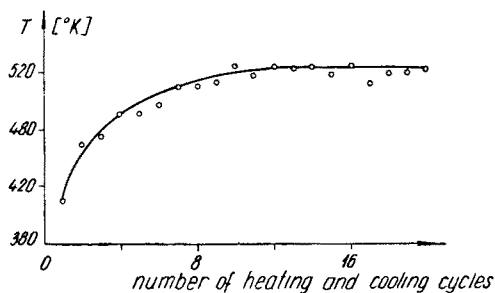


Fig. 4. Dependence of the position of the maximum corresponding to the Néel point for NiO on the number of heating-cooling cycles to which the sample was subjected

corresponding to the first maximum on the number of heating-cooling cycles (n) to which the sample was subjected. As a result of these measurements it was found that the position of the maximum is shifted towards higher temperatures until it becomes established at about 520°K. It is well known that this temperature corresponds to the Néel point of NiO.

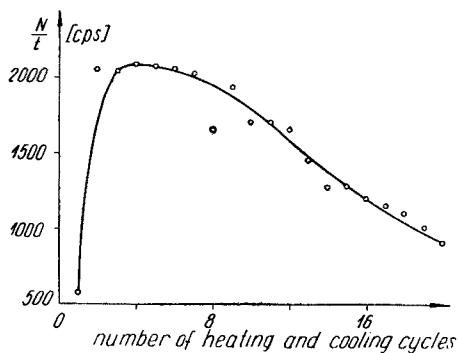


Fig. 5. Dependence of the height of the maximum I corresponding to the Néel point of NiO on the number n of heating-cooling cycles to which the sample was subjected

The dependence of the height of the first maximum on the number of heating-cooling cycles (n) is shown in Fig. 5. Only the maximum on the $\frac{N}{t} = f(T)$ curve occurring during the heating was taken in consideration.

In order to find to which extent the effects observed depend on the presence of ethyl alcohol in the atmosphere surrounding the sample (catalytic decomposition of alcohol)

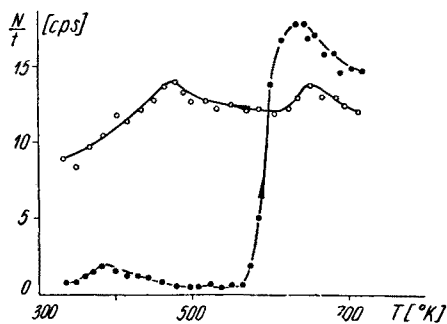


Fig. 6. Temperature dependence of the emission intensity $\frac{N}{t} = f(T)$ measured by means of a point counter without quenching vapour for a virgin nickel sample

test measurements were carried out using as the detector an air point counter without quenching vapour. Fig. 6 shows the curve $\frac{N}{t} = f(T)$ for a virgin sample, measured with the

air point counter. Similarly as in the case of counter with quenching vapour of ethyl alcohol there are two maxima on the emission curve. The position of the first maximum shifts towards higher temperatures whereas the position of the second remains the same. Measurements with a counter without quenching vapour are, however, more difficult because of large instability of the detector. The investigated effects are less distinct than in the case of a point counter with ethyl alcohol as quenching vapour.*

b) Chromium

The exoemission of electrons during the heating and cooling of chromium sample was investigated in the temperature range from 290 to 600°K. The measurements were made several times and on many samples. In all cases two emission maxima were observed, one at the temperature of about 320°K and another one at about 480°K (Fig. 7). In many cases in addition to the two above-mentioned maxima there appeared an additional maximum in the vicinity of 420°K (Fig. 8).

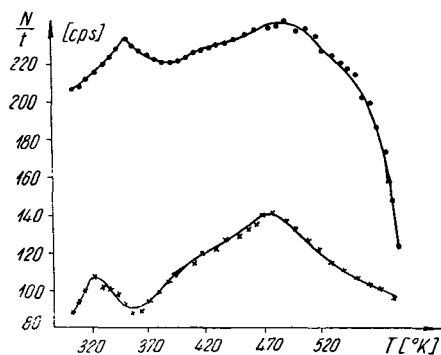


Fig. 7. Dependence of the emission intensity on temperature for a chromium sample. Arrows indicate the direction of temperature change

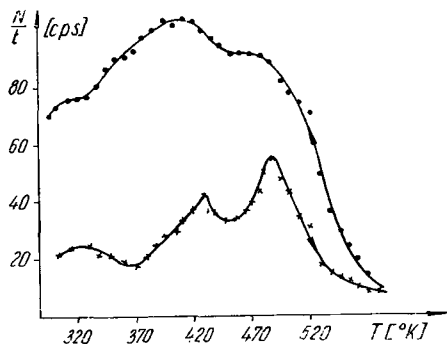


Fig. 8. Dependence of emission intensity on temperature for chromium sample. Arrows indicate the direction of temperature change

4. Discussion of the results

a) Nickel

It follows from the experimental data given in previous sections that the maxima observed on the $\frac{N}{t} = f(T)$ curve are associated with phase transitions. The maximum I corresponds to the transition of NiO from the antiferromagnetic to paramagnetic state (Néel point). The maximum II corresponds to the transition of nickel from ferromagnetic to paramagnetic state (Curie point). As it is known from literature (Kubashevski 1953) only NiO is produced on the surface of nickel oxidized in air atmosphere below 1000°K. The thickness of the oxide layer grows with the time according to the parabolic law of oxidation. On the other hand it is known that the Néel point for massive NiO samples is at 523°K (Nagamiya *et al.* 1955). It is also known that the position of the phase transition point depends on thickness of the investigated sample (Klein, Smith 1951; Ruske 1954; Hellenthal 1958; Drigo 1951; Crittenden, Hoffman 1953; Thun 1956; Votova 1961), and for lower thicknesses shifts towards lower temperatures. These data permit the conclusion that the first maximum is associated with the phase transition at the Néel point and that the shift of its position towards the temperature of 520°K is due to the increase in thickness of the oxide covering the sample. After the thickness has become sufficiently large the nickel oxide behaves as a massive sample.

The second maximum can be explained as associated with the phase transition of nickel at the Curie point. One may guess that the increase in emission intensity in the phase transition points is due to processes occurring during these transitions on the surface of the sample. Such processes may be stress or plastic strain (*e. g.* failure) of oxide covering the sample (Sujak *et al.* 1966; Sujak, Całusiński 1967) due to sudden change of thermal expansion coefficients, photoadsorption processes (Stown 1963) and local decrease in work function due to increased diffusion of dislocations towards the surface of the sample (Andreyev, Palige 1963). One also cannot exclude the contribution of various processes of heterogeneous catalysis (*e. g.* decomposition of ethyl alcohol) occurring on the surface of the sample.*

The dependence of emission intensity on thickness of oxide layer covering the sample (Fig. 5) indicates that there is an optimal thickness of oxide coating for which the electron exoemission is the greatest.

b) Chromium

Fountain (1961), basing on original data states that in the vicinity of 310°K such properties of chromium as elasticity modulus, internal friction, specific resistivity, thermoelectric force and linear expansion coefficient are subject to sudden changes. At first there was the opinion that these changes are associated with the presence of admixtures, but now they are connected with the properties of chromium. There is now evidence indicating allotropic transformations of chromium at this particular temperature. Above as well as below 310°K the crystal structure of chromium is space centred and changes of the lattice

show only very small bending. Above this temperature the structure is characterized by more compact packing. The temperature at which the above-mentioned anomalies occur decreases with compressive stress and degree of contamination.

It is also known from literature (Kubaszewski 1953) that during the heating the sample becomes covered with a Cr_2O_3 layer. Chromium oxide Cr_2O_3 is antiferromagnetic. The transition from antiferromagnetic to paramagnetic state occurs at 310°K (Nagamiya *et al.* 1955; Szczeniowski 1954). In this situation the exoemission maximum on the $\frac{N}{t} = f(T)$

curve in the vicinity of 310°K can be connected with sudden changes of the properties of chromium and with changes of the magnetic properties of Cr_2O_3 covering the sample at the Néel point. So far we have not succeeded in detecting exoemission of electrons during the heating and cooling of powdered Cr_2O_3 in spite of maintaining the same experimental conditions as in the case of electrolytically deposited nickel and chromium. It is known, however, that in the case of powdered materials the ability of electron exoemission is much smaller than in the case of solid materials (Gašior *et al.* 1964).

In contrast to other transition elements chromium is characterized by antiferromagnetic properties. The values of the Néel temperature for chromium reported by various authors are different: Szczeniowski 420°K , Fountain 473°K , Nagamiya *et al.* 480°K . The antiferromagnetism of chromium has been discovered quite recently by neutronographic methods. These properties have not been confirmed, however, by measurements of magnetic permeability (Fountain 1961).

The above-mentioned data indicate that the maximum in exoemission intensity on the $\frac{N}{t} = f(T)$ curve observed in the present experiment in the vicinity of 480°K is associated with the change of magnetic properties of chromium at the Néel point. The temperature at which the intermediate maximum of exoemission intensity appears is close to the Curie point of CrO_2 which amounts to 390°K (Nagamiya *et al.* 1955). It is difficult to connect the occurrence of this maximum with the magnetic transition of CrO_2 , as this oxide has not been found so far by analytical methods to be present on the surface of chromium oxidized in air. On the other hand it is known (Bergstein, Bohun 1957; Biernacki *et al.* 1967) that magnetic transitions are accompanied by increased exoemission of electrons and that the exoemission method is suitable for the detection of traceable crystal contaminations (Sujak 1967). The fact that the intermediate maximum does not always appear distinctly seems to indicate that in certain conditions in addition to Cr_2O_3 there may be produced some traceable amounts of CrO_2 which later is transformed into Cr_2O_3 . This presumption seems plausible since according to Kubaszewski (1953) almost all chromium oxides are rather unstable and go over into Cr_2O_3 . This latter process is irreversible and occurs in any temperature.

The exoelectron detector used in the present experiment also counts water molecules (Sujak 1958). Thus one could think that the maximum in question may be due to dehydration of hydroxides or oxide hydrates produced temporarily on the surface of the sample. The latter hypothesis is favoured by the fact that the intermediate maximum lies above the transition temperature of CrO_2 from ferromagnetic to paramagnetic state. Since, as it has

been already mentioned in the text, if CrO_2 is formed on the surface of the sample then only in trace amount we should observe for such thin layer a decrease in the Curie point rather than its increase with respect to massive material (which has been shown in the present paper for NiO layers).

In view of these considerations the question of the interpretation of the occurrence of the maximum at about 410°K on the $\frac{N}{t} = f(T)$ curve should be regarded as open. It seems that decisive information on this subject may be provided by investigation of exoemission carried out in a possibly largest humidity interval of the surroundings of the chromium sample.

5. Conclusions

From the results presented in this paper one can conclude that the electron exoemission method may be useful not only for studies of various types of phase transitions but can be also applied in investigations of gas corrosion of metals as well in other problems connected with the coating of solids with thin films of metals and dielectrics.

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* Added in prof: Further studies revealed that only a virgin nickel sample shows the emission picture given in Fig. 6 when an air point counter without quenching vapour is used. These and other experiments (which will be published in due course) show strong influence of the presence of alcohol vapour on the described phenomena — most probably the mechanism of a catalytic action on the ethyl alcohol vapour contributes to the observed emission mechanism.