EXOELECTRON EMISSION OF SURFACE-OXIDIZED NICKEL DURING PLASTIC DEFORMATION IN VACUUM

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When nickel, which was earlier annealed at a temperature higher than 670°K, undergoes plastic deformation in vacuum, it emits exoelectrons without any participation of light.

The intensity of this emission reaches maximum value at a deformation of $\varepsilon \cong 3$ per cent, after which it keeps on dropping to nil at sample rupture. The kinetics of this emission is like that of emission in the dark during plastic deformation of aluminum covered with a thick film of oxide.

It is shown that the following factors bear an effect on dark emission during plastic deformation of nickel :

a) temperature of sample annealing — T_w,

b) duration of sample annealing — ϑ,

c) rate of sample deformation — v_r,

d) ageing of sample after annealing — θ.

The observed dark emission of exoelectrons is most probably due to the influence of strong local electric fields occurring in the fissures of the oxide film which arise during deformation, similary as assumed for the case of dark emission from deformed aluminum covered with a thick film of oxide.

1. Introduction

Comprehensive research on exoelectron emission from deformed metals had hitherto primarily been conducted for aluminum, while relatively little attention was paid to other materials.

Likewise, the work done in the Department of Solid State Physics of the Wrocław University dealing with the role of the surface layer in the mechanism of exoelectron emission from plastically deformed metals primarily concerned aluminum.

The conceptions put forth in these studies regarding the control of exoelectron emission by electrized fissures developing in the layer of oxide proved fruitful as regards interpretation

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of the obtained results of measurements (Sujak, Gieroszyński, Pega 1965; Gieroszyński, Sujak 1965; Gieroszyński 1968). They also found application in the emission microscope designed by Veerman (1968).

Verification of these conceptions for other metals in which there is exoelectron emission during deformation would confirm the correctness of their assumptions.

It appears that the dark emission described now and which appears during the plastic deformation of oxide-covered nickel is due to the effect of strong electric fields occurring in fissures in the nickel oxide. With the use of the model introduced for dark exoelectron emission from oxidized and deformed aluminum it is also possible to explain the effect of various external factors on the dark emission from deformed nickel.

2. Equipment and samples

Measurements of the emission of exoelectrons from plastically deformed nickel in vacuum were done on a measuring arrangement and deforming device identical to those used in the case of studies on the emission of exoelectrons from plastically deformed aluminum (Sujak, Gieroszyński, Pega 1965). The operational conditions of the electronic multiplier and the vacuum conditions were also identical to those described earlier (Sujak, Gieroszyński, Pega 1965).

The transmission gear driving the tensile testing machine enabled the use of six useful rates of sample deformation: 0.025, 0.05, 0.1, 0.2 and 0.4 per cent per sec. Hereafter, unless the deformation rate is clearly specified, it is understood to be always equal to 0.2 per cent per sec.

The samples were prepared from nickel sheet of technical purity. The sheet thickness was 0.01 cm. The nickel samples had the same shape and dimensions as earlier specified for the aluminum samples (Gieroszyński, Mader, Sujak 1964). The samples were soaked in acetone prior to oxidation.

In order to form a nickel oxide film on the sample, it was annealed for a definite time (over 90 sec) at a temperature higher than 670°K.

To get an oxide covering of different thickness the samples were annealed at temperatures ranging from 670°K to 925°K or were annealed for different times ranging from 90 to 8×10^3 sec.

Once the oxide layer formed on the sample, it was stored in a dry atmosphere until measurements were initiated.

3. Emission of exoelectrons from nickel without the action of light

During plastic deformation of nickel samples covered by a layer of oxide formed by annealing them in air at a temperature higher than 670°K for 360 sec, the curve of exoelectron emission intensity N/t as a function of deformation ε, $N/t(\varepsilon)$, displays a maximum (Fig. 1). This maximum of emission intensity $(N/t)_{max}$, in general, appears at a deformation value ε_{OM} between 2.5 and 3.5 per cent. A measurable intensity of dark emission appeared once a deformation ε_{od} of 1.5 to 2.5 per cent was exceeded.

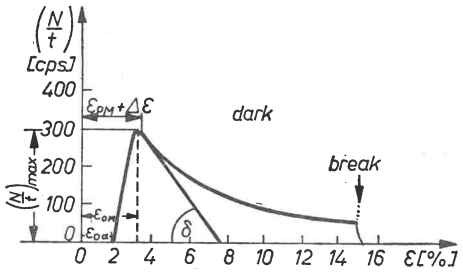

Fig. 1. Intensity of dark electron emission during plastic deformation of nickel in vacuum. $(N/t)_{max}$ is emission intensity corresponding to maximum of $N/t=f(\varepsilon)$ curve, ε_{od} is magnitude of strain at which measurable emission intensity appears, ε_{OM} is magnitude of strain at which maximum emission intensity appears, $\Delta\varepsilon = 0.5\%$

The value of $(N/t)_{max}$ on the $N/t(\varepsilon)$ curve does not depend on illumination at all. The light source was a tungsten filament lamp (6V, 50 W).

The dark emission intensity immediately drops below background level the instant the sample is ruptured, as seen in Fig. 1. Holding up the deformation process yet before sample rupture also brings about an immediate drop in emission intensity below background level, just as had been observed for dark emission from deformed aluminum (Gieroszyński, Sujak 1965).

4. *Effect of annealing temperature* T_w

The influence of the temperature of prior sample annealing on the value of deformation ε_{od} at which a measurable emission intensity appears and on the value of deformation ε_{OM} at which there is maximum dark emission was examined. The duration of annealing of samples was always the same and equalled 360 sec.

It was found that with a rise in annealing temperature T_w both the value of initial strain ε_{od} and the value of deformation ε_{OM} decrease (Fig. 2).

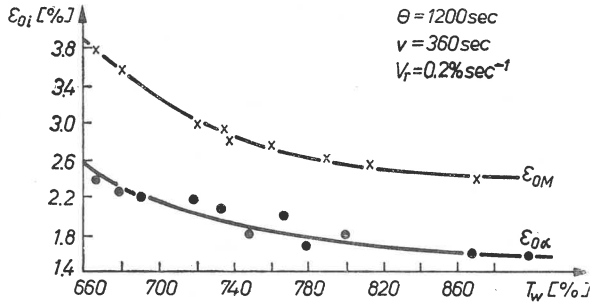

Fig. 2. Effect of temperature T_w of earlier annealing of sample on value of strains ε_{od} and ε_{OM}. Annealing time $\vartheta = 360$ sec, duration of ageing after annealing $\theta = 1200$ sec, deformation rate $v_r = 0.2\%$ sec^{-1}

If the samples were annealed for 360 sec at a temperature lower than 670°K no dark exoelectron emission from deformed nickel was observed. Emission appeared only after the samples were annealed at a temperature higher than 670°K. The emission intensity at

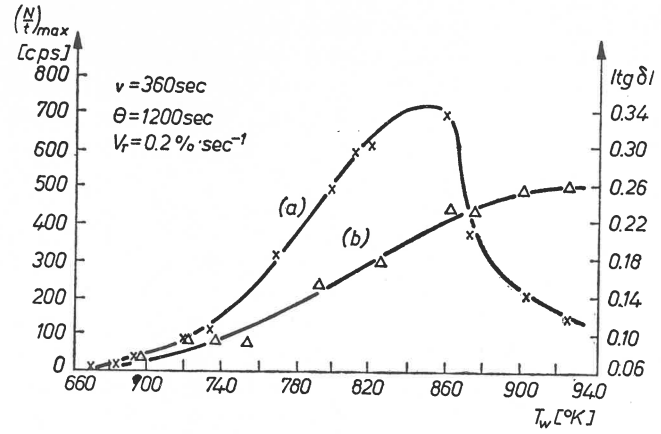

Fig. 3. Effect of annealing temperature T_w on emission intensity $(N/t)_{max}$ (curve *a*) and absolute value of tan δ (curve *b*). Annealing time $\vartheta = 360$ sec, duration of ageing after annealing $\theta = 1200$ sec, deformation rate $v_r = 0.2\%$ sec^{-1}

maximum value, $(N/t)_{max}$, then rises with increasing annealing temperature, reaches its highest value for $T_w = 850$ °K, and then drops (Fig. 3).

The annealing temperature T_w also affects the rate at which emission intensity decreases with sample deformation. The decrease in emission intensity with deformation was investigated after the strain of $\varepsilon_{OM} + \Delta\varepsilon$ was reached, with $\Delta\varepsilon = 0.5$ per cent. The tangent of the angle δ of the slope of the tangent line to the decay curve at a point near $\varepsilon_{OM} + \Delta\varepsilon$ (Fig. 1) was accepted as a measure of decay rate. It was found that with a rise in temperature T_w of sample annealing the absolute value of tan δ increases in the manner shown in Fig. 3.

5. *Effect of annealing time* ϑ

The value of the initial strain ε_{od} and that of the strain ε_{OM} corresponding to the maximum in the $N/t = f(\varepsilon)$ curve change accordingly to the sample annealing time ϑ. As shown in Fig. 4, both ε_{od} and ε_{OM} decrease with an increase in annealing time ϑ.

In the case of samples annealed at 827 °K the emission intensity $(N/t)_{max}$ is affected by the annealing time ϑ in a similar way as the annealing temperature T_w. Figure 5 shows

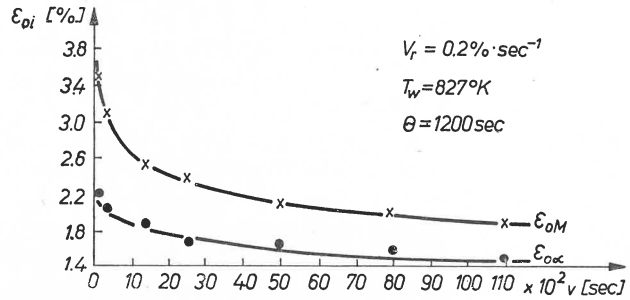

Fig. 4. Effect of duration of sample annealing on value of strains ε_{od} and ε_{OM}. Annealing temperature $T_w = 827$°K, duration of ageing after annealing $\theta = 1200$ sec, deformation rate $v_r = 0.2\%$ sec^{-1}

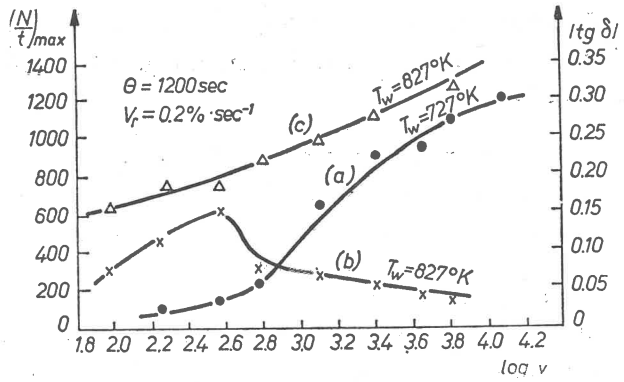

Fig. 5. Dependence of emission intensity $(N/t)_{max}$ on duration of earlier sample annealing, plotted in $(N/t)_{max}$ *versus* log ϑ coordinates (ϑ in sec) for different values of annealing temperatures, $T_w = 727$°K and $T_w = 827$°K (curves *a* and *b*, respectively), and dependence of $|\tan \delta|$ on log ϑ (curve *c*). Sample ageing after annealing $\theta = 1200$ sec, deformation rate $v_r = 0.2\%$ sec^{-1}

that $(N/t)_{max}$ increases with increase of ϑ, attains a maximum at $\vartheta = 400$ sec, after which decreases slowly.

In the case of samples annealed at 727 °K the value of $(N/t)_{max}$ increases with increased ϑ in the entire range of examined values of ϑ.

Depending on the annealing time ϑ, the rate of emission decay during deformation of the sample measured after achievement of maximum emission intensity also varies. The value of $|\tan \delta|$ also rises with increased ϑ (Fig. 5).

6. *Effect of ageing period after annealing* θ

The time during which a sample is aged after annealing bears no effect on the value of strains ε_{od} and ε_{OM}. On the other hand, it does affect the emission intensity $(N/t)_{max}$. With prolonged ageing θ the emission intensity $(N/t)_{max}$ decreases, reaching after several days a value which is almost constant (Fig. 6).

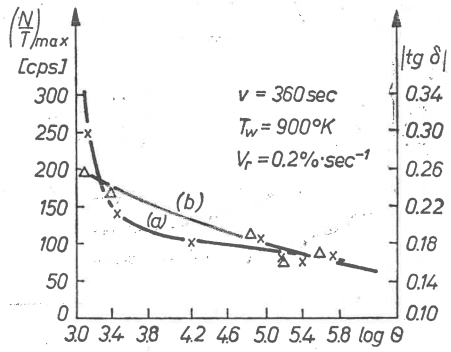

Fig. 6. Effect of ageing after annealing θ on emission intensity $(N/t)_{max}$ (curve *a*) and on the absolute value of tan δ (curve *b*). Sample annealing temperature $T_w = 900$°K, annealing duration $\vartheta = 360$ sec, deformation rate $v_r = 0.2\%$ sec^{-1}

The duration of ageing also bears some influence on the rate of emission intensity decay with advancing sample deformation. As is seen in Fig. 6, the absolute value of tan δ decreases with increased θ.

7. *Effect of deformation rate* v_r

The sample deformation rate $d\varepsilon/dt$, denoted for simplicity by v_r, does affect the value of initial strain ε_{od} or the value of strain ε_{OM} at which the maximum in the $N/t = f(\varepsilon)$ curve appears.

On the other hand, there is observed an effect of the deformation rate v_r on the emission intensity $(N/t)_{max}$ and on the rate of emission decay with deformation.

As was found in the case of dark emission from deformed aluminum (Gieroszyński, Sujak 1965), with a rise in the deformation rate there follows a linear increase of the emission intensity $(N/t)_{max}$ (Fig. 7). For comparison, Fig. 7 also includes the measurement points obtained for aluminum covered with oxide, the layer being $D = 126$ mμ thick (curve *b*).

Like for oxide-covered aluminum, the deformation rate v_r of oxidized nickel affects the rate of emission decay with deformation. With increased deformation rate v_r the value of $|\tan \delta|$ decreases (Fig. 8).

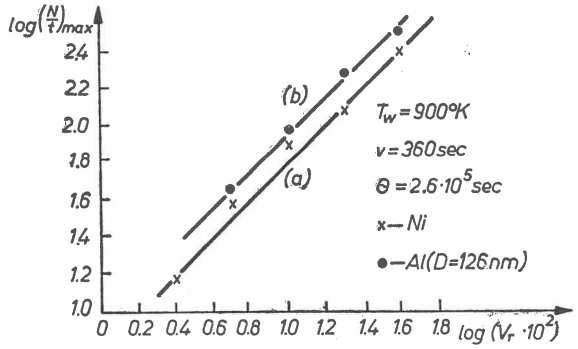

Fig. 7. Dependence of emission intensity $(N/t)_{max}$ on deformation rate v_r for nickel samples presented in double logarithmic coordinates ($(N/t)_{max}$ in pulses per sec, v_r in% sec^{-1}). Annealing temperature T_w= 900°K, annealing duration ϑ = 360 sec, duration of ageing after annealing $\theta = 2.6 \times 10^5$ sec (curve *a*). As a reference the figure includes the same dependence $(N/t)_{max} = f(v_r)$ for aluminum covered with a D= 126 mμ thick layer of oxide (curve *b*)

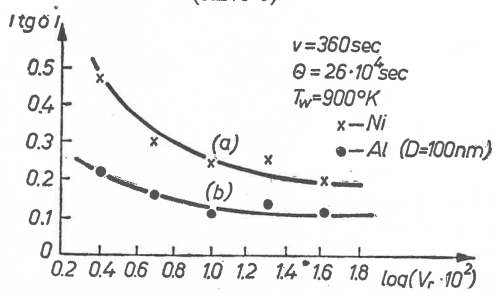

Fig. 8. $|\tan \delta|$ *versus* deformation rate v_r of nickel sample, presented in double logarithmic coordinates (v_r in % sec^{-1}). Sample annealing temperature T_w = 900°K, duration of annealing 360 sec, duration of ageing after annealing $\theta = 2 \cdot 6 \times 10^5$ sec (curve *a*). As a reference the figure includes the corresponding dependence $|\tan \delta| = f(v_r)$ for aluminum covered with a D= 100 mμ thick layer of oxide (curve *b*)

8. Discussion

As is seen, the dark emission of exoelectrons measured during the plastic deformation of oxidized nickel described here is linked with the layer of nickel oxide on the sample being deformed.

It was found that dark emission associated with plastic deformation appears only when the sample was previously annealed for a long enough period of time at a temperature higher than 670 °K. For nickel this time is at least 360 sec.

Since the thickness of the oxide layer on nickel increases with higher annealing temperature and longer duration it is to be expected that the dark emission accompanying plastic deformation may arise only when the sample has on it an oxide layer of appropriate thickness, just as in the case of aluminum oxide on aluminum.

On the basis of microscopic investigations of the nickel sample surfaces it was found that the layer of oxide on the surface undergoes cracking during deformation, forming microfissures. This is similar to the observed phenomena for oxidized and deformed aluminum (Gieroszyński, Mader, Sujak 1964). Moreover, it was ascertained that the first cracking of the thermally formed nickel oxide takes place at a strain of about 1 to 2 per cent.

The use of the results of research on the effect of various external factors on the value of strain ε_{od} at which measurable emission intensity builds up during plastic deformation in the dark enabled to ascertain that the value of ε_{od} undergoes a change if there is a change in the thickness of the oxide layer. This is exactly what the effect of T_w and ϑ on the value of ε_{od} is. On the other hand, the value of ε_{od} remains constant if the thickness of the oxide on the sample is unchanged. Because of this there is no effect of θ and v_r on ε_{od}.

It may thus be assumed that the appearance of electron emission in the dark during plastic deformation of oxide-covered nickel is due to the formation of emissively active microfissures in the oxide. Therefore, it appears that the observed dark emission of exoelectrons during plastic deformation ensues from the oxide layer as a result of strong electric fields arising in the microfissures during its cracking.

The effect of various factors on dark electron emission during deformation of nickel found now may be explained by applying the model of emission for aluminum (also deformed in the dark) presented in the paper by Sujak and Gieroszyński (1969). It was assumed in this model that electrons emitted by the influence of a strong electric field arising at the side wall of the fissure knock out secondary electrons from the opposite wall, of which some emerge and are recorded as dark emission of exoelectrons. The intensity of dark emission in this case will depend on the area of the emitter and the strength of the electric field in the fissure, what in turn depends on the thickness of the cracking oxide layer.

The observed effect of annealing temperature T_w on the value of $(N/t)_{max}$ (Fig. 3) can be explained by assuming that it is due to the superposition of two processes competing with each other. The first is the thickening of the oxide (area of emitter), causing an increase in maximum emission intensity $(N/t)_{max}$. The other is the weakening of the electric field strength occurring in the fissure,[1] causing a drop in the value of $(N/t)_{max}$. As is seen in Fig. 3,

[1] It was shown in one of the papers by Gieroszyński and Sujak (1965) that annealing of an aluminum sample, prior to measurement, which had an oxide layer formed on it electrolytically, brought about a decrease in dark emission intensity, probably due to weakening of the electric field in the fissures.

the former process predominates the latter up to an annealing temperature $T_w = 850°K$, whereas above this temperature the process of weakening of the electric field in the fissure prevails (probably due to the strong diffusion of atoms of the metal into the oxide).

In like manner, it is also possible to explain the influence of annealing duration ϑ on the value of $(N/t)_{max}$. With a rise in annealing time ϑ the thickness of the oxide increases. It should also be assumed that the intensity of the electric field in the fissures is decreased. For due to the diffusion of metal into the oxide the transitory oxide-metal layer has more defects and therefore exhibits a much lower electric resistance. For the samples annealed at $T_w = 827\,°K$ and annealing times shorter than 400 sec the increase in oxide thickness will prevail over the weakening effect of the electric field in the fissures, what causes $(N/t)_{max}$ to rise with longer ϑ. At an annealing time of $\vartheta = 400$ sec the weakening of the electric field begins to predominate, and with an increase in ϑ the value of $(N/t)_{max}$ decreases (Fig. 5). On the other hand, when the effect of annealing duration on $(N/t)_{max}$ is examined for samples annealed at a lower temperature ($T_w = 727\,°K$), the weakening of the electric field within the entire ϑ range does not yet show up and only an increase of $(N/t)_{max}$ with longer ϑ (Fig. 5) is observed.

The influence of the ageing time after annealing θ on the emission intensity at ε_{OM}, $(N/t)_{max}$, may be resolved by assuming that with increased θ there is a decrease of field strength in the formed fissures.

As shown in a recent paper (Sujak, Gieroszyński 1969) the rate of emission decay is augmented with an increase of the electric field strength in the fissures and with an increase of oxide layer thickness. It is likewise possible to explain the effect of such factors, as found now, on the rate of emission decay (absolute value of tan δ) as annealing temperature T_w and duration ϑ, and the time of sample ageing after annealing θ (Figs 3, 5 and 6).

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