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Temperature Dependence of the Work Function of Metals (Mo,Ni)

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The temperature coefficient of the work function (TCWF) of polycrystalline Mo and Ni has been measured in the temperature ranges 600–1100°K and 475–1025°K, respectively, using the electron beam method (EBM). Special precautions have been taken in order to avoid systematic errors due to the effect of residual gases, of stray magnetic fields, of incorrect temperature measurement, of cathode temperature variations, etc. During determinations made upon Ni surfaces, the terrestrial magnetic field has been compensated. Random error sources have been likewise reduced as much as possible. The main results obtained on surfaces outgassed for many thousands of hours at pressures of $1\text{–}3\times10^{-9}$ torr are

$$\left\langle\left(\frac{d\Psi_{\text{Mo}}}{dT}\right)\right\rangle_{\text{av}}=(7.84\pm0.07)\times10^{-5}\text{ ev/°K},$$

$$\left\langle\left(\frac{d\Psi_{\text{Ni}}}{dT}\right)_{T>\theta_{\text{ Curie}}}\right\rangle_{\text{av}}=(-3.12\pm0.05)\times10^{-5}\text{ ev/°K}.$$

At the Curie point of Ni a theoretically expected variation of the TCWF has been observed:

$$\left\langle\left(\frac{d\Psi_{\text{Ni}}}{dT}\right)_{T<\theta}-\left(\frac{d\Psi_{\text{Ni}}}{dT}\right)_{T>\theta}\right\rangle_{\text{av}}=(-0.99\pm0.17)\times10^{-5}\text{ ev/°K}$$

but no jump of the work function (WF) has been found at this point. Special experiments have shown that the results have not been significantly affected by residual gases. A relation between the TCWF measured on polycrystalline surfaces of Ni and the TCWF of the various facets of these surfaces has been obtained.

INTRODUCTION

THE temperature variation of the work function (WF) of metals in the temperature range below 1200°K has been studied in relatively few works. This range is, however, interesting, as a series of metals (for instance the ferromagnetic ones) have critical points within this range; the behavior of the temperature coefficient of the work function (TCWF) near these points is of interest for solid-state physics.[1]

The methods employed belong evidently to the class characterized by the fact that the investigated metals do *not* emit thermoelectrons. Thus in the most important works the following methods have been used: Fowler's method (photoelectric effect) for molybdenum,[2] iron,[3] and nickel[4]; the vibrating condenser method for tungsten[5]; the space charge method for tungsten[6]; the electron beam method (EBM) for copper and nickel[7]; and the field emission method used by one of the authors for nickel.[8] In these works, the random errors in the determination of the WF or of its variations lay in the interval from 5×10^{-3} to 5×10^{-2} ev. As the temperature interval within which the determinations were performed spreads over several hundred degrees, it is obvious that the errors were of the same order as the TCWF ($10^{-4}-10^{-5}$ ev/°K). Therefore no variations of the TCWF around any interesting points could be discerned.

The results obtained in the above-mentioned works were influenced decisively by systematic errors proceeding from the following causes:

1. The investigated surface was not sufficiently clean. In some of the quoted papers measurements were carried out at pressures higher than 10^{-8} torr,[2,6] whereas in other ones they lasted too long,[3,4,5,7] so that contamination occurred even during measurement. For this reason Böttger's results are evidently inconclusive; his measurements, performed at 10^{-8} torr, lasted a few hours at temperatures between 20°C and −190°C, in which interval the investigated surface worked as a trap.

2. Presence of a disturbing magnetic field, either due to the heating current of the metal under investigation[3–6] or arising from the very method of measurement. Such a field disturbs the path of the electrons (in the first case the disturbance depends upon the intensity of the heating current, leading thus necessarily to an erroneous TCWF) and besides brings forth parasitic effects in the case of ferromagnetic materials below the Curie point.

3. The temperature of the metals investigated was generally determined by extrapolation into a wide region, as a function of the heating current,[3–6] an operation which does not sufficiently guarantee confidence.

4. The potential drop along the investigated surface depending upon the heating current[6] and other errors caused by unsuitable measuring circuits.[7]

We have tried to adapt correctly the EBM[9] to the measurements of the TCWF. Removing as far as possible the causes of systematic errors[10,11] and reducing the random errors to less than 10^{-6} ev/°K, we believe that we have succeeded in determining quantitatively

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[1] S. V. Vonsovski and A. V. Sokolov, Doklady Akad. Nauk S.S.S.R. **76**, 197 (1951).

[2] L. A. DuBridge and W. W. Roehr, Phys. Rev. **42**, 52 (1932).

[3] A. Cardwell, Phys. Rev. **76**, 125 (1949).

[4] A. Cardwell, Phys. Rev. **92**, 554 (1953).

[5] J. Potter, Phys. Rev. **58**, 623 (1940).

[6] D. B. Langmuir, Phys. Rev. **49**, 428 (1936).

[7] O. Böttger, Z. Physik **144**, 269 (1956).

[8] G. V. Spivak and A. Gelberg, Doklady Akad. Nauk S.S.S.R. **94**, 455 (1954).

[9] P. A. Anderson, Phys. Rev. **47**, 958 (1935).

[10] G. Comşa, A. Gelberg, B. Iosifescu, and G. Musa, Studii Cercetări Fiz. (Bucharest) **9**, 429 (1958).

[11] A. Gelberg, B. Iosifescu, G. Comşa, and G. Musa, Radiotekh. i Elektron. **3**, 1000 (1958).

the TCWF of molybdenum[12] and nickel.[13] For nickel we have established the existence of an anomaly of the TCWF at the passage through the Curie point.[14]

All the determinations made at temperatures below 1200°K have been performed on polycrystalline surfaces. The TCWF determined in this way is a function of the TCWF of the various facets and of the corresponding WF. The form of this function depends on the method employed and, given the method, on the specific conditions of work. These were taken into account when interpreting the results obtained on polycrystalline nickel.[15]

METHOD

Variations of the WF in temperature ranges in which thermoemission of the metals is practically absent can be detected by four main methods: photoelectric effect, field emission, measurement of contact potential difference (cpd), and EBM.

In order to obtain the TCWF with a precison better than 10% it is necessary to determine the variations of the WF, in temperature ranges of several hundred degrees, with an error of less than 10^{-3} ev. In this respect the first two methods have been found unsatisfactory.

We have chosen the EBM which is *not* based, as is usually stated, on the measurement of cpd, but which at most *allows* the measurement of the cpd between two metals, introduced successively in the electron beam, by determining the shift of the volt-ampere characteristics.[16] The shift of characteristics in the region of initial currents is not affected by variations of the cathode WF (if the method is correctly applied). Consequently the results will not depend on the constancy of the cathode WF, which is a parameter very difficult—if not impossible—to control. From this point of view the EBM is superior to all methods based on cpd measurement. In fact, the latter involve measurements of the variation of the difference between the WF of the studied metal and that of a reference metal; therefore the results depend on uncontrollable variations of the WF of the latter.

Furthermore, contrary to the vibrating condensor and magnetron methods, the EBM does not involve the existence of a magnetic field and can thus be applied as well to ferromagnetic metals below the Curie point.

By means of the EBM, results may be obtained with very small random errors.

Anderson[9] has shown that the WF variation may be obtained either by plotting the volt-ampere characteristics and by measuring their shift (variant I) or by measuring the variation of the retarding potential necessary to maintain the anode (target) current constant (variant II). The measurements made according to variant II can be carried out in a particularly simple and efficient manner. The heating current which keeps the target at the outgassing temperature is disconnected, the target cools down, and its WF varies accordingly. Meanwhile the current on the target is kept constant and the WF variation results from the variation of the retarding potential. Thus the entire variation of the WF is measured in the shortest time possible (i.e., the time necessary for the cooling of the target), and what is more, in a *continuous* way, which favors the ascertaining of possible jumps of the WF. The heating current being switched off, the magnetic field, as well as the spurious potentials that might disturb the measurement, is avoided. Therefore the EBM seems ideal for our purpose.

Herring[17] has stated that, in TCWF measurements by cpd methods, a correction must be introduced in order to compensate the effect of the temperature variation of the electrochemical potential. This correction must be applied likewise in the EBM.

POLYCRYSTALLINE SURFACES

In the present work, as well as in all those dealing with temperatures lower than 1200°K, the metal under study had a polycrystalline structure. Now the question arises what meaning can be ascribed to the experimentally determined TCWF and what is the connection between this coefficient and the TCWF of the various crystalline facets which appear on a surface? No exact answer can be given. To this purpose we should know the WF, the shape, the dimensions, and the relative abundance of each type of facet as well as their arrangement on the polycrystalline surface. Without knowing these details, or knowing them only very approximately, the problem can only be solved by making simplifying assumptions and consequently the result will have merely a qualitative character.

In order to obtain the significance of the experimentally determined TCWF it is necessary to discuss it from the energetic point of view, that is to say, to ascertain the possibility for electrons of a given speed to pass through regions of given potential, as well as from the electron optical point of view (as suggested by Anderson[18]), i.e., to establish the real trajectory of electrons (of which the majority are of very low energy) in the field of patches. In this respect the EBM is also more convenient, the results obtained being independent of the WF of the cathode and consequently neither on its being polycrystalline or not, while things become very complicated for methods based on cpd measure-

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[12] B. Iosifescu, Studii Cercetări Fiz. (Bucharest) **10**, 177 (1959); Rev. Phys. **4**, 345 (1959); dissertation, Institute of Atomic Physics, Bucharest (unpublished).

[13] G. Comşa, Studii Cercetări Fiz. (Bucharest) **10**, 163 (1959); Rev. Phys. **4**, 337 (1959); dissertation, C. I. Parhon University, Bucharest (unpublished).

[14] G. Comşa, A. Gelberg, and B. Iosifescu, Studii Cercetări Fiz. (Bucharest) (to be published); Fiz. Tverdogo Tela (U.S.S.R.) (to be published).

[15] G. Comşa, Studii Cercetări Fiz. (Bucharest) **10**, 145 (1959).

[16] B. Gysae and S. Wagener, Z. tech. Physik **19**, 264 (1938).

[17] C. Herring, Phys. Rev. **59**, 889 (1941).

[18] P. A. Anderson, Phys. Rev. **88**, 655 (1952).

ments, as the polycrystalline structure of both surfaces has to be taken into account.

Herring and Nichols[19] have pointed out the meaning of the shift of the characteristics for polycrystalline surfaces, in the special case in which the external electric field at the surface of the target is zero, without however taking into account the focusing effect of the field of patches. Arizumi[20] has deduced the significance of the TCWF determined on polycrystalline surfaces by various methods, but not by the EBM. Besides he, too, does not consider any arguments of electron optics.

One of the authors[15] has tried to obtain a relation between the TCWF determined experimentally by means of the EBM, taking into account the specific conditions of the experiment, i.e., the value of the external electric field on the surface under examination, the mean size of the microcrystals (determined by means of a metallographic microscope), and the data given in literature concerning the WF of the various crystalline facets of nickel.[8,21] Denoting by $d\Psi_A/dT_A$ the experimentally determined TCWF; by $d\Psi_{A_i}/dT_A$ and p_i, the TCWF and the relative abundance of the facets of type i; and by $\bar{d}_i$ a "transmission coefficient by focusing" (depending upon the WF of the facet of type i and its near neighbors and taking values <1 or >1), the relation obtained is

$$\frac{d\Psi_A}{dT_A}\approx\sum\nolimits_i p_i\bar{d}_i\frac{d\Psi_{A_i}}{dT_A}, \tag{1}$$

where the sum is to be extended only over facets with small WF (for which $\bar{d}_i>1$). Let us assume that the TCWF of a crystalline facet is the sum of a volume term and of a term conditioned by the double layer on the surface of the metal.

$$\frac{d\Psi_i}{dT}=\frac{d\Psi^V}{dT}+\frac{d\Psi_i^D}{dT}. \tag{2}$$

Let us further assume, as is very likely the case, that in a transition point where a change in the magnetic properties of the metal occurs, the TCWF components are related by the inequality:

$$\Delta\frac{d\Psi^V}{dT}\gg\Delta\frac{d\Psi_i^D}{dT}. \tag{3}$$

Here Δ denotes the variation of the mentioned quantities over a narrow temperature interval containing the transition point. Therefore

$$\Delta\frac{d\Psi_i}{dT}\approx\Delta\frac{d\Psi^V}{dT}. \tag{4}$$

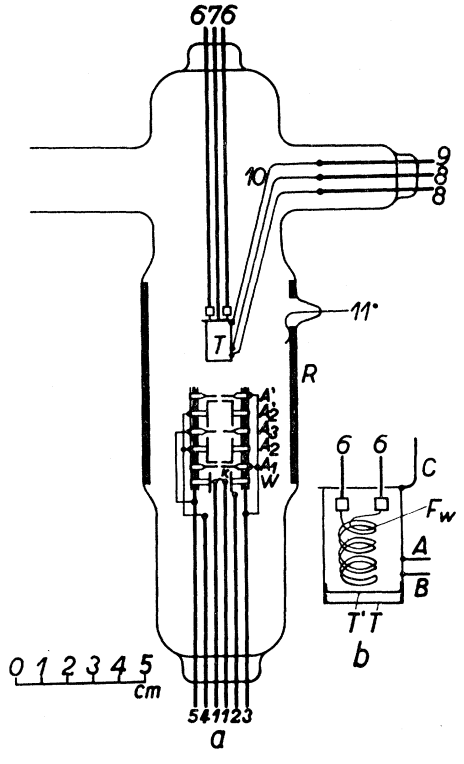

FIG. 1. (a) The experimental tube. T—metal target investigated (Mo or Ni); K—cathode (tungsten wire, $\phi=0.1$ mm); W—Wehnelt cylinder (sheet of Ta, 0.1 mm); A_1, A_2, A_3, A_2', A_1'—accelerating electrodes of the electronic gun (sheet of Ta); R—coated guard ring; 1–10—inlet wires of Mo or W ($\phi=1.5$ mm) through glass: 6–6 for the heating filament of the target, 7 the target holder, 8–8 for the thermocouple wires (made of W–Ta for the Mo target and of Ni-NiCr for the Ni target), 9 for the electric contact of the target, 10 strip made of the investigated metal (Mo or Ni), 11 electric contact of the guard ring. (b) Detailed scheme of the target. T—target; T'—double bottom of the box which screens the target; F_w—heating filament of the target (tungsten wire $\phi=0.2$ mm) wound as a double spiral; 6–6 supporting wires of F_w; A-B welding points of the thermocouple; C—electric contact of the target.

As may be easily proved, $\sum_i p_i\bar{d}_i\approx 1$, and thus

$$\Delta\frac{d\Psi_A}{dT_A}\approx\Delta\frac{d\Psi_i}{dT_A}, \tag{5}$$

the variations $\Delta(d\Psi_i/dT_A)$ having the same value for any facet with small WF [according to Eq. (4)].

Thus although the correctly applied EBM completely displays its advantages only in the study of monocrystalline surfaces, results from polycrystalline surfaces may equally be simply enough interpreted, especially at the above-mentioned transition points.

EXPERIMENTAL

Figure 1(a) represents the experimental tube. It contains a Myers[22] electronic gun which, although rather complicated, has a good focusing power. (The accelera-

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[19] C. Herring and M. H. Nichols, Revs. Modern Phys. **21**, 185 (1949).

[20] T. Arizumi, J. Phys. Soc. Japan **3**, 1 (1948); **3**, 143 (1948).

[21] P. Asadulin and G. N. Shuppe, J. Tech. Phys. (U.S.S.R.) **24**, 205 (1954).

[22] H. Myers, Proc. Roy. Soc. (London) **215A**, 329 (1952).

ting potential applied on electrodes A_1 and A_1' is of about 20 volts, referred to the mid-point of the cathode). Thus the target can be kept at a distance of 10–15 mm away from the last electrode of the gun. Were it not so, the large temperature variations of the target could lead to deformations of the gun during the experiment and thereby disturb the beam.

The *target* (anode) has the form of a cylindrical box [Fig. 1(b)] made of the metal under investigation. One of the lids is the studied surface, i.e., the target itself (T). The lining of this lid with a sheet (T') of refractory matter (Ta or Mo) prevents the falling of evaporated tungsten atoms, emitted by the heating filament F_w, on the back of the lid, and their diffusion (facilitated by the high outgassing temperature) towards the surface on which measurements are made (an effect observed in the absence of the double lid). The connection between the target and the measuring circuits is established by means of a strip made out of the *same* metal as the one under investigation, so as to ensure that the entire temperature gradient should lie within the same metal and that the Herring correction could be correctly applied.

The heating *filament* of the target, F_w has the form of a double spiral in order to reduce as much as possible the magnetic field of the heating current, which has a disturbing action upon experiments carried out according to variant I. The heating by radiation ensures the equipotential character of the target.

The *temperature* of the investigated surface is determined by measuring with a potentiometer the emf of a thermocouple welded to the side surface of the box [Fig. 1(b)] (variant I). The wires of the thermocouple are welded directly and separately to the box. If the wires are first welded together, one cannot make sure that the adhesion between this welding and the surface of the box is intimate enough to avoid the appearance of an uncontrollable temperature gradient.

The calibration of the thermocouple has been made according to the target temperature (T_A), determined by a pyrometer for temperatures higher than 800°C, and also with the aid of a Pt-PtRh thermocouple applied, in a separate experiment, on this surface itself; the latter calibration has been performed in the whole temperature range studied, thus avoiding extrapolation.

The *electrical charging of the tube wall* was avoided by depositing a metallic layer (R) of nickel or gold, which has the function of a guard ring.

The *electrical circuit* used in variant I is in many respects similar to those used by Anderson. We want however to emphasize the performance of the heating circuit of the cathode, which ensures the strict maintainance of a constant cathode temperature (T_K) and which differs from those mentioned in the literature. It is known that the constancy of the parameter T_K is essential for obtaining correct results by means of the EBM. In order to obtain a precision of 10^{-3} ev in the determination of the WF variations it is necessary that the fluctuations of the cathode temperature (ΔT_K) should be sufficiently small so that $|\Delta T_K/T_K|<10^{-4}$. To this end, some authors[7,9] maintain the emission current of the cathode (measured on the first anode of the gun) at a constant value, which is a wrong procedure. Indeed in this case, the results become dependent on the uncontrollable value of the cathode WF, and thus the main advantage of the EBM is lost; moreover, it can be shown that for a variation $\Delta\Psi_K$ of the cathode WF, an apparent variation of the target WF $|\Delta\Psi_A|>|\Delta\Psi_K|$ is obtained. We have noticed that even if the electric power supplied to the cathode remains unchanged, the cathode temperature still varies, as it is influenced by the temperature variations of the target.

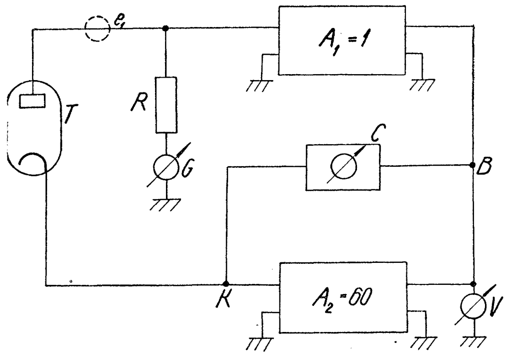

FIG. 2. Block scheme of the measuring device. T—experimental tube; A_1—cathode follower; A_2—regulating amplifier; C—semiautomatic potentiometer measuring $e\Delta U_A$; e_1—variable voltage source.

We have considered that the cathode temperature may be kept constant with the required accuracy, maintaining the resistance of the cathode (R_K) within the limits $|\Delta R_K/R_K|<10^{-4}$, where ΔR_K are the fluctuations of the cathode resistance. Continually comparing—by means of a Thomson bridge—the actual values of R_K to that of a standard resistor and slightly varying the heating current of the cathode, we satisfied the condition mentioned above.

The *electrical circuit* used in *variant II* differs from the one used in variant I (and accordingly from those used in the literature). It permits one to keep the target current at a constant value (10^{-9} A) during the rapid falling of the target temperature, by automatically varying the retarding potential, and also the *continuous* and *simultaneous* determination of the target temperature (T_A) and of the retarding voltage (U_A).

For this purpose an electronic device has been set up[23] (see block scheme in Fig. 2) which, owing to a tension electronically regulated by the target current (by means of a negative feedback system) allows the constant maintainance of this current. The retarding potential can be read on the dial of the ZIP-R2/1 semiautomatic potentiometer (C in Fig. 2). In order to check the performance of the device, a source of variable

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[23] G. Comşa, A. Gelberg, A. Georgescu, and V. Grabari, Studii Cercetări Fiz. (Bucharest) 9, 445 (1958).

voltage (0–40 mv) was connected in series with the tube simulating the variations of the WF; the errors found were smaller than ±0.5 mv.

In order to read the target temperature continuously, the emf of the thermocouple was measured by means of a millivoltmeter.

The simultaneous record of the values of U_A and T_A was ensured by photographing the dials of the semi-automatic potentiometer and of the millivoltmeter on the same film at short intervals, as the target cools down. In this way each photograph represents a point of the plot $e\Delta U_A = f(T_A)$.

Compensation of the terrestrial magnetic field. Although according to variant II the heating current of the target is interrupted during the measurements and thus its magnetic field cancelled, the determination of the TCWF of a ferromagnetic substance below the Curie point implies special precautions in order to cancel any magnetic field (even the terrestrial one) in the vicinity of the investigated surface. If this precaution were neglected, as soon as the temperature of the ferromagnetic target descends below the Curie point, it would become magnetized in this "residual" field, the electronic current composed of slow electrons being thereby disturbed. We performed the compensation of the terrestrial magnetic field by means of a pair of Helmholtz coils, concentrically placed around the experimental tube, which was directed along the magnetic field of the earth.

Screening. In order to minimize external disturbing effects, the experimental tubes have been enclosed in a grounded metallic cage. The connections between the tube and the measuring circuits have been screened likewise.

PRESSURE OF RESIDUAL GASES AND THEIR INFLUENCE ON THE RESULTS

The experiments have been carried out at pressures of about 10^{-9} torr, measured with Alpert-Bayard gauges of our own construction.

Before the assembling of the experimental tube, the electronic gun and especially the targets were outgassed in separate units, until evaporation. Then the assembled experimental tube, the Alpert-Bayard gauge and two ionization pumps (constructed by one of the authors[24]) (Fig. 3) were outgassed in two preliminary stages of one hundred hours each, on a vacuum unit working with oil pumps and two effective liquid nitrogen traps (or alternatively, a liquid nitrogen trap in series with a copper-foil trap). After a thorough outgassing of the metallic and glass parts (targets at 1925°K for Mo and 1350°K for Ni) the entire vessel was sealed off at a pressure of $5\times10^{-9}-10^{-8}$ torr. After sealing off, the pressure increased about ten times and was then lowered and maintained around the value of 10^{-9} torr for thousands of hours, with the help of the ionization pumps. During this interval the investigated target was continuously heated (Mo at 1650°K and Ni at 1250°K).

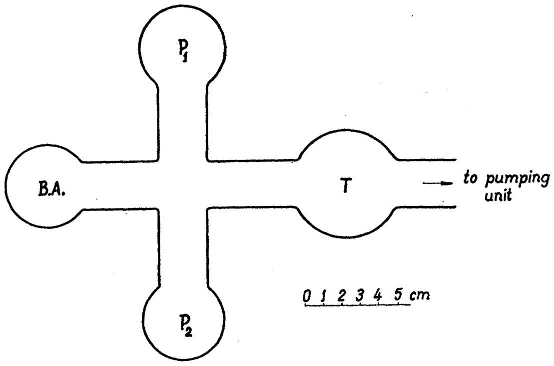

FIG. 3. Vacuum complex to be sealed off from the pumping unit. T—experimental tube; B.A.—Bayard-Alpert gauge; P_1, P_2 —ionization pumps.

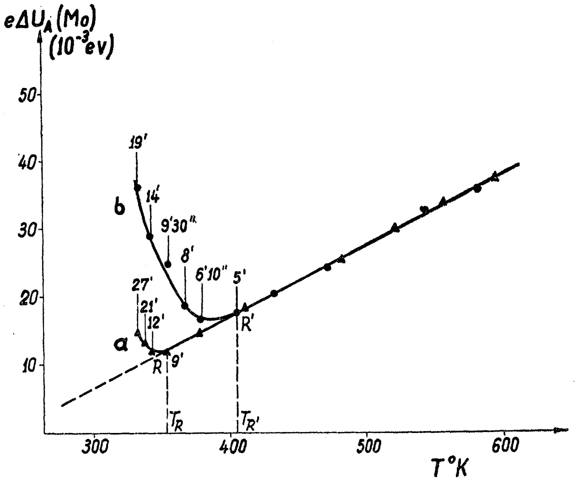

FIG. 4. Retarding potential variation during the cooling of the Mo target, showing the effect of residual gases. The time elapsed from the interruption of the heating current of the target is indicated for each point. Curve a is plotted at a pressure of 3×10^{-9} torr, and curve b at 10^{-8} torr.

Heating at higher temperatures deteriorated the vacuum in the case of molybdenum, or caused an intense evaporation of the nickel target which led to its perforation in time.

Although the measurements were carried out at low pressures and each one lasted a relatively short time, an analysis of a possible alteration of the results owing to the action of the residual gases is still necessary.

The contamination of the investigated surfaces caused by the residual gases, may alter the results in two distinct ways:

1. By covering the target surface *during the measurement* (while the metal cools down from the outgassing temperature), thus leading to the appearance of a supplementary variation of the WF.

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[24] G. Comşa, and G. Musa, Studii Cercetări Fiz. (Bucharest) **7**, 119 (1957); J. Sci. Instr. **34**, 291 (1957).

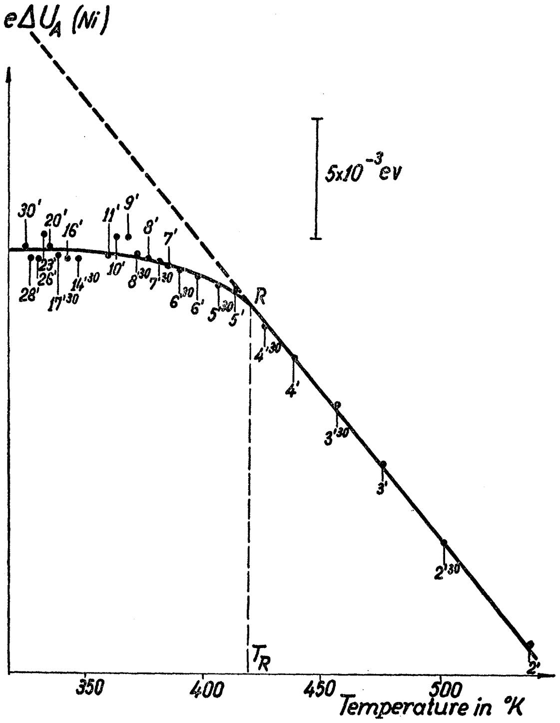

FIG. 5. Retarding potential variation during the cooling of the Ni target, showing the effect of residual gases. The curve is plotted at 1×10^{-9} torr.

2. By covering the target surface also *during the outgassing process* and in spite of it; in this case the investigated surface is originally covered by impurities, the TCWF being that of a contaminated surface, i.e., appreciably different, as a rule, from that of a clean metal.

We present a series of observations or cases which enable us to conclude to what extent our results were affected by the existence of residual gases, in one of the two ways mentioned above.

a. We have plotted the retarding potential variations vs the molybdenum target temperature, indicating for each point the time elapsed from the interruption of the heating current of the target. Curve *a* in Fig. 4 was taken at a pressure of 3×10^{-9} torr, while curve *b* at 10^{-8} torr. (The increase of pressure was obtained by cutting off the accelerating voltage in the ionization pumps.) Figure 4 refers to a lower temperature interval then the one in which the actual TCWF measurements for molybdenum were performed (600°–1100°K). We want to emphasize that in this last interval, both curves are coincident. At a certain point (R') the curves separate: curve *b* obtained at a higher pressure shows a marked increase of the WF, while curve *a* obtained at the working pressure still maintains its initial trend till point R, where it also deviates from this trend.

Similar results were obtained with nickel. Figure 5 represents the curve taken from a nickel target, at a pressure of 1×10^{-9} torr. It is noticeable that in this case the deviation from the general trend of the curve has an opposite direction than in the former case.

b. The TCWF obtained in two successive runs (r_1 and r_2 in Fig. 6) has the same value, provided that the first run is interrupted and the target reheated before it attains the point where the WF variation deviates from its customary trend, as mentioned under *a.* (That is, $T_M > T_R$ and $t_M < t_R$).

c. If the Ni target is cooled down to room temperature in 30 minutes, then reheated quickly to 1250°K (dashed curve in Fig. 6), and a new run (r_2') is performed, then the obtained TCWF is 80% higher in absolute value than that measured on a freshly outgassed surface.

d. Subsequent to the performing of the "contamination" mentioned in *c*, the TCWF restores its usual value *only* after an outgassing of about 24 hours at 1250°K.

e. No measurable change of pressure appears during the cooling down of the target in the measuring process and its successive heating up to the outgassing temperature (A_1-M-A_2 in Fig. 6).

f. During the heating period $M'-A_2'$ in the $A_1-M'-A_2'$ process, the pressure increases by $2\times10^{-9}-5\times10^{-9}$ torr, and decreases to its working value (1×10^{-9} and 3×10^{-9} torr, for Ni and Mo, respectively) only after several hours.

Before drawing any conclusions from the above-mentioned cases, we must examine the observations presented in *b* and *c*. The question is whether the TCWF determined during the second run (r_2 or r_2', respectively, in Fig. 6) corresponds or not to the state of the surface in the moment M or M', respectively.

There is no doubt that during the heating of the target, which inevitably precedes every run, a fraction of the adsorbed molecules leave its surface. We shall evaluate their number in case *c*.

As stated in *f*, the increase in pressure during the heating of the target ($M'-A_2'$), does not exceed 5×10^{-9} torr. Considering that the volume of the sealed-off vessel (Fig. 3) is about 1.5 liters; that for the emission current used, the total pumping speed of the ionization pumps is 0.1–0.2 liter/sec; and that the heating of the target ($M'-A_2'$) lasts about 50 seconds, we can evaluate that in this time interval the target desorbs at most 1.5×10^{12}–3×10^{12} molecules. As the target has a total surface of about 15 cm², each square cm has lost at most 1×10^{11}–2×10^{11} molecules, which represent 10^{-4} monolayers. The effect upon the TCWF of such a difference in the coverage of the surface is absolutely negligible. Therefore the value of the TCWF determined in run r_2' corresponds to the state of contamination of the surface at moment M'. So much the more can we consider the TCWF measured in run r_2 (point *b*) as corresponding to the state of the surface at moment M, as in point *e* it was stated that during the heating period $M-A_2$ there is no measurable change of pressure in the tube, and thus the difference in the surface

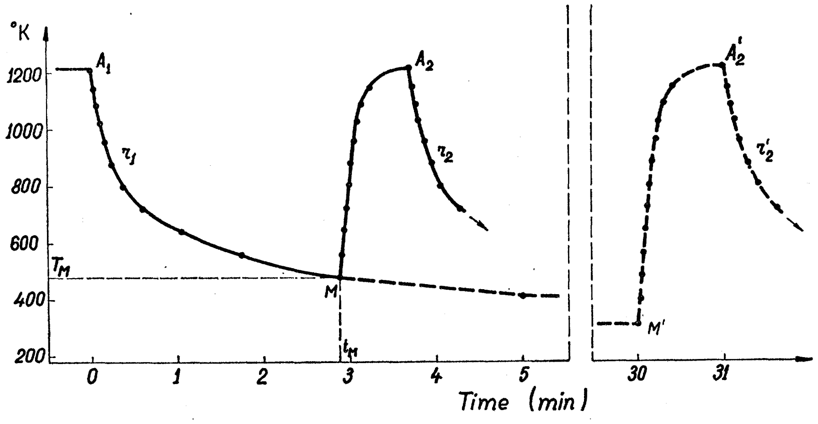

Fig. 6. Temperature variation of Ni target versus cooling time. A_1, A_2, A_2'—beginning of a measuring run; M—end of the measuring run; M'—end of a contamination process; r_1, r_2, r_2'—measuring runs.

coverage is at least one order of magnitude smaller then the one calculated above.

These considerations, based essentially on the desorption speed of the molecules during outgassing, are confirmed by case *d*, which states that 24 hours are necessary to remove these adsorbed molecules from the surface under investigation; therefore those desorbed in 50 seconds represent a negligible quantity.

The coincidence of the $U_A=f(T_A)$ curves plotted at different pressures, in temperature domains where $T_A>T_{R'}$ (as stated in *a*), leads to the conclusion that even a pressure several times higher than the usual working pressure, does not influence the obtained results. This means that either the surface is completely covered from the beginning of the experience, or that it is clean and that at the mentioned pressures and temperatures the residual gases have no detectable effect upon the target during *the outgassing process* or *the measurement itself*. The first assumption is contradicted by the observations reported for case *c*, which show that the surface is far from being saturated and also by case *a*, where the effect of residual gases at lower temperatures is mentioned, an effect which increases with the rise in pressure.

The experience reported in case *b* is another proof for the assumption that the surface does not get contaminated during the measurements, taking into account the arguments we brought forth concerning the significance of TCWF measurements in the second run (r_2) and the impossibility of the surface being totally contaminated.

Let us consider more closely the influence of residual gases upon the WF at lower temperatures, during the contamination process. The coincident part of the $U_A=f(T_A)$ curves, plotted at different pressures, can be considered as unaffected by the presence of residual gases. As has been established, these segments of the curve are linear, both for Mo and for Ni (excepting the Curie point). Moreover, as shown in Fig. 4, the curve plotted at higher pressures (*b*) deviates from linearity at a time denoted by R', while the curve *a* plotted at lower pressures first continues the linear trend and deviates at point R only after some time has elapsed and the target has reached a lower temperature. These experimental facts enable us to assume that in the absence of residual gases the curve would continue as an extrapolation of the linear part. We can therefore consider that the size of the deviation from the straight line represents the WF variation due to contamination of the surface by residual gases.

Figures 7 and 8 show a plot of these deviations, both for molybdenum and nickel, as they result from Figs. 4 and 5.

As may be seen in Figs. 7a and 8, the whole variation of the Mo or Ni WF, after 30 minutes of contamination, reaches only 10^{-2} ev, which at first could seem a rather small value. But we can make sure that this result is likely to be true, by estimating in a completely different way the number of molecules adsorbed during the contamination. We start from the fact stated in *f*: After the contamination process described in *c* and the subsequent heating of the target, the pressure increases and can be restored to its initial value only after several hours of pumping with the ionization pumps.

Considering the pumping speed of the ionization pump, the number of molecules desorbed in the first 50 seconds of heating, and introducing a time constant of about an hour for the decrease of pressure in the vessel, there results a number of adsorbed molecules during the 30 minutes of contamination of about 10^{14}–10^{15}. As the surface of the target has about 15 cm^2, the covering of the surface does not exceed a few percent. Thus the small variation of the WF value seems justified.

The reduced coverage of the surface is due to the fact that the residual gases are composed mainly of helium. The diffusion of helium through glass walls is well known (e.g., Alpert[25]). The extremely prolonged working time (thousands of hours) of the tube under the action of the ionization pumps and the relatively large area of the evacuated vessels justify the assertion supported also by the experiments of Alpert and

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[25] D. Alpert, J. Appl. Phys. **24**, 860 (1953).

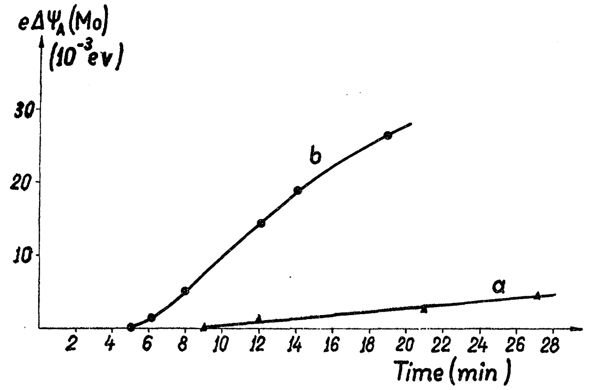

FIG. 7. Variation of the WF of Mo owing to contamination. Deviation of the points in Fig. 4 versus time elapsed from the interruption of the heating current.

Buritz,[26] that the residual gases are composed mainly of helium.

Another fact seems to confirm this supposition: The TCWF determined in a vessel which had a minute leak had a value ten times larger than the usual one, although the pressure did not exceed 6×10^{-9} torr. "Fresh" gases, rich in active components, were continuously leaking into the vessel and these active gases had a marked influence upon the TCWF measurements.

Although the pressure was systematically higher in the experimental tubes containing Mo targets, nevertheless the WF variations due to contamination were essentially like those for Ni. However, for Mo the residual gases increased ΔU; for Ni they decreased ΔU (see Figs. 4 and 5).

Since for the investigation of molybdenum, the tubes were made of Pyrex glass, which has a higher permeability for helium than the borosilicate glass used with nickel, we believe that the increased pressure was mainly due to helium, which has unimportant effects on the WF variations.

We must also consider the possibility of a target contamination with carbon, due to oil vapors, during the outgassing of the vessels on a vacuum unit with oil pumps. Such a contamination is considered to be improbable, because the vacuum unit was provided with two effective traps.

But even if minute quantities of oil vapor could escape through the traps, their action upon the surface studied would be negligible. Indeed, the carbon either diffuses into the bulk of the metal (which seems most probable) during the many thousands of hours of outgassing and represents an impurity negligible as compared with those mentioned in the purity certificate of the target material; or the carbon remains at the surface of the metal and evaporates together with the superficial layers of the target, during the thousands of hours of outgassing. The evaporated nickel formed on the walls of the tube a thick opaque layer, which played the role of a guard ring (R in Fig. 1). In the case of molybdenum the evaporation was not so intense, but still the walls were covered in time with a faint blackish hue.

RESULTS

In order to check the method, the electrical setup, and the performance of the experimental tube, we carried out the first determinations according to variant I. Thus the linearity and the parallel shift of the characteristics, as well as the precision in the determination of the WF, were investigated.

Figure 9 shows two volt-ampere characteristics, obtained at two distinct temperatures of the nickel target. The straight lines have been traced by the method of least squares. The standard deviation of the points from the straight line is of 1.5×10^{-3} ev. A careful examination discloses systematic deviations of the points from linearity. A curve of parabolic form, adjusted likewise by the method of least squares, fits still better and reduces the standard deviation of the points to 0.5×10^{-3} ev. From this value we can infer that in variant I, the errors made in determining the variations of the WF are of the order of 0.7×10^{-3} ev. The nonlinearity of the characteristics is due to the fact that the cathode and the anode are not infinite parallel planes, as well as to their polycrystalline character.

The final measurements of the TCWF were carried out in variant II, at a rate of at most one measurement in 24 hours.

For Mo (of 99.92% purity), 67 curves of the retarding potential (U_A) versus temperature were recorded within the temperature interval $600°\text{K}<T<1100°\text{K}$ using two experimental tubes. One of these curves is represented in Fig. 10. The points fit satisfactorily enough the straight line traced by least squares. The TCWF can be deduced from the slope of these straight lines only after applying the Herring correction. This correction has been computed using the Herring rela-

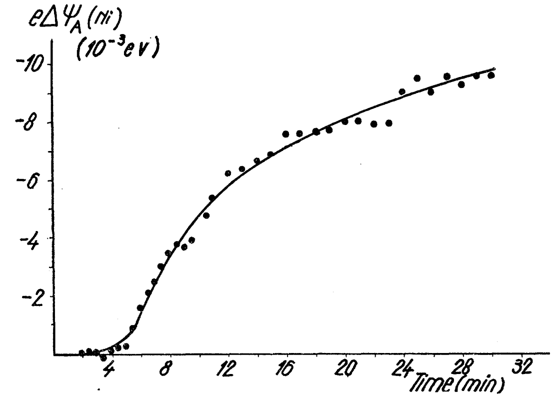

FIG. 8. Variation of the WF of Ni owing to contamination. Deviation of the points in Fig. 5 versus time elapsed from the interruption of the heating current.

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[26] D. Alpert and R. S. Buritz, J. Appl. Phys. 25, 202 (1954).

tions[17] and the tabulated data.[27] In the range of temperatures considered, the Herring correction for Mo may be approximated (using the method of least squares) by a straight line with slope $(1.49\pm0.03)\times10^{-5}$ ev/°K. Taking into account the correction, one obtains from the slopes of the 67 experimental curves

$$\left\langle\left(\frac{d\Psi_{\mathrm{Mo}}}{dT}\right)\right\rangle_{\mathrm{av}}=(7.84\pm0.07)\times10^{-5}\ \mathrm{ev/°K}. \tag{6}$$

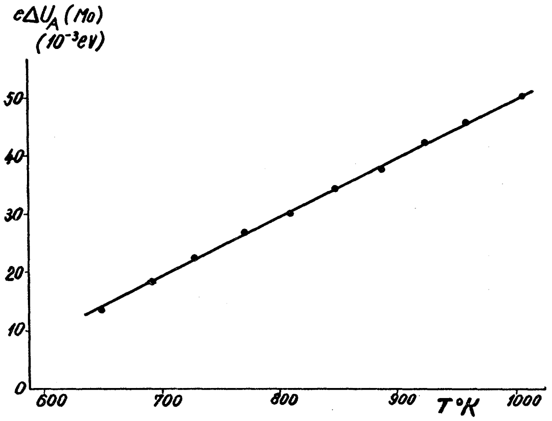

FIG. 10. Temperature variation of the retarding potential for Mo.

The TCWF of Ni (of 99.98% purity) has been determined in the same way. Figure 11 represents the retarding potential variation measured in the presence and in the absence of the terrestrial magnetic field, in the temperature range from 475° to 1025°K. To a good approximation the points fit two straight lines above and below the Curie point, respectively. It is to be noticed that the slopes of the straight lines are not influenced by the presence of the terrestrial magnetic field. The hump which appears in the neighborhood of the Curie point, and which is strongly attenuated when the terrestrial magnetic field is compensated, is due to the magnetization of the nickel target in this field, which implies variations of focusing. The hump does not disappear completely, probably owing to a residual field existing either because of the incomplete compensation of the terrestrial field, or because of the nickel layer deposited on the surface of the experimental tube, which layer is magnetized. The extension of the hump mainly towards the high-temperature region may be explained by the fact that the upper part of the nickel box cools down first, passing through the Curie point before the investigated surface itself, the temperature of which has been taken as a standard. Anyway we may assert that this hump does not reflect the real variation of the WF and therefore there is no jump of the WF at the Curie point. A difference is, however, to be noticed between the slopes of the straight lines above and below the Curie point; as has already been pointed out, this difference persists also in the absence of the terrestrial magnetic field. Consequently there exists a jump in the TCWF value at this point.

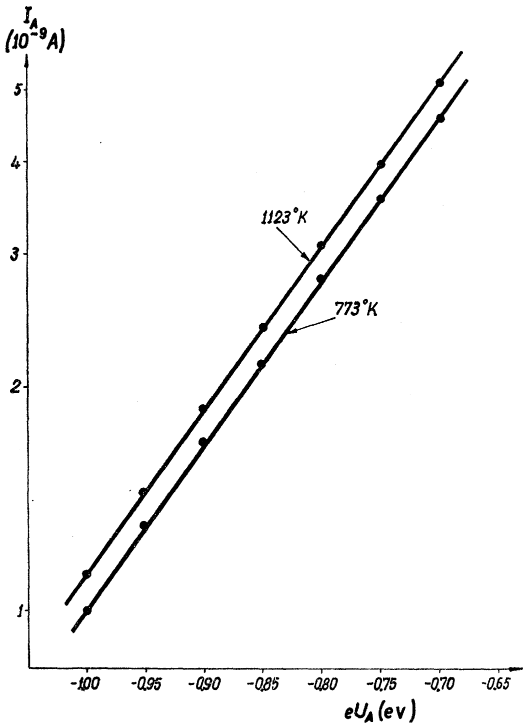

FIG. 9. Volt—ampere characteristics drawn for two temperatures of the Ni target. Saturation current about 5×10^{-8} A.

In the case of nickel the Herring correction can also be approximated by a straight line of slope $(-2.21\pm0.01)\times10^{-5}$ ev/°K in the whole interesting temperature range.

The TCWF of nickel, determined in the temperature range between 720 and 1025°K, i.e., above the Curie point, from a set of 54 curves, obtained with a tube in which the metal was outgassed during 20 000 hours, has the value:

$$\left\langle\left(\frac{d\Psi_{\mathrm{Ni}}}{dT}\right)_{T>\theta\,\mathrm{Curie}}\right\rangle_{\mathrm{av}}=(-3.12\pm0.05)\times10^{-5}\ \mathrm{ev/°K}. \tag{7}$$

On the other hand, averaging the differences between the slopes determined in the intervals 475–625°K and 725–1025°K, respectively, from 36 curves obtained with two experimental tubes, it has been found[14] that

$$\left\langle\left(\frac{d\Psi_{\mathrm{Ni}}}{dT}\right)_{T<\theta}-\left(\frac{d\Psi_{\mathrm{Ni}}}{dT}\right)_{T>\theta}\right\rangle=(-0.99\pm0.17)\times10^{-5}\ \mathrm{ev/°K} \tag{8}$$

which differs from zero by more than 5 standard errors.

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[27] H. H. Landolt and R. Börnstein, *Zahlenwerte und Funktionen* (Springer-Verlag, Berlin, 1959), Vol. 2, Part I; *Smithsonian Physical Tables* (Baltimore Press, Baltimore, Maryland, 1956).

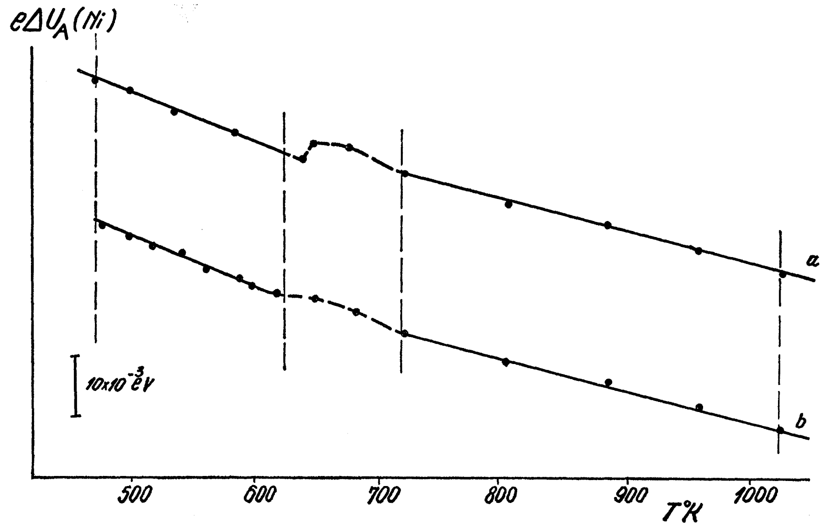

FIG. 11. Temperature variation of the retarding potential for Ni, (*a*) in presence of the terrestrial magnetic field; (*b*) after compensation of the terrestrial magnetic field.

From Vonsovski's considerations[1] there results the expression of the difference between the TCWF in presence of a spontaneous magnetization and in its absence:

$$\left(\frac{d\Psi}{dT}\right)_{T<\theta}-\left(\frac{d\Psi}{dT}\right)_{T>\theta}\approx-\delta_1\mu\frac{d}{dT}y^2, \qquad (9)$$

where δ_1 is a coefficient dependent on the exchange integrals, μ is the chemical potential, and y the relative magnetization. It can be shown that $(d/dT)y^2$ is negative. Therefore, according to Eq. (8), it follows that δ_1 is also negative.

CONCLUSIONS

By correctly applying the EBM and by taking all the steps considered as necessary to avoid systematic errors and to reduce random errors, we have determined the TCWF of Mo and Ni with a precision of the order of one percent. We established the existence of an anomaly of the TCWF of nickel at the Curie point. No jump of the WF of nickel at the Curie point has been observed. Under the given experimental conditions the approximate shape of the TCWF dependence, determined on a polycrystalline surface, upon the TCWF of the facets forming the surface, has also been obtained.

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