

UNCLASSIFIED

AD NUMBER
AD805602
NEW LIMITATION CHANGE
TO Approved for public release, distribution unlimited
FROM Distribution authorized to U.S. Gov't. agencies and their contractors; Foreign Government Information; AUG 1966. Other requests shall be referred to Air Force Foreign Technology Division, Wright-Patterson AFB, OH 45433.
AUTHORITY
ftd, usaf ltr, 7 oct 1971

THIS PAGE IS UNCLASSIFIED

805602

FTD-TT-65-1914

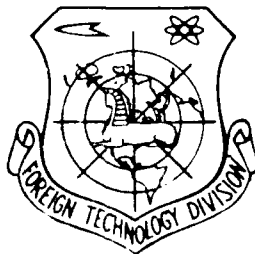
FOREIGN TECHNOLOGY DIVISION



CONTRIBUTION TO THE THEORY OF THE TARNISHING PROCESS. III

By

Carl Wagner and Karl Gruenewald



DISTRIBUTION OF THIS
DOCUMENT IS UNLIMITED



This translation was made to provide the users with the basic essentials of the original document in the shortest possible time. It has not been edited to refine or improve the grammatical accuracy, syntax or technical terminology.

EDITED TRANSLATION

CONTRIBUTION TO THE THEORY OF THE TARNISHING PROCESS. III

BY: Carl Wagner and Karl Gruenewald

English Pages: 26

SOURCE: Zeitschrift Fuer Physikalische Chemie, Vol. 40B,
No. 6, 1938, pp. 455-475.

TP6000199

THIS TRANSLATION IS A RENDITION OF THE ORIGINAL FOREIGN TEXT WITHOUT ANY ANALYTICAL OR EDITORIAL COMMENT. STATEMENTS OR THEORIES ADVOCATED OR IMPLIED ARE THOSE OF THE SOURCE AND DO NOT NECESSARILY REFLECT THE POSITION OR OPINION OF THE FOREIGN TECHNOLOGY DIVISION.

PREPARED BY:
TRANSLATION DIVISION
FOREIGN TECHNOLOGY DIVISION
WP-APB, OHIO.

CONTRIBUTION TO THE THEORY OF THE TARNISHING PROCESS. III*

by

Carl Wagner and Karl Gr $\ddot{u}$ newald

(with 8 figures in the text)

(received on 9 July 1938)

1. The speed of the oxidation of zinc into zinc oxide is, within the unavoidable error limits, not noticeably dependent on the oxygen pressure. This is so because the diffusion gradient of the ZnO-phase is primarily determined by the excess zinc at the Zn-ZnO phase boundary and because changes in the oxygen pressure are of very little influence.

2. The speed of oxidation of copper to copper oxide and of nickel to nickel oxide increases with increasing oxygen pressure. This is so because the diffusion gradient of the Cu₂O or the NiO phase is essentially determined by the oxygen excess = metal deficiency on the oxide-gas phase boundary.

3. The oxidation speed of copper to copper protoxide is determined exclusively by the diffusion of Cu⁺ ions and electrons in the Cu₂O phase if the Cu₂O layers are relatively thick. The observed speed agrees with values calculated from electrical conductivity and the Cu⁺ transference number in the Cu₂O phase.

4. If the Cu₂O or NiO layers are small, the oxidation of Cu or Ni is primarily determined by the speed of the phase boundary reactions. A graphic method is described which permits the individual determination of the speeds of the phase boundary reactions and diffusion pro-

cesses.

5. The formation of Cu_2O nuclei appears to be partially responsible for the speed of oxidation of copper at low oxygen pressures, particularly in the beginning stages.

6. The oxidation of nickel-gold alloys occasionally takes place considerably faster than that of pure nickel. It must be assumed that the scale layer on Ni-Au alloys is not completely dense, permitting the diffusion of some O_2 molecules through the pores.

1. PROBLEM

A virtually pore-free oxide layer is formed during the heating of heavy metals in an oxidizing atmosphere. It was shown in earlier publications* that the diffusion in this layer may be interpreted as a migration of ions and electrons. Formulas for the quantitative calculation of the speeds of oxidation were derived on the basis of these assumptions. It is to be the task of this work to investigate the oxidation speeds of metals in their dependence on oxygen pressure and then to compare them with the earlier predictions. Further, statements concerning the oxidation speeds of alloys are also to be examined.

2. QUALITATIVE PREDICTIONS OF THE THEORY

The following are qualitative considerations for the dependence of the speed of diffusion on the oxygen pressure.

a) Oxidation of Zinc

One may conclude from the reduction of electron conduction capability with increasing oxygen pressure that the zinc oxide contains** a small excess of zinc under finite oxygen pressures. This excess is at least partially in the form of excess zinc ions and quasi-free electrons. This zinc excess is the smaller the larger the external oxygen pressure. The zinc excess is the largest in a zinc oxide which is in equilibrium with a neighboring metallic zinc phase. The graphic presentation in

Fig. 1a is qualitatively derived on this basis. The zinc excess is very small on the phase boundary between oxide and gas at all oxygen pressures between 0.01 and 1 atm. in comparison to the excess zinc on the phase boundary metal-oxide. This may be concluded from the conductivity measurements which were mentioned earlier. Thus, the change of the external oxygen pressure within the indicated range, does not demand a change of the concentration gradient that determines the diffusion. This means that the speed of diffusion should be virtually independent of the oxygen pressure.

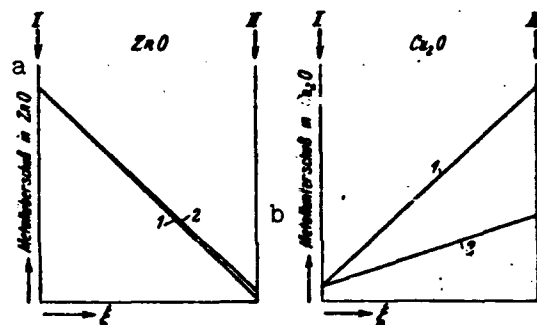


Fig. 1. Schematic presentation of the concentration gradient in ZnO and Cu_2O at various oxygen pressures. ξ) location coordinate; I) boundary surface metal-oxide; II) boundary surface oxide-gas. a) Excess metal in ZnO; b) metal deficiency in Cu_2O .

ZnO: Curve 1: $p_{\text{O}_2} = 1 \text{ Atm.}$; Curve 2: $p_{\text{O}_2} = 0.01 \text{ Atm.}$
 Cu_2O : Curve 1: $p_{\text{O}_2} = 0.1 \text{ Atm.}$; Curve 2: $p_{\text{O}_2} = 0.001 \text{ Atm.}$

b) Oxidation of Copper to Copper Protoxide

The copper protoxide phase (Cu_2O), on the other hand indicates a metal deficiency = excess of oxygen (e.g. 0.11% at 1000°C and with 30 mm Hg oxygen pressure). * The higher the oxygen pressure, the higher is also the oxygen excess of the Cu_2O phase. If only a Cu_2O phase is produced (when the external oxygen pressure is smaller than the equilibrium pressure over the Cu_2O phase + CuO phase, 100 mm Hg at 1000°C), ** an increase of the external oxygen pressure demands, according to Fig. 1b, an increase of the oxygen excess on the Cu_2O - gas phase boundary.

This is equivalent to an increase of the concentration gradient and therefore a corresponding pressure dependence of the oxidation speed. (Similar considerations apply to the oxidation of Ni to NiO).

Experiments of this sort have been carried out particularly by W. Feitknecht.* The speed of reaction increases much more slowly than would correspond to proportionality. But a precise evaluation is impossible since the parabolic tarnishing law is only approximately satisfied in the individual experiments (see also Sections 3 and 4). An extraordinarily strong pressure dependence was determined by N.B. Pilling and R.E. Bedworth** at 800°C and at pressures below 1 mm Hg. A pressure change of approximately a half of a power of ten causes a change in the speed of reaction by two powers of ten. According to our own experiments we should assume that diffusion was not alone the deciding factor (see also Section 6); phase boundary reactions and the formation of nuclei have probably exerted a considerable influence.

When the external oxygen pressure exceeds the equilibrium pressure over the phases $\text{Cu}_2\text{O} + \text{CuO}$, and CuO is produced in a thin layer, then the oxygen excess in the Cu_2O layer of the phase boundary $\text{Cu}_2\text{O}-\text{CuO}$ is, with sufficient speed of the phase boundary reaction, independent of the external oxygen pressure and thus the oxidation speed becomes essentially independent of the oxygen pressure as has already been pointed out by N.B. Pilling and R.E. Bedworth (loc. cit.) and W. Feitknecht (loc. cit.) as well as by K.W. Fröhlich***, ****.

The copper deficiency of the Cu_2O phase in comparison to the integral stoichiometric composition is caused by the presence of Cu^+ vacancies as well as electron defect locations.*****. The movement of Cu^+ ions is facilitated by transitions of Cu^+ ions to a neighboring Cu^+ vacancy. Electron movement is facilitated by electron transitions to neighboring electron defect locations. This may be specifically inter-

preted as electron exchange between Cu^+ ions and Cu^{2+} ions which, in comparison to the normal lattice are deficient by one electron. Since it is necessary for the Cu^+ ions and electrons to diffuse equally rapidly for the maintenance of electroneutrality, the diffusion of the considerably slower Cu^+ ions is essentially the time-determining factor. As was indicated earlier,* the amount of material transported $d\bar{n}/dt$ in equivalents/sec is defined by the following expression:

$$\frac{d\bar{n}}{dt} = 2(B_{\square(\text{Cu}^+)} \cdot kT) \cdot q \cdot \frac{d[\square(\text{Cu}^+)]}{d\xi}. \quad (1)$$

Where $B_{\square(\text{Cu}^+)}$ is the mobility of the Cu^+ vacancies (stationary velocity in cm/sec for the force value of 1 dyn), k is the Boltzmann constant, T the temperature, q the diffusion cross section, $[\square(\text{Cu}^+)]$ the spatial concentration of the Cu^+ vacancies and ξ is the location coordinate. The product $(B_{\square(\text{Cu}^+)} \cdot kT)$ is, at the same time, the self-diffusion coefficient of the Cu^+ vacancies. The factor 2 appears because the diffusion of the slower Cu^+ ions is accelerated by the preceding electrons. This corresponds in turn to the diffusion of H^+Cl^- in aqueous solution according to W. Nernst.**

Actually, this formulation is only approximate, since solution of Cu^+ vacancies and holes in Cu_2O shows certain deviations from the laws of ideally dilute solutions; compare C. Wagner and H. Hammen, loc. cit., and Section 6.

3. QUANTITATIVE PREDICTIONS OF THE THEORY FOR THE OXIDATION OF COPPER

When the diffusion determines the reaction speed virtually exclusively, the reaction per unit time is inversely proportional to the thickness $\Delta\xi$ of the oxide layer. This has already been shown by G. Tamman*** as well as by N.B. Pilling and R.E. Bedworth.**** The material reaction in equivalents per unit time is designated as $d\bar{n}/dt$, the cross section as q and the so-called rational tarnishing constant

$$\frac{d\delta}{dt} = \frac{1}{2} \cdot k. \quad (2)$$

as k .

The tarnishing constant k can usually be calculated from the affinity and ion and electron conductivity values of the oxide layer.* layer.*

$$k = \frac{900}{96500} \cdot \frac{1}{N} \cdot \int_{\mu_X^{(1)}}^{\mu_X^{(a)}} (n_1 + n_2) \cdot n_3 \cdot \kappa \cdot \frac{d\mu_X}{|z_2|}. \quad (3)$$

Where N is Loschmidt's number, e are the elementary charges in absolute e.s.u., n_1 and n_2 and n_3 are the relative conductivity portions for cations (subscript 1), anions (subscript 2) and electrons (subscript 3). κ represents the specific electrical conductivity of the oxide layer (in $\text{ohm}^{-1} \cdot \text{cm}^{-1}$), $|z_2| = 2$ is the valence of the oxygen ions, μ_X is the chemical potential of the oxygen in erg/g-atom, namely $\mu_X^{(a)}$ on the outer surface (phase boundary oxide layer-gas), $\mu_X^{(1)}$ on the inner surface (phase boundary oxide layer-metal). The oxygen equilibrium pressure p_{O_2} may replace the chemical potential. The following is valid in differential form:

$$d\mu_X = \frac{1}{2} d\mu_{O_2} = \frac{1}{2} dRT \ln p_{O_2}. \quad (4)$$

The following statements may be made regarding the oxidation of copper to copper protoxide on the basis of the present experiments:

1. The electron conductivity is by far predominant ($n_3 \approx 1$), anion conductivity may be disregarded; transference number of the cations, $n_1 = 5 \cdot 10^{-4}$ at 1000°C is independent of the respective oxygen excess or p_{O_2} .**

2. The specific electrical conductivity κ is proportional to the seventh root of the oxygen pressure:

$$\kappa = \kappa(p_{O_2} = 1) \cdot \sqrt[7]{p_{O_2}} \quad (\text{for } \nu = 7). \quad (5)$$

preted as electron exchange between Cu^+ ions and Cu^{2+} ions which, in comparison to the normal lattice are deficient by one electron. Since it is necessary for the Cu^+ ions and electrons to diffuse equally rapidly for the maintenance of electroneutrality, the diffusion of the considerably slower Cu^+ ions is essentially the time-determining factor. As was indicated earlier,* the amount of material transported $d\bar{n}/dt$ in equivalents/sec is defined by the following expression:

$$\frac{d\bar{n}}{dt} = 2(B_{\square(\text{Cu}^+)} \cdot kT) \cdot g \cdot \frac{d[\square(\text{Cu}^+)]}{d\xi} \quad (1)$$

Where $B_{\square(\text{Cu}^+)}$ is the mobility of the Cu^+ vacancies (stationary velocity in cm/sec for the force value of 1 dyn), k is the Boltzmann constant, T the temperature, g the diffusion cross section, $[\square(\text{Cu}^+)]$ the spatial concentration of the Cu^+ vacancies and ξ is the location coordinate. The product $(B_{\square(\text{Cu}^+)} \cdot kT)$ is, at the same time, the self-diffusion coefficient of the Cu^+ vacancies. The factor 2 appears because the diffusion of the slower Cu^+ ions is accelerated by the preceding electrons. This corresponds in turn to the diffusion of H^+Cl^- in aqueous solution according to W. Nernst.**

Actually, this formulation is only approximate, since solution of Cu^+ vacancies and holes in Cu_2O shows certain deviations from the laws of ideally dilute solutions; compare C. Wagner and H. Hammen, loc. cit., and Section 6.

3. QUANTITATIVE PREDICTIONS OF THE THEORY FOR THE OXIDATION OF COPPER

When the diffusion determines the reaction speed virtually exclusively, the reaction per unit time is inversely proportional to the thickness $\Delta\xi$ of the oxide layer. This has already been shown by G. Tamman*** as well as by N.B. Pilling and R.E. Bedworth.**** The material reaction in equivalents per unit time is designated as $d\bar{n}/dt$, the cross section as g and the so-called rational tarnishing constant

$$\frac{ds}{dt} = \frac{1}{k} \cdot k. \quad (2)$$

as $\underline{k}$.

The tarnishing constant $\underline{k}$ can usually be calculated from the affinity and ion and electron conductivity values of the oxide layer.* layer.*

$$k = \frac{300}{96500} \cdot \frac{1}{N \cdot \epsilon} \cdot \int_{\mu_2^0}^{\mu_1^0} (n_1 + n_2) \cdot n_3 \cdot \kappa \cdot \frac{d\mu_X}{|z_2|}. \quad (3)$$

Where N is Loschmidt's number, ϵ are the elementary charges in absolute e.s.u., n_1 and n_2 and n_3 are the relative conductivity portions for cations (subscript 1), anions (subscript 2) and electrons (subscript 3). κ represents the specific electrical conductivity of the oxide layer (in $\text{ohm}^{-1} \cdot \text{cm}^{-1}$), $|z_2| = 2$ is the valence of the oxygen ions, μ_X is the chemical potential of the oxygen in erg/g-atom, namely $\mu_X^{(a)}$ on the outer surface (phase boundary oxide layer-gas), $\mu_X^{(1)}$ on the inner surface (phase boundary oxide layer-metal). The oxygen equilibrium pressure p_{O_2} may replace the chemical potential. The following is valid in differential form:

$$d\mu_X = \frac{1}{2} d\mu_{O_2} = \frac{1}{2} dRT \ln p_{O_2}. \quad (4)$$

The following statements may be made regarding the oxidation of copper to copper protoxide on the basis of the present experiments:

1. The electron conductivity is by far predominant ($n_3 \approx 1$), anion conductivity may be disregarded; transference number of the cations, $n_1 = 5 \cdot 10^{-4}$ at 1000°C is independent of the respective oxygen excess or p_{O_2} .**

2. The specific electrical conductivity κ is proportional to the seventh root of the oxygen pressure:

$$\kappa = \kappa(p_{O_2} \approx 1) \cdot \sqrt[7]{p_{O_2}} \quad (\text{for } p_{O_2} \approx 1). \quad (5)$$

and it therefore follows from Eq. (3) that

$$k = \frac{300}{96500} \cdot z(p_{O_2} - 1) \cdot n_1 \cdot \frac{RT}{z_1 \cdot N \cdot t} \cdot \left(\sqrt[7]{p_{O_2}^{(a)}} - \sqrt[7]{p_{O_2}^{(i)}} \right). \quad (6)$$

Where $p_{O_2}^{(i)}$ is the oxygen pressure on the inner surface Cu-Cu₂O (see also section 6) and $p_{O_2}^{(a)}$ is the external oxygen pressure. The tarnishing constant k for the oxidation of Cu to Cu₂O must therefore be a linear function of the seventh root of the external oxygen pressure $p_{O_2}^{(a)}$.

4. FORMULAS FOR THE EVALUATION OF TARNISHING EXPERIMENTS WITH SLOW PHASE BOUNDARY REACTIONS

The mass increase Δm of metal samples was also used as a measure of the speed of oxidation, in much the same manner as in the experiments of N.B. Pilling and R.E. Bedworth (loc. cit.) and of other authors.

If the diffusion alone is the time-determining factor, as is assumed by Eq. (2), then the mass increase per unit surface $\Delta m/q$ should rise proportionally to the square root of time (parabolic tarnishing law), or:

$$\frac{1}{t} \cdot \left(\frac{\Delta m}{q} \right)^2 = k''. \quad (7)$$

The constant k'' may be designated as the "practical tarnishing constant." This rule applies, in our experiments with copper and nickel, only after extended reaction periods. During the initial periods, deviations are found since the phase boundary reactions (metal-oxide as well as oxide-gas) take place with finite speeds. This has already been pointed out by K. Fischbeck, L. Neundeubel and F. Salzer* as well as by H. Reinhold and H. Seidel** on the basis of other systems.

In the boundary case of very thin layers of the reaction product, the phase boundary reactions are solely responsible for the determination of time. The speed (mass increase per unit time and per unit sur-

face) is equal to a constant which is designated as ℓ'' :

$$\frac{1}{\ell} \cdot \frac{\ell_m}{q} = \ell'' \text{ for } \frac{\ell_m}{q} \rightarrow 0. \quad (8)$$

If both phase boundary reactions and diffusion are simultaneously responsible for time, a time-law of the following type must be expected according to K. Fischbeck.* This includes the time-laws (7) and (8) as boundary cases:

$$\frac{\ell_m}{q} \cdot \frac{1}{\ell''} + \left(\frac{\ell_m}{q} \right)^2 \cdot \frac{1}{k''} = t. \quad (9)$$

The following train of thought is determining for the derivation of this formula. The Cu_2O has a very definite Cu deficiency in equilibrium with Cu metal as well as in the equilibrium with a gas phase of specified oxygen pressure. These equilibrium values determine the concentration gradients as long as the conversion is relatively small per unit time. In the case of large conversion rates per unit time (i.e., in the case of small Cu_2O layer thicknesses), no equilibrium is present on the phase boundaries with the neighboring phases. Instead, we will obtain stationary (or quasi-stationary) concentrations for the copper deficiency on the phase boundaries. These are limited by the fact that the conversion on the phase boundary Cu- Cu_2O is equal to the diffusion conversion as well as to the conversion on the Cu_2O -gas phase boundary. In connection with this, the following specific assumptions are introduced:

1. The amount of material transported by diffusion is, according to Eq. (1), approximately proportional to the concentration gradient within the Cu_2O layer.

2. The conversion speed on each of the two phase boundaries is made proportional to the difference between equilibrium concentration and the stationary concentration of the copper deficiency. This argu-

ment is a useful approximation for small differences between equilibrium concentration and stationary concentration (= the first term of a series expansion), but it is hardly generally applicable. But a more precise calculation is impossible at this time, see also the experimental results in Section 6.

We divide Eq. (9) by $\Delta m/q$ for the practical evaluation of measurements and obtain the linear relationship between $t/\Delta m/q$ and $\Delta m/q$:

$$\frac{t}{\Delta m/q} = \frac{1}{k''} \cdot (\Delta m/q) + \frac{1}{l''}. \quad (10)$$

The observed values $t/\Delta m/q$ and $\Delta m/q$ are entered in a coordinate system, one against the other for the determination of constants k'' and l'' . The individual measured values should then be on a straight line. It follows from this that

1. The slope of the curve indicates the reciprocal value of the practical tarnishing constant k'' . The rational tarnishing constant k (conversion to equivalents per 1 cm^2 and 1 sec per 1 cm layer thickness when diffusion alone determines the time) is obtained according to a conversion formula given earlier:*

$$k = k'' \cdot \frac{1}{2} \cdot \frac{v}{\tilde{A}_0}. \quad (11)$$

Here v is the volume of 1 equivalent of oxide = $\frac{1}{2}$ mole Cu_2O or $\frac{1}{2}$ mole NiO (= 11.7 and 5.5 cm^3), respectively and $\tilde{A}_0 = 8$ is the equivalent weight of oxygen.

2. The intersection of the lines according to Eq. (10) with the axis of ordinates (extrapolation to a zero Cu_2O layer thickness) produces the reciprocal value of the rate constant l'' of the pure phase boundary reactions. The corresponding constant l for the conversion to equivalents per 1 cm^2 and 1 sec in boundary layer reactions that are the sole determining factors is derived from l'' by dividing it by

the equivalence equilibrium of oxygen:

$$l = \frac{1}{\lambda_0} \cdot l'' \quad (12)$$

5. EXPERIMENTS ON THE OXIDATION OF ZINC

a) Experimental Arrangement

Zinc rods with a length of 10 cm and 0.6 cm diameter were heated in a slow current of oxygen or technical nitrogen during one (or several) days to 400°C ($\pm 5^\circ$). The weight increase of the cooled samples was used as a measure of the speed of oxidation. No sublimation losses due to vaporization of zinc were observed. In order to have as well defined a surface as possible, the individual zinc rods were polished with the finest emery paper. Three rods each were used for the individual experiments. The rods were tied with small circlets of quartz fibers (approximately 0.5 mm diameter) and then placed into a quartz boat. Only a very small part of the zinc surface was in contact with the quartz, while most of it was completely free.

b) Experimental Results

Widely varying results were obtained with identical experimental conditions. It is natural that a precisely equivalent surface preparation cannot be guaranteed. Additional difficulties compounded this. Since zinc oxide crystals are irregular, we must expect varying diffusion speeds depending upon the orientation of the crystals to the diffusion direction.* Additionally, further deviations from the normal course of reaction must be introduced by the initial formation of unstable zinc oxide modifications,** which are transformed into more stable modifications during the further course of the reaction. This will indicate possible causes for variations in the experimental results, but a precise analysis for the causes in individual cases is still lacking.

TABLE 1

Oxidation of Zinc to Zinc Oxide at 400°C

Nr.	Gas	Versuchs- dauer in Std.	Zink- oberfläche in cm ²	d Gewichts- zunahme in g	e Anlaufkonstante $k'' = (1m, g)^2, t$ (g · cm ⁻²) ² · h	
					f Einzelwert	g Mittelwert
1	h O ₂ (rein) p _{O₂} = 1 Atm.	24	57.5	2.0 · 10 ⁻³	0.50 · 10 ⁻¹⁰	0.72 · 10 ⁻¹⁰
2		24	57.3	2.0 · 10 ⁻³	0.51 · 10 ⁻¹⁰	
3		25	56.3	2.8 · 10 ⁻³	0.98 · 10 ⁻¹⁰	
4		24	56.1	1.9 · 10 ⁻³	0.48 · 10 ⁻¹⁰	
5		24	53.6	1.7 · 10 ⁻³	0.42 · 10 ⁻¹⁰	
6		24	57.2	2.6 · 10 ⁻³	0.86 · 10 ⁻¹⁰	
7	1 N ₂ mit 2.19% O ₂ p _{O₂} = 0.022 Atm.	24	56.0	3.0 · 10 ⁻³	1.19 · 10 ⁻¹⁰	0.75 · 10 ⁻¹⁰
8		24	56.3	2.6 · 10 ⁻³	0.89 · 10 ⁻¹⁰	
9		24	56.3	1.4 · 10 ⁻³	0.26 · 10 ⁻¹⁰	
10		47.5	54.4	3.4 · 10 ⁻³	0.82 · 10 ⁻¹⁰	
11		24	56.7	2.8 · 10 ⁻³	1.02 · 10 ⁻¹⁰	
12		24	56.6	2.6 · 10 ⁻³	0.88 · 10 ⁻¹⁰	
13		24	56.8	2.2 · 10 ⁻³	0.63 · 10 ⁻¹⁰	

a) No.; b) duration of experiment (hrs); c) zinc surface (cm²); d) weight increase; e) tarnishing constant; f) individual value; g) average value; h) pure oxygen; 1) N₂ with 2.19% O₂.

On the average, the oxidation in pure oxygen and technical nitrogen with 2.19% O₂ at 1 atm total pressure takes place with approximately equal speed (see also Table 1), in other words, well within the considerable limits of error of our experiments, independent of oxygen pressure as previously (in Section 2) predicted. It may be mentioned for the sake of comparison that a change of conductivity of a ratio of 1:2.7 was found for a variation of the oxygen pressure of p_{O₂} = 1 to p_{O₂} = 0.02.* The tarnishing constant indicated here agrees within an order of magnitude with the results of N.B. Pilling and R.E. Bedworth (loc. cit.) ($k'' = 0.88 \cdot 10^{-10} \text{ (gm/cm}^2\text{)}^2/\text{hr}$ for 400°C and p_{O₂} = 1 atm.

6. EXPERIMENTS ON THE OXIDATION OF COPPER TO COPPER PROTOXIDE

a) Experimental Arrangement

Sheet strips with a thickness of approximately 0.3 mm, a width of 5 mm and a length of 10 mm were used for the oxidation of copper to copper protoxide. The sample was suspended from a quartz fiber which

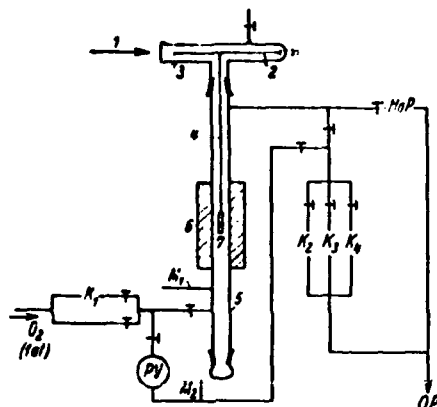


Fig. 2. Experimental arrangement for the measurement of the speed of oxidation of metal foils. 1) Microscope; 2) quartz fiber; 3) counter mark; 4) Pt-wire; 5) quartz tube; 6) furnace; 7) metal sample for the oxidation experiment; M_1 and M_2 pressure gauges; K_1 inlet capillary for O_2 ; K_2 , K_3 , K_4 outlet capillaries; HgP) mercury pump; OP) oil pump; PV) buffer volume. Gas path: $K_1 \rightarrow$ furnace $\rightarrow$ HgP, $p_{O_2} = 0.23$ mm Hg; $K_1 \rightarrow$ furnace $\rightarrow K_2$, $p_{O_2} = 1.70$ mm Hg; $K_1 \rightarrow$ furnace $\rightarrow K_3$, $p_{O_2} = 11.0$ mm Hg; $K_1 \rightarrow$ furnace $\rightarrow K_4$, $p_{O_2} = 63.0$ mm Hg.

was supported horizontally.* Its flexure could be observed with a microscope and it thus directly indicated the mass increase during the oxidation.* Figure 2 shows the experimental arrangement of furnace and capillary system for the adjustment of certain oxygen pressures with stationary flow. The quartz tube (5) was evacuated during the preheating process. Small pressures ($p_{O_2} = 0.23$ and 1.70 mm Hg) were adjusted simply and with sufficient speed by opening and closing of the corresponding petcocks in front of K_1 or HgP or K_2 . In the case of larger pressures ($p_{O_2} = 11$ and 63 mm Hg), the flow of oxygen was initially led through the buffer volume PV and, after arrival at a stationary condition, led to the quartz tube and the sample. The flow speed was $3.5 \cdot 10^{-6}$ mole O_2 /sec = $14 \cdot 10^{-6}$ equiv. O_2 /sec, in other words, sufficiently large in comparison to the speed of oxidation; particularly when one considers the buffering by a corresponding volume reserve.

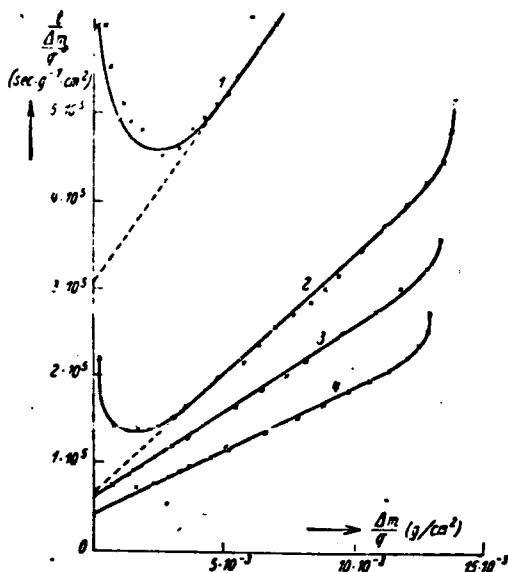


Fig. 3. Diagram for evaluation of copper oxidation experiment (1000°C).

Curve 1: $p_{O_2} = 0.23 \text{ mm Hg} = 3.0 \cdot 10^{-4} \text{ Atm.}$
 Curve 2: $p_{O_2} = 1.71 \text{ mm Hg} = 2.25 \cdot 10^{-3} \text{ Atm.}$
 Curve 3: $p_{O_2} = 11 \text{ mm Hg} = 1.45 \cdot 10^{-2} \text{ Atm.}$
 Curve 4: $p_{O_2} = 63 \text{ mm Hg} = 8.3 \cdot 10^{-2} \text{ Atm.}$

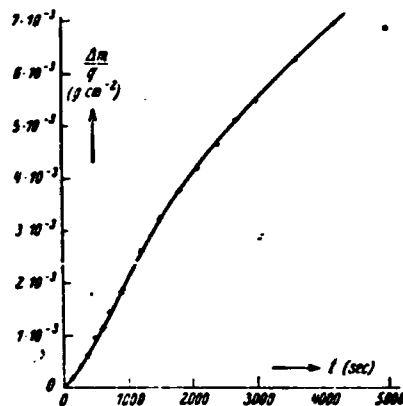


Fig. 4. Conversion values $\Delta m/q$ in the initial stage of the oxidation of copper to copper protoxide as a function of time t . (1000°C; $p_{O_2} = 0.23 \text{ mm Hg} = 3.0 \cdot 10^{-4} \text{ atm.}$)

b) Experimental Results

As has been pointed out in Section 4, the parabolic tarnishing law is not completely satisfied in the case of our experiments. The individual measurements were plotted in a diagram (Fig. 3) in order to separate the speeds of the actual diffusion process from the phase boundary reactions. This is further explained in Section 4 subsequent to Eq. (10).

A turning of the curves takes place when the values of $\Delta m/q$ are large, at that point, namely, when all the copper has been oxidized. When the smallest experimental pressures are applied ($p_{O_2} = 0.23$ and 1.7 mm Hg), the initial part of the curve shows a considerable deviation from the straight line which is demanded by the theory.

The "backward" curve portions for the smallest layer thicknesses are caused by the autocatalytic reaction during the initial stage. Fig. 4 shows, for the sake of clarification, the corresponding mass increase $\Delta m/q$ obtained as a function of time t . The slope of this curve is a direct measure of the corresponding speed of reaction, which initially

rapidly increases with increasing duration of the experiment (convex curve segment). Only later can we observe a reduction in speed corresponding to the larger path of diffusion within the Cu_2O phase (concave curve segment). Analogously to other reactions of similar types,* we may assume that the autocatalytic initial slope is caused by the gradual formation of nuclei.

The characteristic values k'' and l'' and $\underline{k}$ and $\underline{l}$ were calculated from the straight segments of the curve in Fig. 4 (see also Table 2), in accordance to the data in Section 4. The values calculated theoretically according to Eq. (6) were then compared to the tarnishing constants $\underline{k}$ which had been determined experimentally.** The following numerical values were used for the calculation at 1000°C : $\kappa(p_{\text{O}_2} = 1) = 11.7 \text{ ohm}^{-1} \cdot \text{cm}^{-1}$ (electrical conductivity of the Cu_2O phase extrapolated to 1 atm, according to J. Gundermann, unpublished); $n_1 = 5 \cdot 10^{-4}$ (Cu^+ transference value according to J. Gundermann and C. Wagner, loc. cit.); $p_{\text{O}_2}^{(1)} = 6.3 \cdot 10^{-7} \text{ atm}$ (oxygen equilibrium pressure over $\text{Cu} + \text{Cu}_2\text{O}$ according to Gundermann, K. Hauffe and C. Wagner).***

TABLE 2

Oxidation of Copper to Copper Protoxide at 1000°C

p _{O₂} Atm.	Kupferunterschub der Cu ₂ O-Phase in g-Atom auf 1/2 Mol Cu ₂ O B		Konzentra- tionsdiff. bei einge- stellten Gleich- gewichten an den Phasen- grenzen y _g ^{II} - y _g ^I E	Rationelle Anlauf- konstante k (Äqu. · cm ⁻¹ · sec ⁻¹) F		Geschwin- digkeits- konstante l der Phasen- grenz- reaktionen Äqu. · cm ⁻¹ · sec ⁻¹ I	
	Cu ₂ O im Gleich- gewicht mit Cu y _g ^I C	Cu ₂ O im Gleich- gewicht mit O ₂ y _g ^{II} D		k (Äqu. · cm ⁻¹ · sec ⁻¹)			
				(beob.) G	(ber.) H		
A	1	2	3	4	5	6	7
30 · 10 ⁻⁴	0.12 · 10 ⁻³	0.40 · 10 ⁻³	0.28 · 10 ⁻³	20 · 10 ⁻³	21 · 10 ⁻³	0.4 · 10 ⁻⁴	
225 · 10 ⁻³	0.12 · 10 ⁻³	0.02 · 10 ⁻³	0.30 · 10 ⁻³	31 · 10 ⁻³	34 · 10 ⁻³	1.4 · 10 ⁻⁴	
1.45 · 10 ⁻¹	0.12 · 10 ⁻³	0.91 · 10 ⁻³	0.79 · 10 ⁻³	45 · 10 ⁻³	48 · 10 ⁻³	2.1 · 10 ⁻⁴	
83 · 10 ⁻¹	0.12 · 10 ⁻³	1.29 · 10 ⁻³	1.17 · 10 ⁻³	62 · 10 ⁻³	66 · 10 ⁻³	3.4 · 10 ⁻⁴	

A) p_{O_2} (atm); B) copper deficiency of the Cu_2O phase in gm atom per $\frac{1}{2}$ mole Cu_2O ; C) Cu_2O in equilibrium with Cu y_{g}^{I} ; D) Cu_2O in equilibrium with O_2 y_{g}^{II} ; E) concentration difference with set equilibria on the phase boundaries $y_{\text{g}}^{\text{II}} - y_{\text{g}}^{\text{I}}$; F) rational tarnishing constant $\underline{k}$

($\text{equ.} \cdot \text{cm}^{-1} \cdot \text{sec}^{-1}$); G) observed; H) calculated; I) rate constant l of the phase boundary reactions $\text{equ.} \cdot \text{cm}^{-2} \cdot \text{sec}^{-1}$.

The agreement between observed and calculated k -values is very satisfactory and it confirms the general basic viewpoints (migration of ions and electrons). It should be pointed out specifically that a theoretical calculation of k -values generally only takes place for the evaluation of these basic assumptions, while the k -value in the individual case is determined by direct experiment.

But the theoretical prediction on the dependence of the speed of oxidation on oxygen pressure appears to be of practical value. It is especially clear in Fig. 5 that the oxidation speed of copper to Cu_2O as well as the conductivity of the Cu_2O phase are linear functions of the seventh root of the oxygen pressure.

The conversion values for the minutely small Cu_2O layers (see also Table 2, column 7) which are determined solely by the phase boundary reactions, are determined by the extrapolation of the straight portions of the curve in Fig. 3 to the intersection with the abscissa. The values for higher oxygen pressures (11 and 63 mm Hg) appear fairly reliable. In contrast to this, a greater extrapolation with a corresponding uncertainty is required for the smaller pressures (0.23 mm Hg, particularly). The conversion values are the larger, the higher the external oxygen pressure and the larger the difference between the equilibrium - copper deficiency values* $y_g^{\text{II}} - y_g^{\text{I}}$ on the two phase boundaries $\text{Cu-Cu}_2\text{O}$ and $\text{Cu}_2\text{O-Gas}$. But no proportionality with $y_g^{\text{II}} - y_g^{\text{I}}$ is found, such as the specific assumptions for the derivation of Eq. (9) would actually demand. Accordingly, equations of the forms (9) or (10) can only result in a rough approximation. The rapid decrease of the l -values is notable when small pressures are present. It is assumed that

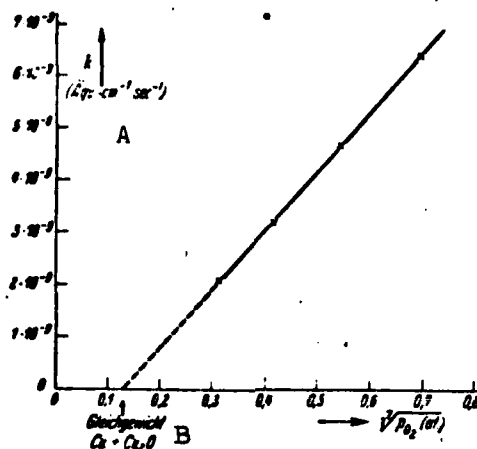


Fig. 5. Tarnishing constant k for the oxidation of copper to copper protoxide at 1000°C as a function of the seventh root of the oxygen pressure (P_{O_2} in atm). A) Equilibrium.

the reaction on the phase boundary Cu_2O - gas becomes the determining factor in this range. The speed of this reaction may be considered, in the simplest case, to be proportional to the oxygen pressure. At larger oxygen pressures, it is assumed that the reaction on the phase boundary $Cu-Cu_2O$ becomes the determining factor.

7. EXPERIMENTS ON THE OXIDATION OF NICKEL

The oxidation of nickel was carried through on the same experimental arrangement as was the copper. The samples were larger in area (20 mm long, 5 mm wide) and, at the same time, thinner (0.1 mm), since the oxidation takes place considerably more slowly. The results are presented in Table 3.

Nickel oxide, much as the Cu_2O phase, contains an oxygen excess = metal deficiency.* Corresponding to the qualitative considerations in section 2, the speed of oxidation should increase with growing oxygen pressure. According to section 3 this should be approximately in the same manner as the conductivity of the NiO phase.** But a precalculation is not possible in this case since the relative contribution of

the Ni^{2+} ions to conductivity is unknown.

The experimental values can be presented in approximate agreement with Eq. (6) by means of the following interpolation formula:

$$k \approx \text{const} \cdot (\sqrt[6]{p_{\text{O}_2}^{(1)}} - \sqrt[6]{p_{\text{O}_2}^{(0)}}). \quad (13)$$

The value $p_{\text{O}_2}^{(1)}$ (equilibrium over $\text{Ni} + \text{NiO}$) = $7.4 \cdot 10^{-11}$ atm* at 1000°C can practically be ignored (also the sixth root!). It may be pointed out for the sake of comparison that the total conductivity of the NiO phase at 1000°C increases approximately proportional to the fourth root of the oxygen pressure.

Table 3 further indicates the conversion values for minutely small NiO layer thicknesses = speed constant l , of the phase boundary reac-

TABLE 3

Oxidation of Nickel to Nickel Oxide at 1000°C

A	p_{O_2} Atm.	B	Rationelle Anlauf- konstante k Aqu. $\cdot \text{cm}^{-1} \cdot \text{sec}^{-1}$	C	Geschwindigkeitskonstante der Phasengrenzreaktionen Aqu. $\cdot \text{cm}^{-2} \cdot \text{sec}^{-1}$
	1		2		3
	$3.0 \cdot 10^{-4}$		$0.6 \cdot 10^{-11}$		$0.7 \cdot 10^{-3}$
	$2.25 \cdot 10^{-3}$		$1.1 \cdot 10^{-11}$		$3.1 \cdot 10^{-3}$
	$1.45 \cdot 10^{-2}$		$1.4 \cdot 10^{-11}$		$4.6 \cdot 10^{-3}$
	$8.3 \cdot 10^{-2}$		$1.8 \cdot 10^{-11}$		$5.3 \cdot 10^{-3}$
	1.00		$2.8 \cdot 10^{-11}$		$6.2 \cdot 10^{-3}$

A) p_{O_2} atm; B) rational tarnishing constant k ($\text{equ.}^2 \cdot \text{cm}^{-2} \cdot \text{sec}^{-1}$); C) rate constant of the phase boundary reactions ($\text{equ.} \cdot \text{cm}^{-2} \cdot \text{sec}^{-1}$).

tions. The sharp drop in the presence of small oxygen pressures is also notable.

8. EXPERIMENTS ON THE OXIDATION OF NICKEL-GOLD ALLOYS

a) Theoretical Predictions

When alloys are oxidized, the oxide layer usually contains more of the less noble metals than were present in the original alloy. Thus the alloy phase exterior presents an enrichment of the nobler consti-

tments = a deficiency of the less noble metal components. Not only the diffusion processes in the oxide phase, but also diffusion processes in the alloy phase are, therefore, responsible for the progress of the reaction. A qualitative discussion will, among others, be found in the work of G. Tammann and H. Bredemeier,* G. Tammann and W. Rienäcker,** L.B. Pfeil,*** J.S. Dunn,**** E. Scheil and K. Kiwit,***** A. Portevin, E. Prétet and H. Jolivet***** as well as K.W. Fröhlich.***** A quantitative treatment of these occurrences is still lacking.

It is noted that as a result of general considerations (dimensional considerations), the parabolic tarnishing law according to Eq. (7) must apply even when there are several time-determining diffusion processes if no role is taken by phase-boundary reactions or time changes in the state of the oxide layers (phase transformations, secondary pore formation) and to the extent that the original composition still obtains in deeper-lying layers of the alloy.

Conditions which are particularly easily understood apparently are available in nickel-gold alloys. Nickel and gold form a continuous series of mixed crystals.***** Further, gold is virtually absent from the oxide phase.

In a manner similar to that in Section 2, it may be predicted that the speed of diffusion within the nickel oxide phase does not considerably depend on the nickel content on the boundary surface Ni-Au mixed crystal - NiO (see also Fig. 6) since the oxygen excess = metal deficiency on the phase boundary NiO-gas is virtually solely responsible for the value of the concentration gradient. This is so, at least as long as the nickel concentration does not drop too far. In actuality, this boundary will be at approximately 1% Ni as may be seen from a more precise calculation.

The nickel concentration of the metal phase on the phase boundary toward NiO is not necessarily identical to the alloy composition. The continued emigration of Ni into the NiO phase causes an impoverishment of nickel or an enrichment of Au. More precise calculation shows that a very definite nickel concentration establishes itself on the metal-oxide phase boundary which is independent of the progress of the reaction as long as only diffusion processes determine the time and as long as alloy of the original composition is available in the deeper layers.

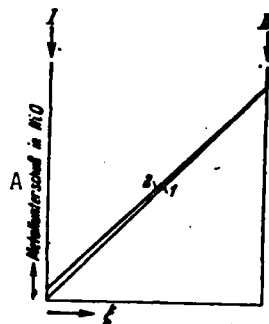


Fig. 6. Schematic presentation of the concentration gradient in NiO during the oxidation of Nickel-gold alloys. x) Location coordinate; I) boundary layer metal/oxide; II) boundary layer oxide/gas. Curve 1: pure nickel. Curve 2: nickel-gold alloy with a stable nickel concentration of 1 atom % on the metal-NiO phase boundary. A) Metal deficiency in NiO.

The stationary nickel concentration on the phase boundary metal-oxide is determined by the fact that the concentration gradient within the alloy always permits an amount of nickel to diffuse to the boundary that is equal to the amount which has been consumed by further diffusion into the NiO phase.

The stationary nickel concentration on the metal-oxide phase boundary becomes ever smaller with increasing gold concentration in the original alloy and, finally effectively reaches a zero point (i.e., less than 1%). The diffusion in the NiO determines the time up to this critical limit and it is equally as fast as in pure nickel. As the gold concentration of the original alloy increases, the corresponding nickel concentration difference toward the phase boundary metal-oxide (here 0% Ni) becomes ever smaller and, accordingly, the nickel diffusion speed in the alloy phase drops off. The Ni diffusion speed is in this range almost entirely the determining factor.

Figure 7 indicates the theoretically calculated overall curve of the oxidation speed as a function of the alloy composition. The more precise calculation shows that a virtual inflection point appears with

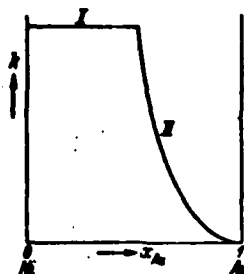


Fig. 7. Schematic presentation of the speed of oxidation of nickel-gold alloys as a function of the composition of the initial alloys (mole fraction (x_{Au})) according to theoretical considerations. Curve segment I: Stationary nickel concentration of the metal phase on the boundary toward the oxide phase $>1\%$; diffusion within the oxide phase always determines the time. Curve segment II: Stationary Ni-concentration of the metal phase on the boundary toward the oxide phase $<1\%$; diffusion within the metal phase always determines the time.

increasing gold concentration toward the area of constant oxidation speed (curve segment I) after that point the speed of oxidation rapidly drops off. The alloy composition which must be assigned to this inflection point is determined by the ratio of the diffusion constants of the alloy phase and the tarnishing constant of pure nickel. Available diffusion measurements of A. Jedelev* in the system Ni-Au result in diffusion constants which are strongly concentration dependent. This precludes a quantitative prediction in individual cases. We can dispense with the reproduction of the calculations since the course of the experiments present very considerable deviations. The application of these general considerations to other systems should be of interest.

b) Experimental Arrangement

The required nickel-gold alloys were made available by the Pforzheim branch of the Deutsche Gold- und Silber-Scheideanstalt. Since it was impossible to roll the material into small sheets, the weighing method could not be used. Instead, the oxygen consumption was measured gas-volumetrically during the oxidation. Experimental arrangements of

this sort have been described by C.N. Hinshelwood,* F.J. Wilkins and E.K. Rideal,** A. Portevin, E. Pr  tet and A. Jolivet*** as well as by G. Valensi**** among others. For the present purposes an apparatus similar to one designed by M. Centnerszwer and J. Kunstinson***** was constructed. Two quartz tubes were placed into an oven. The alloy sample was placed into one of the tubes. The pressure changes in comparison to the other tube were observed by means of a differential pressure gauge. The pressure changes during the experiment (<80 mm Hg at 760 mm Hg) have no specific influence on the speed as may be seen from the measurements in Section 7. Standardization resulted in an oxygen consumption of 0.052 mg at 900  C oven temperature for a pressure difference of 1 mm Hg. The samples were tempered in vacuum or in a flow of nitrogen prior to the beginning of the experiment. The initiation of the experiment was sufficiently well defined by the sudden influx of oxygen into the evacuated quartz tubes.

c) Experimental Results

Contrary to expectations it was found that the oxidation of nickel-gold alloys proceeds faster than with pure nickel, particularly with more extended observations. A selection of experimental results is presented in Fig. 8. The calculation of constants is impossible since the parabolic law of tarnishing does not even apply in approximation.

New samples were oxidized for 11 days and then cut through for further clarification. Microscopic observation and photographic examination of the polished cut surfaces produced the result that a dense nickel oxide phase with a plane boundary surface toward the remaining metal exists only in pure nickel. The reaction zone of the alloys, on the other hand, consisted essentially of a disorganized mixture of Au (or Au-enriched alloy) and an NiO phase. This contrasted with the assumption of the formation of a closed NiO layer in the alloys according

to the theoretical considerations of Section 8. The penetration depth of oxygen into the 25 atom-% Ni + 75 atom % Au alloy was eight times as great as in the case of pure nickel. Individual large fissures were visible along the edges of the samples while pores were not otherwise visible.

J.A.A. Leroux and E. Raub* have observed the formation of a conglomerate of Cu_2O + Ag during the oxidation of copper-silver alloys in the reaction zone. They also found that the oxidation was aided by the presence of silver since oxygen is soluble in solid silver and diffuses relatively quickly. It would therefore have to be determined whether oxygen noticeably diffuses within the gold phase in the case of nickel-gold alloys.

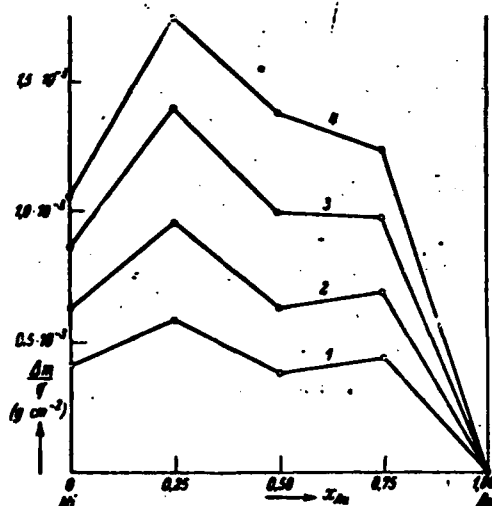


Fig. 8. Oxygen uptake of nickel-gold alloys as a function of the alloy composition (mole fraction x_{Au}). Curve 1: period of the experiment: 1200 sec; curve 2: period of the experiment: 2400 sec; curve 3: period of the experiment: 4200 sec; curve 4: period of the experiment: 6000 sec.

The solubility of oxygen in gold, according to measurements by F.J. Toole and F.M.G. Johnson,** is below the error limit of the measurements. For the purpose of a special investigation of oxygen diffusion into gold,

the oxygen uptake of a gold-plated nickel sheet was investigated. A noticeable reaction could be reached only after extended experiment periods, after the nickel had been able to diffuse through the gold layers to the outside. The ground section indicated NiO to be present only on the outer surface, while K.W. Fröhlich (loc. cit) observed Cu_2O formation particularly in the phase boundary Cu-Ag during an investigation of silver plated copper. This was the case because the oxygen easily diffused through the silver.

Only the assumption that a partial diffusion of oxygen molecules O_2 takes place through the pores of the scale layer, even when such pores cannot be proven to exist in the micro-image remains as an interpretation of our observations on Ni-Au alloys. This interpretation corresponds to the measurements of the speed of oxidation as well as to the observations on the formation of a disordered mixture of phases Au and Ni.

We wish to thank the Deutsche Forschungsgemeinschaft for its grant, the Pforzheim branch of the Deutsche Gold- und Silber-scheideanstalt for the nickel-gold alloy samples as well as gold-plated nickel sheet, as well as the Vereinigung von Freunden der Technischen Hochschule Darmstadt for the purchase of an oil pump.

Darmstadt, Institute for Inorganic and Physical Chemistry of the Technical University.

Part I of this report is available in English as FTD-TT-65-1912.

Part II of this report is available in English as FTD-TT-65-1913.

- 1 Report I: C. Wagner, Z. phys. Chem. [J. Phys. Chem.], (B) 21 (1933) 25. Report II: C. Wagner, Z. physik. Chem. (B) 32 (1936) 447.
- 2* C. Wagner, loc. cit.
- 2** H.H. v. Baumbach and C. Wagner, Z. physik. Chem. (B) 22 (1933) 199. Compare also F. Skaupy, Z. Physik [J. Physics], 1 (1920) 259. M. Kröger, Grenzflächenkatalyse [Boundary-Surface Catalysis], Leipzig 1933. O Fritsch, Ann. Physik [Annals of Physics], (5) 22 (1935) 375.
- 3* C. Wagner and H. Hammen, Z. physik. Chem. (B) 40 (1938) 197.
- 3** H.W. Foote and E.K. Smith, J. Amer. Chem. Soc. 30 (1908) 1344.
- 3*** H.S. Roberts and F.H. Smyth, J. Amer. Chem. Soc. 42 (1920) 2582; 43 (1921) 1061.
- 4* W. Feitknecht, Z. Elektrochem. [J. Electrochemistry], 35 (1929) 142.
- 4** N.B. Pilling and R.E. Bedworth, J. Inst. Metals 29 (1923) 529.
- 4*** K.W. Fröhlich, Z. Metallkde. [Journal of Metals], 28 (1936) 368.
- 4**** For details see also K. Fischbeck and F. Salzer, Metall-wirtsch. [Metals Economy], 14 (1935) 733, 753.
- 4***** Compare, for example, H. Dünwald and C. Wagner, Z. physik. Chem. (B) 22 (1933) 212. C. Wagner and H. Hammen, loc. cit.
- 5* C. Wagner, loc. cit., Report II, Table 1, No. 3.
- 5** W. Nernst, Z. physik. Chem. 2 (1888) 613.
- 5*** G. Tammann, Z. anorg. allg. Chem. [J. Inorg. Gen. Chem.], 111 (1920) 78.
- 5**** N.B. Pilling and R.E. Bedworth, J. Inst. Metals 29 (1923) 529.
- 6* C. Wagner, Report I (loc. cit.). A simplified derivation with electrical equivalent circuits is given by T.P. Hoar and L.E. Price, Trans. Faraday Soc. 34 (1938) 867.
- 6** J. Gundermann and C. Wagner, Z. physik. Chem. (B) 37 (1937) 155.

- 7* K. Fischbeck, L. Neundeubel and F. Salzer, Z. Elektrochem. 40 (1934) 517.
- 7** H. Reinhold and H. Seidel, Z. Elektrochem. 41 (1935) 499.
- 8 K. Fischbeck, Z. Elektrochem. 39 (1933) 316. See also W. Jost, Diffusion und chemische Reaktion in festen Stoffen [Diffusion and Chemical Reaction in Solids], Dresden and Leipzig 1937. Page 32.
- 9 C. Wagner, Report I (loc. cit.).
- 10* In this connection, we see the experimental results obtained for Bi and PbI₂ by W. Seith (Z. Elektrochem. 39 (1933) 538).
- 10** G.J. Finch and A.G. Quarrel, Proc. physic. Soc. 46 (1934) 148.
- 11 H.H. v Baumbach and C. Wagner, loc. cit.
- 12 E. Salvioni, Nuovo Cimento [New Experience], (5) 3 (1905) 386. J. Giesen, Ann. Physik (4) 10 (1903) 830. M. Volmer, Diss. Leipzig 1910. Ostwald-Luther, Hand- und Hilfsbuch zur Ausführung physiko-chemischer Messungen [An Encyclopedia and Reference Aid for the Conduct of Physicochemical Measurements], 5th Edition, Leipzig 1931. Page 95.
- 14* Cf. among others M. Volmer, Z. Elektrochem. 35 (1929) 555.
- 14** An approximate calculation was given in Report I.
- 14*** J. Gundermann, K. Hauffe and C. Wagner, Z. physik. Chem. (B) 37 (1937) 148.
- 15 Calculated as suggested by C. Wagner and H. Hammen, loc. cit.
- 16* M. Le Blanc and H. Sachse, Z. Elektrochem. 32 (1926) 58.
- 16** M. Le Blanc and H. Sachse, Abh. sächs. Akad. Wiss., math.-physik. Kl. [Trans. Sax. Acad. Sci., Math.-Phys. Class], 82 (1930) 133. H.H. v. Baumbach and C. Wagner, Z. physik. Chem. (B) 24 (1934) 59.
- 17 Equilibrium $\text{Ni} + \text{CO}_2 = \text{NiO} + \text{CO}$ after M. Watanabe (Sci. Rep. Tohoku Imp. Univ. 22 (1933) 892); Equilibrium $2\text{CO} + \text{O}_2 = 2\text{CO}_2$ after R.W. Fenning and H.T. Tizard, Proc. Roy. Soc. London (A) 115 (1927) 324.
- 18* G. Tammann and H. Bredemeier, Z. anorg. allg. Chem. 136 (1924) 337.
- 18** G. Tammann and W. Rienäcker, Z. anorg. allg. Chem. 156 (1926) 261.
- 18*** L.B. Pfeil, J. Iron Steel Inst. 119 (1929) 501.
- 18**** J.S. Dunn, J. Inst. Metals 46 (1931) 25.

- 18***** E. Scheil and K. Kiwit, Arch. Eisenhüttenwesen [Archives of Iron Metallurgy], 9 (1935/36) 405.
- 18***** A. Portevin, E. Prétet and H. Jolivet, Rev. Métallurg. [Review of Metallurgy], 31 (1934) 101, 186, 219. J. Iron Steel Inst. 130 (1934) 219.
- 18***** K.W. Fröhlich, Z. Metallkunde 28 (1936) 368.
- 18***** W. Fraenkel and A. Stern, Z. anorg. allg. Chem. 166 (1927) 161. G. Grube and F. Vaupel, Z. physik. Chem., Bodenstein Commemorative Volume (1931) 187. M. Hansen, Der Aufbau der Zweistofflegierungen [The Structure of the Binary Alloys], Berlin 1936. Page 243.
- 20 A. Jedele, Z. Elektrochem. 39 (1933) 691. Compare also C. Matano, Proc. physic. math. Soc. Japan (3) 15 (1933) 405.
- 21* C.N. Hinshelwood, Proc. Roy. Soc. London (A) 102 (1922) 318.
- 21** F.J. Wilkins and E.K. Rideal, Proc. Roy. Soc. London (A) 128 (1930) 394.
- 21*** A. Portevin, E. Prétet and A. Jolivet, loc. cit.
- 21**** G. Valensi, Bull. Soc. Chim. [Bull. Chem. Soc.], (5) 3 (1936) 1405.
- 21***** M. Centnerszwer and J. Kunstinson, Z. physik. Chem. 124 (1926) 225.
- 22* J.A.A. Leroux and E. Raub, Z. anorg. allg. Chem. 188 (1930) 205.
- 22** F.J. Toole and F.M.G. Johnson, J. physic. Chem. 37 (1933) 331.