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ON THE SCALING OF METALS AND ALLOYS

(Z. Metallkde. 29, 209, 1937)

Ву

Erich Scheil

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Translated by

D. J. Wright

Ottawa

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| Title: | On the Scaling of Metals and Alloys. | | |
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On the Scaling of Metals and Alloys*

While they are being treated, many metals are freely exposed to air during annealing and their surfaces thus become oxidized. The noble metals alone are an exception, since the decomposition pressures of their oxides are above the oxygen partial pressure of the air. Nitrides apparently do not form when annealing commercially used metals in air, or at least not in appreciable amounts. More exact investigations have not yet been made. Moreover, if one disregards the gaseous (e.g. MoO_3) or liquid (e.g. V_2O_5) reaction products which are only rarely obtained, it appears that scaling in air results in the formation of a crystallized or even glassy oxide layer, on the permeability and adhesive strength of which the further course of scaling and the development of the metal surface under the scale layer depends.

Scaling of Pure Metals

The oxides are formed on the metal in the order of their oxide content; metallic oxides may even appear, or one of the stable oxides may be lacking. The first monomolecular scale layer forms very quickly. Further thickening takes place due to diffusion in the scale layer. Cracks or splits in the scale reduce the diffusion path, thereby accelerating the scaling.

If the scale layer consists of only one type of crystal, then its rate of thickening dn/dz is inversely proportional to the thickness n of the scale layer already present

^{*} Paper presented to the Deutsche Gesellschaft fuer Metallkunde, 11 December 1936, in Berlin.

at the time z (1, 2):

dn/dz = 1/Kn

or, by integrating

 $n = z/\sqrt{2K} = z/K^{1}$

K³ represents the extent to which scaling is checked by the scale layer which already exists. Pilling and Bedworth — abbreviated from now on to P. and B. — found that this time law was valid for the majority of metals, even when the oxide layer consisted of several oxides of the metal. By careful experiment, W. Feitknecht (3) found that the scaling of copper at first takes place more rapidly than the quadratic law suggests. In the initial stage Feitknecht found structural changes in the scale layer to which he attributed the deviations. Within the range of oxidation tints, i.e. when the scale layers were very thin, G. Tamm- ann and W. Koester (4) discovered an exponential time law which is still difficult to explain (5). If we disregard these initial phenomena, the quadratic law is well corrob- orated by the experiments.

A few metals, however, are subject to a completely different time law of scaling. Fig. 1 shows three scale isotherms of tungsten. The increase in weight was determined by weighing the sample in the furnace. The deviations in the measurements are due to variations in temperature; the furnace was not regulated during the night. At 900° the scale no longer adhered to the sample but fell into a small receiving pan and was weighed together with it (6). The amount of scale on the isotherms 500° and 700°

··· 2 ···

increased in proportion to the time. P. and B. found the same linear time law in the case of calcium and magnesium. The author checked their findings for magnesium and can corroborate them.

The linear time law means that protection against scaling does not become greater as the scale layer is reinforced. This, however, does not explain why the existing scale layer in no way checks further scaling for, due to the great rapidity of the cleavage plane reactions, the metals obeying the linear time law of scaling would have to scale completely so quickly that it would no longer be possible to follow the reaction by weighing. The linear time law, however, is also satisfied when splits occur periodically in the scale layer. The appearance of the scale layer, which is to be discussed below, substantiates this assumption.

The acceleration of the scaling which is noticeable in the isotherm 900° can be attributed to an increase in the temperature of the sample due to the heat of exidation. A much more marked acceleration of the scaling above a certain temperature was found by P_o and B_o in the case of calcium and magnesium_o

In the case of these two metals, P. and B. explained the linear time law by the decrease in volume during the formation of oxide. According to K. Fischbeck $(7)_p$ in the following metals the metal has a greater volume than the oxide with the same number of metal atoms:

Li, Na, K, Cs, Rb, Mg, Ca, Sr. Tungsten is not included in this series; its volume incr-

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eases almost threefold during oxidation. As is now shown, it is even doubtful in the case of calcium and magnesium whether the decrease in volume is responsible for the behaviour of the linear time law.

The form of the scale substance varies according to the time law of the scaling. Fig. 2 indicates the appearance of an oxidized copper sample (quadratic law) and Fig. 3 that of an oxidized tungsten sample (linear law). With the scaling of copper, a scale layer forms on the originally sharp-cornered sample. the dimensions of which (apart from the somewhat rounded corners and edges) are proportional to the dimensions of the original sample. The thickening of the scale layer on copper must therefore result from the formation of layers of the size of the scale surfaces which at times exist; i.e. the scale layer develops at the scale-air interface (8).

In the case of the tungsten sample in Fig. 3, however, the formerly projecting edges have shrunk inwards. This type of scaling is illustrated even more clearly by the Widia sample shown in Fig. 4 (tungsten carbide in a cobalt groundmass) (9) in which the scale layer is more compact and has a smooth surface, even where the edges have shrunk inwards. The recession of the edges is explained by the development of a layer with the same dimensions as the metal-scale surface. Generally speaking, in the case of the type of reaction substance in Fig. 2 the thickening of the reaction layer takes place in the outer surface while in the case of a reaction substance such as

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that in Figs. 3 and 4 it does so on the inner surface,

While the test-piece such as shown in Figs, 3 and 4 is understandable in the case of tungsten which increases in volume as it scales, we cannot explain the appearance of this test-piece in the case of calcium (10) and magnesium. Since they decrease in volume during scaling, the surfaces should fall inwards instead of standing out in relief. The decreas in volume must therefore be more than balanced by a substantial increase in volume which is probably due to the formation of splits. It thus appears that even with calcium and magnesium, the reduction in volume is not the main factor to have a bearing on the scaling.

P. and B. have found that aluminum and cadmium are in a special position with regard to the course of scaling in relation to time; after a slight, relatively rapid scaling attack, it almost comes to a complete standstill. C. Wagner (11) sees a possible explanation for this in the fact that in the case of aluminum (12) and of cadmium (13) the oxides which are formed are primarily unstable.

The thickening of the scale layer is caused by diffusion. Since the compounds are heteropolar the ions and electrons, rather than the neutral atoms, migrate (14). It is necessary to assume the migration of electrons, for otherwise high electrostatic charges would be huilt up at the points from or to which an ion migrated and such charges would not permit the movements which have taken place. We do not wish to deal with these attendant phen-

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omena here but will limit ourselves to the ionic migrations. One must differentiate between the diffusion of the anions and the cations, since the rate of the two reactions generally differs so greatly that only the diffusion of the one type of ion is to be considered.

This is particularly true when one of the two types of ion is present in less quantity than is required to achieve the ideal lattice structure of the oxide. This is the case, for example, with ferrous oxide. According to R. Schenk (15), ferrous oxide has a lower iron content than the stoichiometric combination of FeO demands. By comparing the volume obtained by a determination of the density with that calculated from X-ray determinations, E. R. Jette and F. Foote (16) have shown that the ferrous oxide lattice lacks sites in the Fe⁺⁺ partial lattice. According to G. Haegg the same thing is true of FeS (17) and FeSe (18).

In a lattice of this structure, of **cour**se, the iron ions near an unpopulated place can easily change over to it. The diffu**si**cn of the iron ions will therefore be extensive in comparison with the diffusion of the anions.

Similarly, H. Duenwald and C. Wagner (19) also assume that there are unpopulated sites in the copper ion partial lattice of cuprous oxide, because of the following observations. In electrolytic transport experiments, the Cu⁺ ions migrated. Moreover, the conductance of the cuprous oxide increased as the oxygen pressure rose, i.e. as the oxygen content of the cuprous oxide increased and the number of defects therefore increased. From measurements made for a

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pressure of 30 mm Hg at 1000°, Duenwald and Wagner calculated that there was a copper deficit of about 10⁻³ g atoms of Cu. The deviations from the stoichiometric combination are therefore several powers less than in the case of ferrous oxide. In contrast to this result, we have K. W. Froehlich's (20) analytical determinations of the copper content of cuprous oxide, according to which a copper excess of about 0.2% Cu (average of the analyses given) was supposed to exist. No explanation for the difference in the results has yet been found.

The author regards Wagner's experimental method as more certain than the analytical observations and assumes as Wagner does that there is a copper deficit in the cuprous oxide.

With regard to the oxides of other metals, it is a known fact that in the case of zinc oxide (21), cadmium oxide (21), aluminum oxide (22) and tantalum oxide (22), the conductance decreases with the oxygen pressure, i.e. there is an excess of the metal. On account of the small size of the metallic ions $(Zn^{++} = 0.85 \text{ Å}, Cd^{++} = 0.05 \text{ Å}, A1^{+++} = 0.55 \text{ Å} and Ta^{+++++} = 0.7 \text{ Å}) (23), von Baumbach and Wagner assumed the arrangement of the excess metallic ions on intermediate lattice spaces.$

No study has yet been made, however, of the majority of the metallic oxides. The lengths of the ionic radii lead one to believe that only metallic ions migrate in the oxides for the ionic radius of oxygen, which increased to 1.3 $\stackrel{\circ}{A}$

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due to the absorption of two electrons, exceeds the ionic radius of commercially used metals whose length has been reduced by the rejection of electrons (23). Accordingly, the new lattice planes of the scale layer are formed at the scale-air interface. When the scale layer is correctly formed it is therefore like that shown in Fig. 2.

If the anions were to migrate, however, the new lattice planes would then be formed at the scale-metal interface, giving a scale substance like that shown in Figs. 3 and 4. One dare not conclude, however, on the basis of the appearance of this type of scale substance alone, that the anions migrate. Due to the periodic formation of cracks, the new formation of the lattice planes - even when it takes place at the scale-air interface - can always be transferred to the neighbourhood of the scale-metal interface. When the metallic ions migrate, both types of scale substance may therefore appear. One can conclude from the foregoing that, in the case of the oxides of tungsten, magnesium and calcium too, the metallic ions migrate.

In previous investigations, no consideration was given to the fact that some metals form scale layers of several oxides. Of the metals which are of commercial importance, iron (FeO, Fe₃O₄ and Fe₂O₃) and copper (Cu₂O and CuO) are included in this category. According to the investigations made by H. H. von Baumbach and H. Duenwald and C. Wagner, the conductance bears hardly any relation to the oxygen pressure. The transport number of the Cu⁺⁺ ions was likewise very

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low $(n_{Cu}^{++} < 5 \ . \ 10^{-3})$ and was still within the margin of experimental error. The cupric oxide was therefore supposed to limit the scaling of the copper to a considerable extent. According to Feitknecht's measurements (3), the rate of scaling at low oxygen pressures below the equilibrium pressure of $Cu_20 + Cu0$ increases as the oxygen pressure of the gas rsies, and becomes constant when the equilibrium pressure is achieved. As Cu0 forms, the scaling rate of copper therefore diminishes but is not completely arrested; further scaling is merely restricted. Probably the Cu0 layer does not form a compact crust. This is confirmed by the fact that the volume decreases as the Cu_20 changes into Cu0. The phenomena have still not been thorocughly explained.

Both in copper and in iron, the metallic ions move most easily in the oxide which is poorest in oxygen; it is this layer, therefore, which has the greatest breadth.

Scaling of Alloys

<u>The order of oxide formation</u>. In the case of alloys the oxides of the various alloying elements, and sometimes even combinations of these oxides $(e_{\circ}g_{\circ} Fe_2SiO_4)_{\circ}$ are formed. Fig. 5 represents the simplest case of an alloy of two components, in which only the two metals and their oxides appear as types of crystal. Let us consider the changes in a thin boundary layer of a mixture. Due to oxidation the structure of the layer shifts along the line XO from X to O; in doing this, the structure of the layer first enters the field A + B + BO. At first, therefore, only the crystal type B is oxidized so that when the line XO bisects the line A + BO all the B of the layer in question is oxidized. As the oxidation progresses further, the boundary layer reaches the field A + AC + BO and the oxidation of A begins. It is complete when the line XO has reached the line AO + BO.

Fig. 6 represents a somewhat more complicated case: in addition to the oxides AO and BO, we also have the combination of them, AO . BO. As oxidation occurs, BO forms first, then AO . BO forms as A oxidizes and the resultant AO reacts with the BO which is already present, and finally AO also forms. The more complicated cases can be similarly described.

In both the cases under consideration, one will say that A is nobler than B. By limiting ourselves to the lowest stage of oxidation of each metal and to alloys of two metals, the metals can be arranged in a series in such a way that each metal oxidizes sooner than the one following it in the series (25). For the corresponding sulphide series, G. Tammann and H. von Samson-Himmelstjerna (26) have determined the sequence of the metals experimentally. Although suitable experimental data are lacking for the oxidation series, one can arrange the metals by order of oxidation by classifying the elements according to diminishing heats of formation of their lowest oxides, converted to the heat of formation of one oxide, MeO.

Coubts have been expressed as to whether it is

correct to base investigations on the heats of formation converted to MeO. This question may be discussed in the light of Fig. 7. It is assumed that only the heats of formation provide any standard for the free energy. The oxide B₂O is less noble than AO because the straight line A + Bo"O lies beyond the dotted line B-AO'. In order for this to be valid for other oxides $B_{\chi}O_{\chi}$ as well (e.g. for B0), the straight line B0" must lie beyond B0'. One can now either use, as Guertler (25) did, the angle between BO and BO" or the value which the line BO" assumes at a certain point, e.g. for the composition BO, as a measure of the affinity. The second of these measures was used in Table 1. In column 1 of this Table we give the chemical symbol, in column 2 the formula of the oxide which is poorest in oxygen, in column 3 its heat of formation and in column 4 the heat of formation converted to the oxide MeO.

The sequence of the Table corresponds to the oxidation series at room temperature, assuming that the determination of the free energy is based primarily on the heat of formation. When the values are very close to one another deviations may appear because, on the one hand, other factors play some part in the determination of the free energy and, on the other hand, it would be most fitting to use the heats of formation at scaling temperature for the basis of the study. For this reason, for example, copper does not appear in the series in the order of its heat of formation but in accordance with observations

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made during scaling.

Changes in the sequence may also be produced, moreover, in the case of alloys of three or more metals due to the formation of combinations of the individual oxides. Thus, for example, the sequence for silicates will not always agree with that for oxides. To achieve a complete synopsis, the oxide series would have to be extended to include further series of combining components, but this is not possible at the present time.

The distribution of the oxides in the scale layer. In connection with the development of the scale structure it is significant that the oxides of the added metals are generally enriched at particular points in the scale layer, namely at the scale-metal interface.

In deriving this rule we assume that the oxide AO does not dissolve B and likewise BO does not dissolve A, and furthermore the nobler A should be present in considerable excess. Then the less noble oxide BO forms on the surface first. The case of acompletely compact coating of the surface by the oxide BO, which is particularly important in the production of scale resistant alloys, will be mentioned below. It is assumed in the following discussion that the BO layer has gaps in which AO can form. In both types of crystal, further development takes place due to diffusion through the scale crystals, i.e. because of the lack of dissolving power of the two oxides, the A ions migrate only through the AO layer and the B

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ions only through the BO layer and form new lattice planes of the scale-air interface. Since the concentration of B or A plays an essential part in the speed of this process, more AO is formed in a certain unit of time than BO. The AO would eventually outgrow the BO because it always develops at the scale-metal interface. Moreover, the A atoms will partially migrate around the BO particles so that BO takes some part in the shifting of the surface towards the centre of the metal sample.

This results in an enrichment of the BO at the scale interface. This could be proved in the case of iron alloys by analysis of the individual scale layers which could be separately detached (6). Fig. 8 gives as an example the measurements of iron-aluminum alloys. The distance from the lines representing equal distribution gives the indication of the extent to which they had been enriched or impoverished. At temperatures of over 1000° the enrichment of the alumina in the scale-alloy interface layer is particularly great. The enrichment of the less noble admixture at the scale-metal interface occurs with all iron alloys with the exception of manganese steel (6). According to K. W. Froehlich (20), this law has also proved true repeatedly for copper alloys.

If the metal A which is present in excess is less noble than B, the AO forms first and B is enriched at the scale-metal interface. It cannot oxidize here, however, because the more easily oxidizable A is always present. Since the thickening of the layer takes place at the scale-air interface, nothing is changed until the concentration of B at the scale boundary forms a layer occluding the A and the further oxidation then takes place as if the nobler B were present in excess. B0 now appears too until the excess has again been reduced to a certain amount. All in all, enrichment of the nobler substance at the scale-metal interface is the result of these changes in concentration. Its existence was detected in the scale of several iron alloys (6) and in copper-silver alloys which were rich in copper (20).

It is therefore established that as a rule the elements which are present in slighter amounts are enriched at the scale-metal interface, as oxide when the admixed substance is less noble and in metallic form when it is nobler than the metal present far in excess.

The picture given of the scaling process is very sketchy, but it shows the main features. Further insight is afforded by a glance at the structure of the scale boundary. Fig. 9 gives as an example the structure of a steel with 4% Al which was subjected to scaling for 5 hours at 1000° . The alumina, easily distinguishable from the iron oxides by its colour, projected into the iron layer. These advancing oxides can only have been formed by the oxygen, in spite of

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its slight diffusability in iron, penetrating the iron and there oxidizing the aluminum. It is probably not a case of true diffusion but of an advance along cleavage planes or grain boundaries. As soon as this oxygen encounters an aluminum atom, it will react with it and be added to already existing alumina crystals as alumina or will form new alumina nuclei. In this way, threads of alumina would gradually form inside the steel, unless the metal boundary grew inwards at the same time due to the formation of iron scale. Because of the fact that the iron changes into scale, the iron between the threads of alumina disappears and the alumina is enriched near the scale boundary.

The advance of the alumina threads from the scale boundary will continue longer, the less the oxidizing strength of the gas. In the case of weakly oxidizing gases, therefore, the special scaling can project deeply into the material, causing considerable harm because of the long attack. This has occurred in the case of cast iron, in which the graphite seams provide paths for the penetration of the oxygen into its inside layers. The oxidation starts in the graphite seams. The oxygen concentration, however, is so slight that at first no iron oxides but only iron silicates are formed from the silicon content of the cast iron (27). Only after this has made considerable progress and the graphite seam is mostly gasified, do iron oxides form in place of the graphite seams. Fig. 10 shows a cast iron which has

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been subjected to scaling. In place of the graphite seams, ferrosoferric oxide for the most part has already formed. Emanating from the graphite seams, a very finely dispersed amount of iron and iron silicate

has formed.

Scale resistant alloys .- The question now arises as to whether one should mix nobler or baser substances. Both are enriched at the metal-scale interface, and one might think that a compact layer might form which would effectively check the further development of scaling. It must be observed, however, that the noble metals can be penetrated by oxygen. Froehlich (20) has shown that silver plating does not protect copper against scaling. The compactness of the layer plays some part of course, but it can hardly be expected that scaling would produce a more compact layer than silver plating. In many cases, particularly in the scaling of nickel steels (28), a strong nickel layer mixed with scale is frequently formed. Quite apart from the cost involved one can hardly expect to achieve any real protection against scaling by alloying a noble metal to the basic metal.

All scale-resistant alloys contain a baser element intended to reduce the scaling. The scale-resistant chromium-nickel-steels, made of iron to which a nobler element, nickel, and a baser element, chromium, have been added, are no exception for the additive introduced to increase the scale resistance is chromium exclusively (6).

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In order to achieve real scale resistance, a tightly sealed layer must be formed on the alloy by the oxide of a baser secondary metal. The rate of migration of the metallic ions in this layer must be very low because the thickening of the layer depends on it.

The extent of the difference in scaling attack is shown in Fig. 11, taken from a paper by A. Portevin, E. Pretet and H. Jolivet (29). As long as the aluminum steel with 8.5% Al was covered only by the white alumina scale, the increase in weight due to scaling was very slight. From a certain moment on, which varied for the individual samples, a considerably stronger scaling attack combined with the formation of iron oxide set in because somehow the alumina layer was defective. It is therefore also necessary that the special oxide form a tightly sealed crust.

Moreover, the melting point of the special oxide layer, as well as the melting point of its mixture with the oxide of the basic metal and with other secondary substances in the alloy, must lie well above the scaling temperature. Thus, for example, the extent of the scale resistance of silicon steels is limited by the melting point of the eutectic mixture of ferrous oxide and fayalite (Fe_2SiO_9) which is 1240° . Even at 1200° , silicon steels are no longer resistant to scaling. Likewise, contact with substances which can enter into a reaction with the special oxide may result in the change from protection against scaling to violent attack. Most metallic oxides, which may stem for example from the decreased scaling of the material to be annealed, may enter into such a reaction with the special oxide layers of the scale resistant alloys.

Conditions for the formation of good protective oxide layers are best fulfilled in the case of substances which are used as refractories in the ceramic industry, e.g. alumina, silicic acid, chromic oxide, magnesia and beryllium oxide.

Summary

The scaling of metals is due to diffusion of the metallic ions through the scale layer. The new lattice planes are therefore formed on the surface of the scale. If splits occur, the point at which scale forms shifts to the inner surface adjacent to the metallic surface. Due to periodic splittings, the attack progresses linearly in relation to time.

In alloys, the oxides of the various alloying elements form in the first approximation in order of the heats of formation. For the arrangement of the oxides in the scale layer, the principle that the alloying additives are enriched at the scale-metal interface holds true, regardless of whether they are nobler or baser than the metal which is present in excess. The conditions for the formation of scale-resistant layers on alloys are stated.

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Fig. 2

Fig. 3

Fig. 4

Oxidized Copper Sample

Oxidized Tungsten Sample

Oxidized Widia Sample









Order of Oxide Formation. B baser than A.

Fig. 6

Order of Oxide Formation. Combination of oxides, B baser than A.



Fig. 7 - Relation Between Heats of Formation and Equilibria.



Fig. 8 - Aluminum Contents of Various Scale Layers of Aluminum Steel.





Fig. 9 - Structure of the Scale Boundaries of a Steel with 4% Al after Annealing for 5 Hours at 1000° .

Fig. 10 - Scale Structure (Iron Silicates) in the Cast Iron.



Fig. 11 - Scaling Isotherms of an Aluminum Steel with 8.5% Al at 1000° (according to Portevin, Pretet and Jolivet).

| Table 1. | Oxidation | n Sequence | of Oxides |
|----------|---------------------------------|------------|-----------|
| | Oxide | Heats of | formation |
| Element | | of comple | converted |
| | | or comp a | |
| | | | to Meu |
| Ta | $Ta_{P}O_{5}$ | 498.4 | 849 |
| Al | Al_2O_3 | 898,8 | 828 |
| v | V205 | 302 | 252 |
| Cr | Cr ₂ O ₃ | 288,9 | 241 |
| в | B ₂ O ₃ | 282 | 285 |
| Th | ThO ₂ | 292 | 219 |
| Li | Li ₂ 0 | 142,8 | 214 |
| U | UÕ, | 269,7 | 202 |
| Zr | ZrŌ, | 257.4 | 193 |
| Ce | CeO, | 282.9 | 175 |
| Ti | TIO | 218.1 | 164 |
| Na | Na _s Õ | 100,7 | 160 |
| Si | SiO ₂ | 205,1 | 154 |
| Ca | CaÕ | 152.1 | 152.1 |
| Mg | MgO | 145,8 | 145.8 |
| Sr | SrO | 142,2 | 142.2 |
| Be | BeO | 185 | 135 |
| Ba | BaO | 183.4 | 183.4 |
| K | K ₂ O | 86.8 | 130 |
| Rb | Rb ₂ O | 83,5 | 125 |
| Cs | Cs.O | 82.7 | 124 |
| Mn | MnO | 123 | 123 |
| Bi | $\mathbf{Bi}_{2}\mathbf{O}_{3}$ | 137.8 | 115 |
| Mo | MoO | 142.8 | 107 |
| W | WO ₂ | 181.4 | 98.5 |
| Zn | ZnÕ | 83 | 88 |
| Sn | Sn O | 66.8 | 66.8 |
| Cd | CdO | 65,2 | 65,2 |
| TI | Ti_2O | 43,2 | 65 |
| Fe | FeO | 64,6 | 64,6 |
| Ni | NIO | 58,9 | 58,9 |
| Os | OsO_4 | 98,3 | 58,4 |
| Co | CoO | 57,5 | 57.5 |
| Cu | Cu_2O | 48 | 64,5 |
| Pb | PbŌ | 52,7 | 52,7 |
| Ru | RuO_2 | 52,5 | 89,4 |
| Rh | Rh_2O | 22,7 | 34,1 |
| Jr | $\mathbf{Jr}\mathbf{O}_2$ | 40,1 | 80,2 |
| Hg | HgŌ | 21,5 | 21,5 |
| Pđ | PdO | 20,4 | 20,4 |
| Ag | Ag_2O | 6,5 | 9,8 |
| Au | Au_2O_3 | | |