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OXIDATION CHARACTERISTICS OF MOLYBDENUM-ZIRCONIUM OXIDE CERMETS

B. Heitzinger

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16. Abstract

The oxidation of molybdenum is affected by the factors of temperature, the oxygen pressure in the oxidizing atmosphere, and the time of exposure. Studies of the oxidation characteristics of molybdenum show that the oxidation rate increases strongly when the temperature exceeds 600° C. Investigations of the behavior of cermets with various percentages of zirconium oxide are discussed, taking into account oxidation conditions at temperatures under and above the melting point of molybdenum trioxide.

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Oxidation Characteristics of Molybdenum-Zirconium Oxide Cermets

F. Heitzinger
Metallwerk Plansee AG., Reutte, Austria

In recent years, materials on a Mo-ZrO_2 base have become increasingly more important in technology. These are employed as materials with high proportion of oxide, above all, in the iron and steel industry, as protective pipes for thermoelectrical temperature measurements, as nozzles and aperatures for maintaining certain flow cross section constant, as continuous casting iron molds, but also as parts subject to wear and tear [1], [2]. Materials with less ZrO_2 are employed mainly as extrusion materials [3]. These are materials with the metal and ceramic portions penetrating one another to form a grid where the ceramics fill the interconnected pore volume of the porous metal grid (Fig. 1). /1*

As a result of the considerable proportion of molybdenum in every case, these materials are sensitive to oxidation at higher temperatures. Precise knowledge of oxidation behavior therefore deserves special attention, because the material is usually employed in air at high temperatures.

Of course, oxidation is mainly determined by the molybdenum, so that we will first turn to the oxidation behavior of molybdenum.

1) Oxidation of Molybdenum /2

The oxidation of molybdenum is determined by time, as well as by temperature and oxidation pressure of the oxidizing atmosphere [4-8]. This is carried out at lower temperatures up to 300° C following a parabolic relationship (time - increase in weight). Molybdenum is oxidized to MoO_2 and effects a certain amount of automatic protection. If the oxidation temperature increases, the parabolic course of oxidation converts to a linear relation-

*Numbers in the margin indicate pagination in the foreign text.

ship with increasing formation of MoO_3. Moreover, MoO_3 begins to evaporate above 600° C and the oxidation is characterized by a reduction in weight.

Above 600° C, the oxidation of molybdenum was determined in our own experiment, although it is known from the literature. The experiments were carried out in a retort furnace with slowly moving air up to the melting point of MoO_3. Beyond this, our own quite simple experimental arrangement was employed, to be described later.

The reason for this work was to gain a clear basis for comparison, since the oxidation of molybdenum, above all above 600° C, is clearly determined by the content of oxygen so that data in the literature cannot be directly employed.

For a further discussion of the oxidation behavior of molybdenum, our own results will be briefly discussed. The rate of oxidation increases greatly with increasing MoO_3 evaporation with further temperature increase above 600° C (Fig. 2).

At 795° C at the melting point of MoO_3, the rate of oxidation increases by more than a power of 10, but then is altered unsubstantially up to 900° C (Fig. 3). /3

Since the previously selected experimental arrangement was unsuitable for experiments at temperatures above 900° C, the following experimental arrangement was employed for high temperature experiments above the melting point of MoO_3 (Fig. 4). The results with this experimental arrangement are presented in Fig. 5. This also shows again the slight alteration in oxidation rate between 800° C and 900° C, while the rate of oxidation increases in a steep linear relationship with temperature above 900° C. The experiments were stopped at 1400° C for practical reasons. Most published experiments with molybdenum already terminate at approximately 1000° C and there are hardly comments on higher oxidation temperatures.

2) Oxidation of Mo + ZrO_2 Cermets

2.1. Oxidation below the MoO_3 melting point

The rate of evaporation of MoO_3 is still so low at 600° C that the oxidation is essentially characterized by an increase in weight. The relationship between MoO_3 evaporation and MoO_3 scale is less than 0.02 %. At this temperature, molybdenum was compared with an Mo + ZrO_2 cermet, containing 40 percent by volume of ZrO_2 and the following surprising result was obtained (Fig. 6).

In the beginning, oxidation is greatly delayed by the sinter /4 skin. After about five hours, the oxidation process proceeds in the case of the cermet at a rate increasing by more than a power of 10. Th.s result was the occasion for more careful study of the entire Mo + ZrO_2 (Fig. 7). The sensitivity to oxidation of such a material is considerably increased by the zirconium oxide content in the molybdenum. As a result of the high oxygen mobility in the zirconium oxide grid, the deposit can be considered equally as roughening the molybdenum surface and also increasing the reaction surface. Only in the range of formation of an oxide grid by about 15 percent by volume is this effect weakened through bridge formation.

At 80 percent by volume, the molybdenum grid is destroyed and the ZrO_2 encompasses the molybdenum deposits. At the same point, the boundary surface is also reduced between Mo + ZrO_2, with further increases of ZrO_2 substantially, so that a clear steep drop occurs, above all at the curve for weight increase as a function of the molybdenum surface (a' the cut sample).

2.2. Oxidation above the Melting Point of Molybdenum Trioxide

While the intake of oxygen through oxidation was measured simply by determination of the weight after various oxidation times up to 600° C, a completely erroneous picture is obtained in a simple representation of the oxidation behavior through testing the change in weight with further temperature increase up to the melting point of molybdenum trioxide, because the increase in weight through formation of MoO_3 is accompanied with increasing temperature to an increasing extent by a weight reduction caused by the evaporation of MoO_3.

Above the melting point of MoO_3, e.g. between 800° C and /5
900° C, the oxidation of Mo + ZrO_2 cermet can again be characterized well by a representation of the loss in mass over time and temperature (Fig. 8). These experiments were carried out with the high-temperature experimental arrangement as was employed for molybdenum over 800° C. In contrast to oxidation, essentially below the melting point of MoO_3, the oxidation of Mo + ZrO_2 cermet does not follow a linear course as is the case for molybdenum, but a parabolic ΔG-time relationship. It would be incorrect, however, to conclude that the oxidation almost comes to a standstill with increasing time. The curve of the loss in mass over time represents instead a result from the increase in weight through inner oxidation and decrease in weight through MoO_3 evaporation. Inner oxidation is understood as the oxidation of Mo over the ZrO_2 grid, preceding the growing scale layer in the depth of the material. At the beginning of oxidation, inner oxidation plays almost no role. With increasing time of oxidation and formation of a scale layer increasing in time, the rate of evaporation of MoO_3 drops. The reason lies in the construction of a diffusion barrier, first for the oxygen itself into the material through the scale layer and secondly for the MoO_3, leaving the material through the scale layer. In practical situations this is expressed such that the MoO_3 evaporation rate decreases by about two powers of 10 after only a few minutes. If the oxidation temperature is increase to above 1000° C in the range of 1100 to 1200° C, the oxidation converts from the parabolic characteristic to a linear ΔG-time relationship. I designate this temperature range as the area of catastrophic oxidation of Mo + ZrO_2 cermet.

The cause for this strange shape in the course of oxidation /6
as a function of temerature may lie in the great increase of MoO_3

vapor pressure in this temperature range. The MoO_3 vapor pressure achieves 760 mm Hg at 1155° C (Fig. 9).

Above 1300° C, the course of oxidation already discussed in the temperature range between 800 and 1000° C is observed. Above approximately 1300° C a liquid oxide surface layer is formed during observation, characterized by an increase of ZrO_2 at the surface to the reaction atmosphere, i.e. air.

The next figure shows a range of pure molybdenum to pure ZrO_2 in the temperature range discussed above. The figure presents four clear areas in a rough observation. The oxidation of molybdenum in this high temperature range is substantially decreased by the addition of small amounts of ZrO_2. This can be easily explained because even with a small amount of ZrO_2, the ZrO_2 is increased at the surface because of evaporation of the molybdenum trioxide. This is hardly altered with further increase of ZrO_2. Only with a 40 percent by volume of ZrO_2 and more will the strong oxide grid have an effect on the formation of the scale layer, i.e. the zirconium oxide determines the formation of the scale layer, at least over a certain period of time. Above 60 percent by volume of ZrO_2, the oxidation is characterized by a transition range from weight decrease to weight increase and finally in the range of the ZrO_2, having molybdenum present only as enclosed particles, that is between 80 and 100 percent by volume of ZrO_2, the oxidation is exclusively characterized by an increase in weight as a result of the inner oxidation of molybdenum to MoO_2, as I assume on the basis of metallurgical study.

Finally, it is mentioned briefly that the oxidation tempera- /7 ture was always the furnace temperature, but this is only identical with the temperature of the sample surface in the range above 80 percent by volume of ZrO_2. As can be seen clearly from Fig. 11, the surface temperature increases considerably more than the furnace temperature with the molybdenum portion as a result of the strong exothermic reaction. In the case of pure molybdenum and a furnace temperature of 1300° C, for example, the surface temperature is 200° C above the oxidation temperature.

3) Summary

An attempt was made in somewhat compressed form to provide a picture of the interesting oxidation behavior of Mo + ZrO_2 cermet.

The oxidation rate of molybdenum is substantially increased below the MoO_3 melting point by zirconium oxide deposits. Above the MoO_3 melting point, the entire oxidation characteristic of the molybdenum is altered and the linear course of oxidation is converted into a parabolic Δ G-time relationship. Only in the range of 1100 to 1200° C, the so-called area of catastrophic oxidation, does the linear oxidation course reappear as in molybdenum. Nevertheless, the rate of oxidation is lower by about one power of 10 than in this same range with pure molybdenum.

The oxidation behavior of Mo + ZrO_2 cermet can be expressed simply by stating that below the MoO_3 melting point the oxidation rate of molybdenum is substantially increased by ZrO_2 deposits, while it is substantially reduced over the MoO_3 melting point by ZrO_2 deposits.

REFERENCES

[1] Truppe, M., Probleme der kontinuierlichen Messung der Badtemperatur mit Thermoelementen beim "LD"-Verfahren" [Problems of Continuous Measurement of Bath Temperature with Thermoelements in "LD" Procedures], Dissertation, Mont. Hochschule, 1968.

[2] Truppe, M., "Stahl und Eisen," 90 (1970), 1315.

[3] Rönigk, B. and H. Leibold, "Ceramic and Metal-Ceramic Materials for Extrusion Molds Subject to Heavy Wear and Tear," lecture at the Symposium on Extrusion in Frankfurt am Main, November 12 and 13, 1970.

[4] Gulbransen, E.A., Trans. Electrochem. Soc. 91 (47) 594.

[5] Lustman, B., Metal Progress 57 (1950) 629.

[6] Simnad and Spilners, Journal of Metals 7 (1955) 41.

[7] Harwood, J.J., The Metal Molybdenum, 420, 1958.

[8] Speiser R. and G. Pierre in the Science and Technology of Tungsten, Tantalum, Molybdenum, Niobium and their Alloys edited by Promisel N.E., 304, 1964.

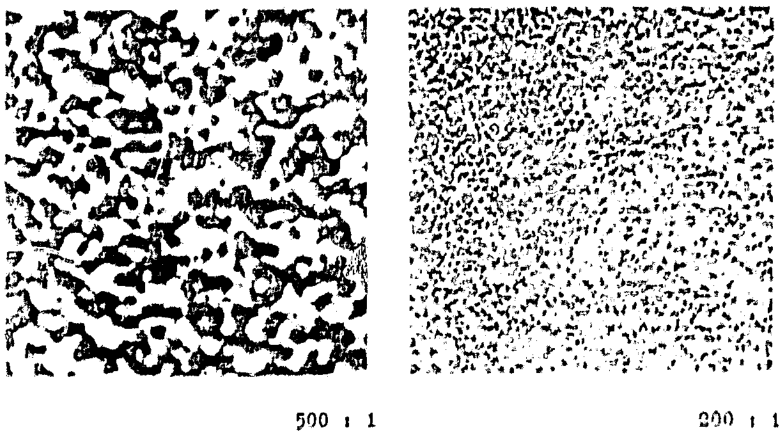

Fig. 1: Mo + ZrO_2 (60 percent by volume Mo to 40 percent by volume ZrO_2).

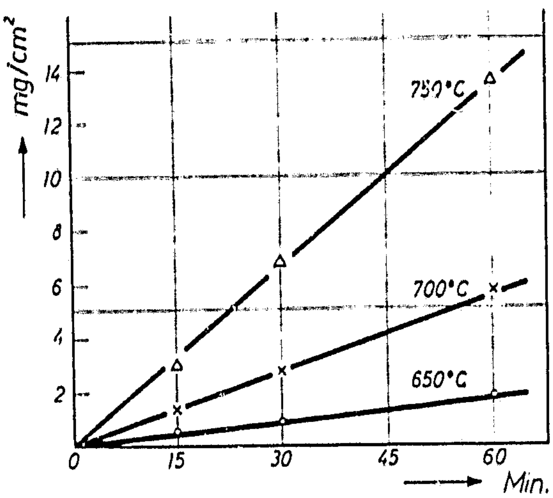

Fig. 2: Weight Loss of Molybdenum below the Melting Point of MoO_3.

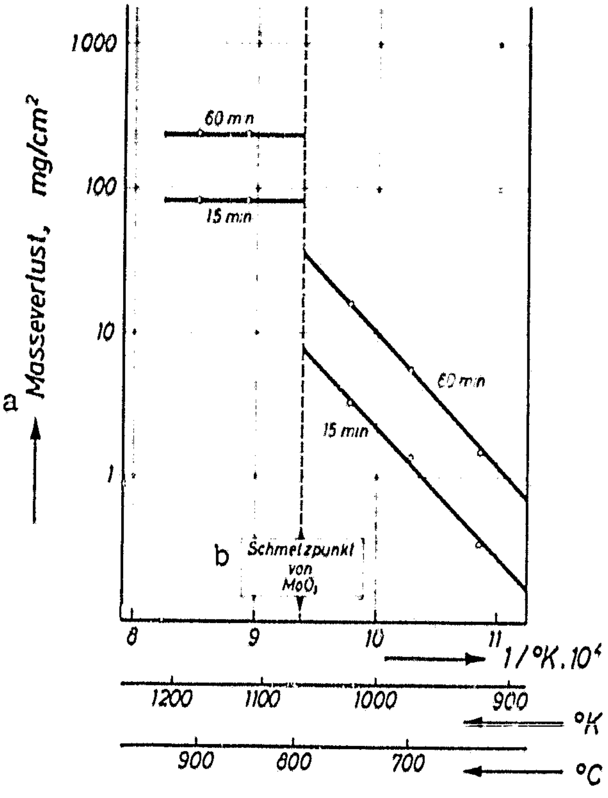

Fig. 3: Oxidation of Molybdenum in the Range of the Melting Point of MoO_3.

Key: a. loss in mass b. melting point of MoO_3

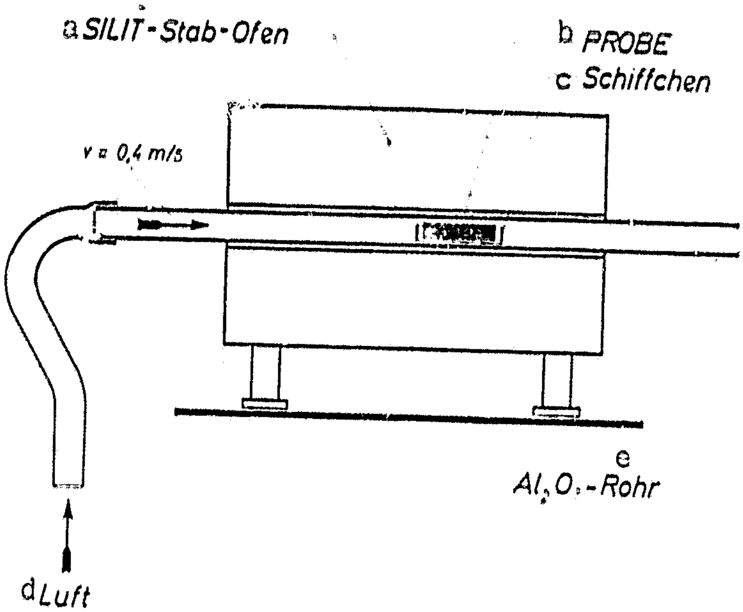

Fig. 4: Experimental Arrangement.
Key: a. silit rod furnace b. sample
c. shuttle d. air e. pipe

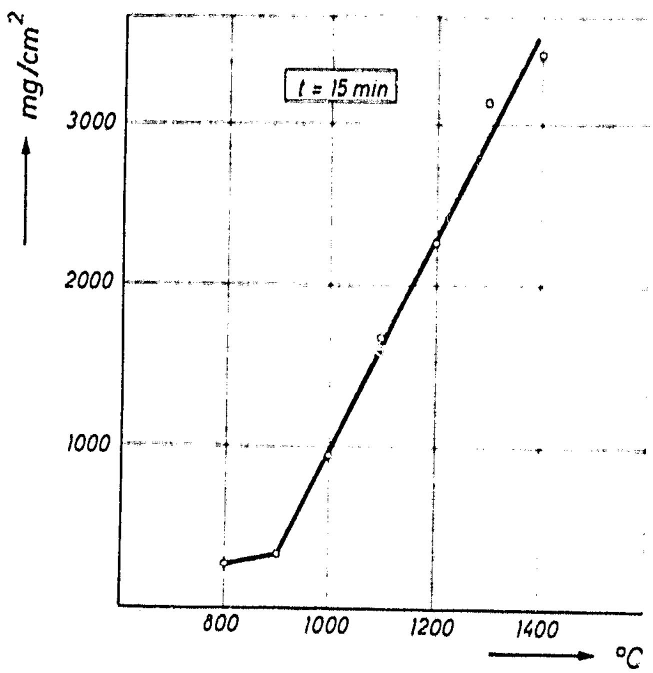

Fig. 5: Weight Loss of Molybdenum at Temperatures above the Melting Point of MoO_3.

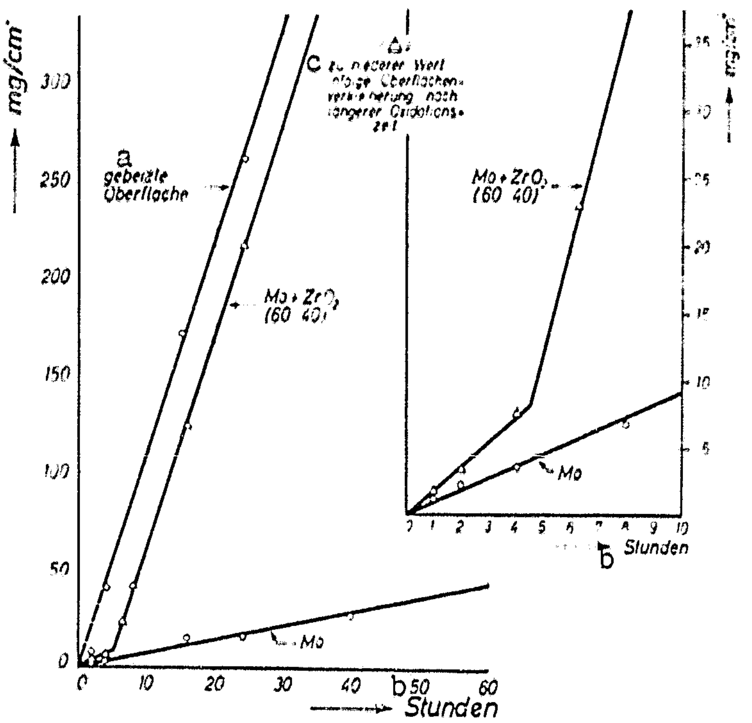

Fig. 6: Increase in Weight at 600° C for Molybdenum and Mo+zrO_3 (60 : 40).

Key: a. etched surface b. hours

c. value too low as a result of surface reduction after extended oxidation time

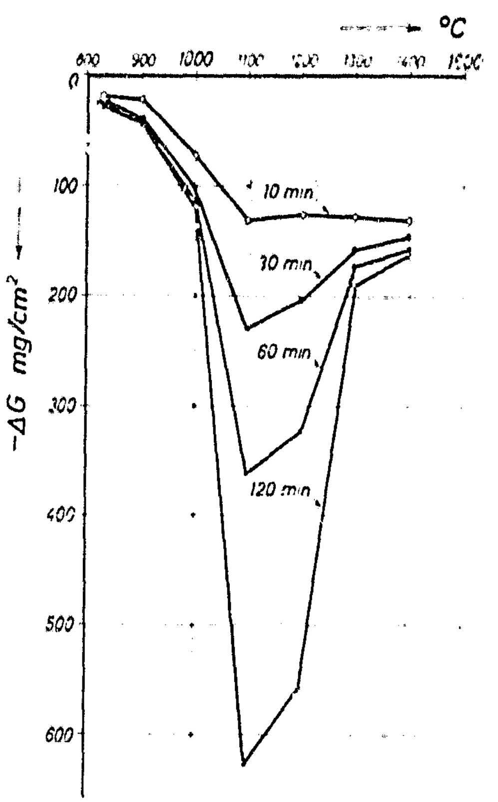

Fig. 7: Increase in Weight of Mo+ZrO_2 at 600° C (Oxidation Time of 30 hours).

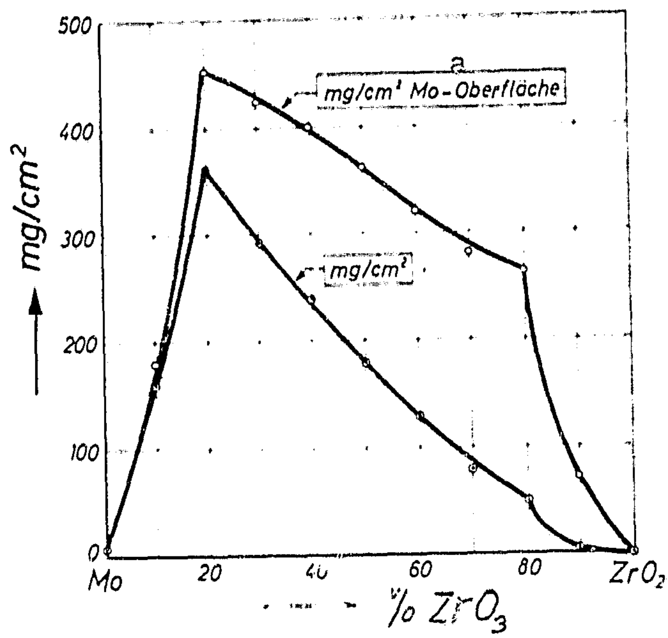

Fig. 8: Weight Change for Mo+ZrO_2 (60:40) at Temperatures over the Melting Point of MoO_3.
Key: a. surface

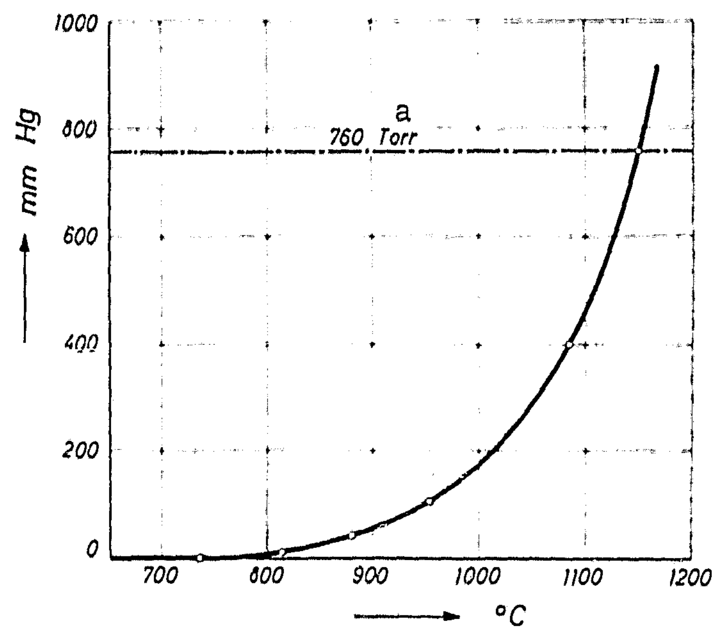

Fig. 9: Vapor Pressure Curve of MoO_3.
Key: mm Hg

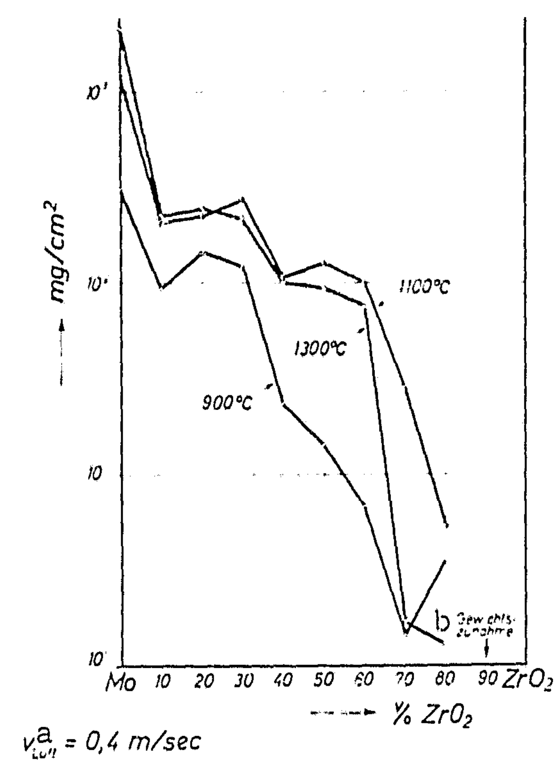

Fig. 10: Loss in Weight for $Mo+ZrO_2$ during Oxidation above the Melting Point of MoO_3 (Oxidation time 12 min.).

Key: a. air b. increase in weight

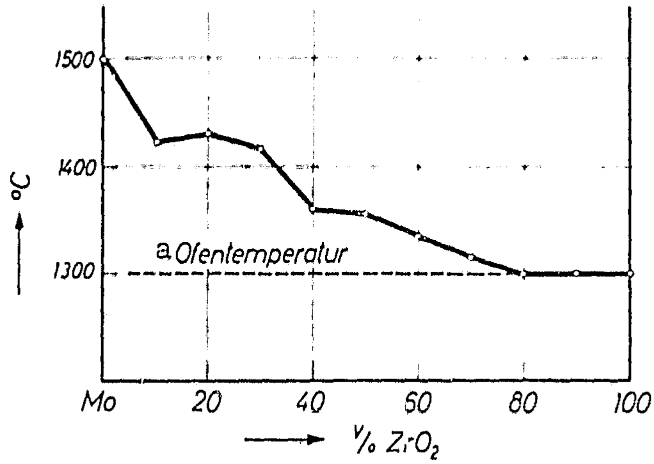

Fig. 11: Surface Temperature of Oxidizing Mo+ZrO_2 Samples.
Key: a. furnace temperature.