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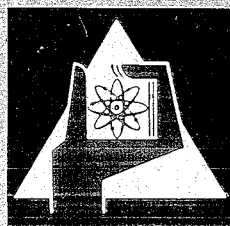
Juli 1970

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Institut für Material- und Festkörperforschung

Relations between Stereometric Microstructure and Properties
of Cermets and Porous Materials

S. Nazaré, G. Ondracek, F. Thümmeler



GESELLSCHAFT FÜR KERNFORSCHUNG M. B. H.
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RELATIONS BETWEEN STEREOMETRIC MICROSTRUCTURE AND
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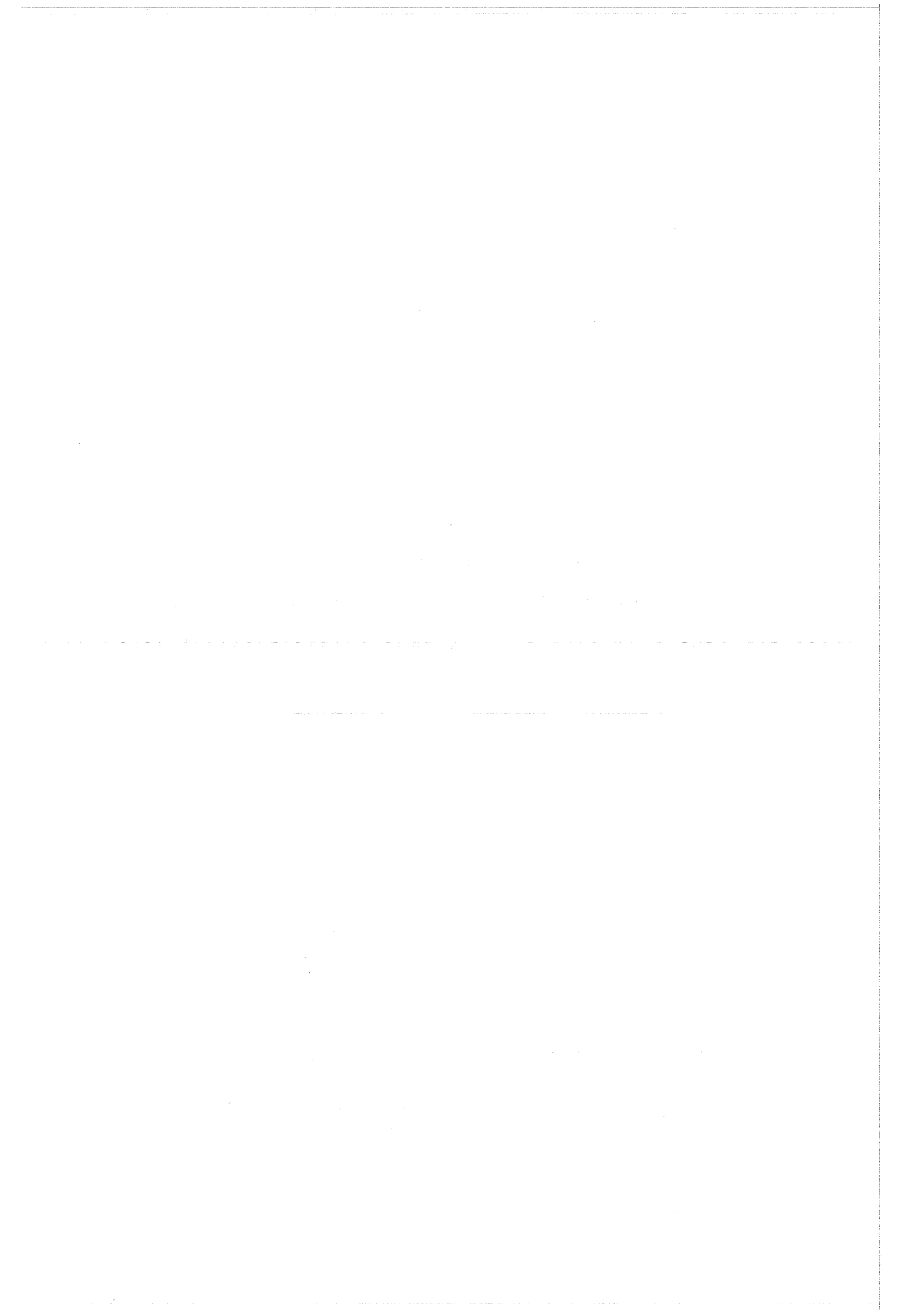
von

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<sup>+) Speaker, paper presented at the International Powder Metallurgy
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<sup>++) Work partly performed at the University of Surrey, Dept. of
Metallurgy, U.K., during a stay as a visiting
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Zusammenfassung

Die Eigenschaften eines zweiphasigen Materials können sehr stark durch die charakteristischen Parameter des Dispergenten beeinflusst werden. Dies gilt besonders für Cermets, deren Komponenten sehr unterschiedliche Eigenschaften aufweisen, weil eine Phase metallisch, die andere keramischen Charakter hat. In dieser Hinsicht sind poröse Werkstoffe, die auf pulvermetallurgischem Wege hergestellt werden, ein Sonderfall der Cermets. Daher wird in dieser Arbeit der Einfluss von verschiedenen Parametern der eingelagerten Phase auf einige Eigenschaften von Cermets allgemein behandelt.

Zunächst werden die theoretischen Beziehungen für die elektrische Leitfähigkeit von Cermets diskutiert. Andere Eigenschaften wie magnetische Permeabilität und thermische Leitfähigkeit werden auch behandelt. Diese Beziehungen können zur Abschätzung des Einflusses von Partikelgrösse, -gestalt und -verteilung des Dispergenten auf die Cermeteigenschaften benutzt werden. Im Grenzfall gelten sie auch für poröse einphasige Materialien. Die theoretischen Beziehungen werden mit den vorhandenen experimentellen Daten verglichen. Der Zusammenhang zwischen dem stereometrischen Aufbau von Cermets und porösen Werkstoffen und den genannten Eigenschaften wird diskutiert.

Abstract

The characteristic parameters of a dispersed phase in a matrix of another phase may strongly influence the properties of a two-phase material. This is especially true for cermets, which consist of a phase having often very different properties, because one phase is a ceramic, the other is a metal. In this sense, porous specimens, as achieved generally with powder metallurgical methods, are a special case of cermets. This is why the effects of several parameters of a dispersed phase in a matrix on some properties shall be considered here in a more general manner.

At first theoretical considerations are discussed for the concentration function of the electrical conductivity of cermets. Some other properties like permeability and thermal conductivity are also mentioned. The limiting cases of the equations enable us to consider the influence of pores in single phase material as well as particle shape, distribution and size of the dispersed phase on cermet properties. These considerations from a theoretical point of view are then compared with experimental results available. Conclusions are drawn about the relationship between the stereometric microstructure of cermets and porous materials and the properties mentioned.

Summary

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1. Introduction

In determining the properties of materials prepared by powder metallurgical methods, the question of porosity and its influence on the properties becomes relevant. Basically a porous material is a special case of a two phase material, in which the properties of the two phases are extremely different. Such materials are called cermets and can be defined as combinations with at least one phase with predominantly metallic and at least another with predominantly nonmetallic bonding [1]. The theoretical considerations for the concentration functions of cermets must therefore also be valid for porosity and furthermore in simplified form. The electrical conductivity and other similar properties of cermets will be considered here in relation to the concentration. The expressions shown here will be used for porous materials.

Whilst considering cermets, it is useful to differentiate between the structure as related to the materials involved, and the structure as given by the stereometric arrangement of the phases in the composite. The structure as related to the materials describes the interaction between the constituents and the bonding at the interfaces, and is dependent e.g. on the concentration and thermodynamic properties of the phases involved. Without considering this point any further, it should be noted that the following discussion is valid for stable cermet combinations. Unlike unstable cermets the components of the former do not react with one another [1]. The stereometric structure describes the geometry and the arrangement of the phases in the cermet. Its parameters are therefore independent of the material [2], and we shall consider its influence on the properties.

2. Stereometric Structure of Cermets

The density of UO_2 -Cu cermets as a function of the concentration is shown in fig. 1. It can be seen that within a certain interval,

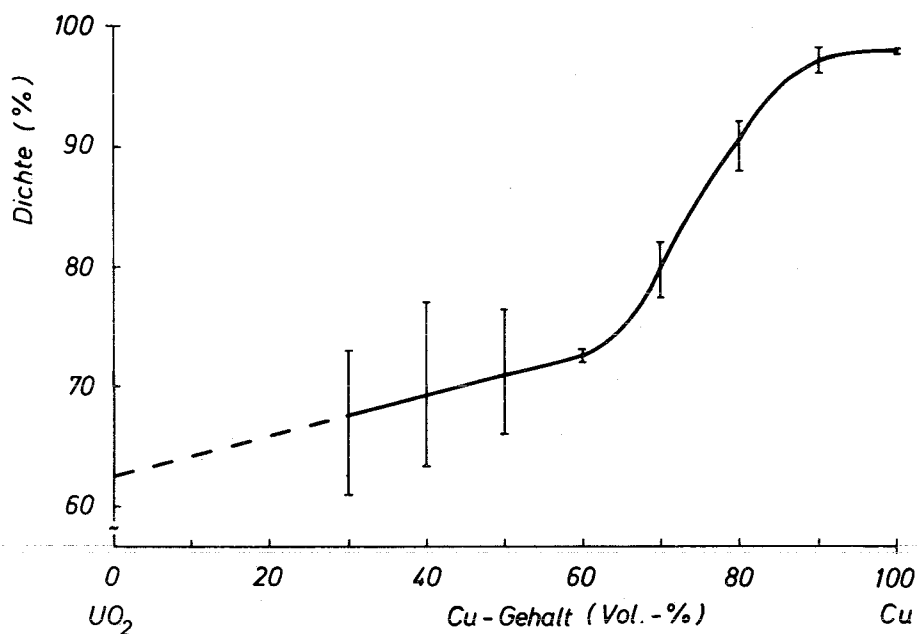


Fig. 1: Density of UO_2 -Cu cermets as a function of concentration [2]

a change in the slope of the curve takes place. A similar relationship has been found for the variation of density and other properties for various cermet combinations [3-5]. It should be mentioned, however, that in general the concentration function of the density must not show such a slope, because of their dependance of the production technique. But, nevertheless, it shows one of the first characteristics of the stereometric structure of cermets - the change in the matrix. In the case of a two phase cermet combination, there exists a region with a

metallic and a region with a ceramic matrix, i.e. the particles of one phase are separated by a continuum of the other phase, in which they are dispersed (matrix structure). With porous materials it would correspond to the case of non-interconnected porosity. The two regions with a matrix structure are separated by a region where the matrix change occurs. Here both phases are continuous. The corresponding case for porosity would be where the pores are interconnected.

The region where these two types of structures exist depends on the preparation method, on the particle size and shape of the starting powders. The particle size can be characterised as a stereometric factor by the mean particle diameter. The particle shape can be defined by using a form factor, which generally gives the deviation from a spherical shape. Particles with an irregular shape are roughly characterised through the three axis of the ellipsoid. Other stereometric factors for the matrix structure are shown in fig.2

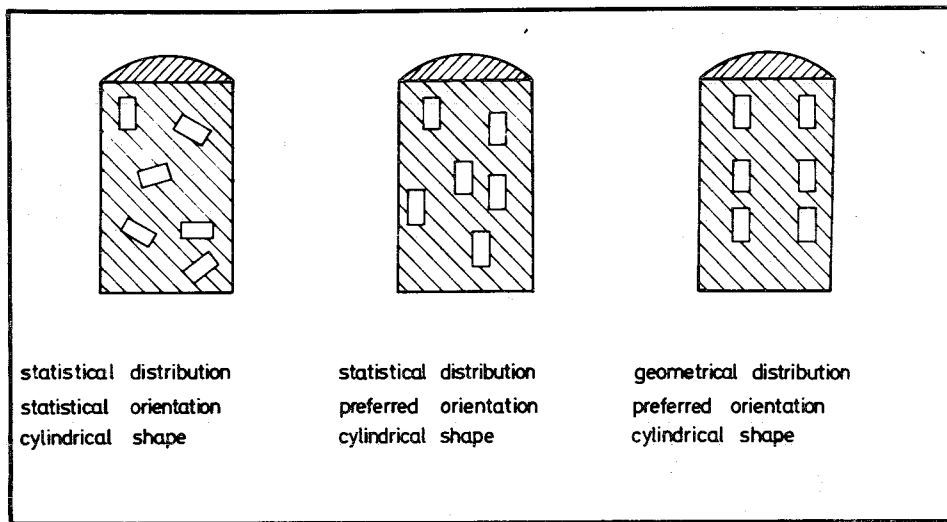


Fig.2: Stereometric factors in a cermet with a matrix structure [8]

and comprise the orientation and distribution of the dispersed phase. The orientation can be defined by means of texture parameter and the distribution through its degree [2]. When various preferred orientations exist, the distribution function of the texture parameters must be considered.

The various parameter of the stereometric structure of cermets e.g. particle shape and size, orientation and distribution can also be adapted to porous materials. Instead of the particles of the second phase we have the pores. We shall now consider in which way the stereometry influences the concentration function of the electrical resistivity of cermets and porous materials.

3. The Concentration Functions of Cermet Properties

We shall at the outset deal with variation of the electrical resistivity with concentration. A study of various existing equations for cermets [8] and porous materials [14-30, 51] shows that the following two relations are most general and have a minimum of restrictions [9]:

$$\left[\left(1 - V_K \right) \left(\frac{1}{\rho_m} - \frac{1}{\rho_c} \right) \sum_{i=x}^z \frac{\cos^2 \alpha_{im}}{\frac{1}{\rho_c} + \left(\frac{1}{\rho_m} - \frac{1}{\rho_c} \right) F_{im}} \right] + \left[V_K \left(\frac{1}{\rho_K} - \frac{1}{\rho_c} \right) \sum_{i=a}^c \frac{\cos^2 \alpha_{iK}}{\frac{1}{\rho_c} + \left(\frac{1}{\rho_K} - \frac{1}{\rho_c} \right) F_{iK}} \right] = 0 \quad (1)$$

$$\int_0^{V_D} \frac{dv}{1-v} = - \int_{\rho_M}^{\rho_C} \frac{d\rho}{\rho \left(\frac{1}{\rho_D} - \frac{1}{\rho} \right) \sum_{i=x}^z \frac{\cos^2 \alpha_{iD}}{\frac{1}{\rho} + \left(\frac{1}{\rho_D} - \frac{1}{\rho} \right) F_{iD}}} \quad (2)$$

The suffixes mean:

K = ceramic phase ; m = metallic phase ; D = dispersed phase ;
 M = matrix phase ; C = cermet ; i = x,y,z = ellipsoid axis ;
 ρ = electrical resistivity ; V = concentration of the phases
 in vol.-% ; α = angle between the axes of the ellipsoid and the
 direction of the field ; F = form factor ($F_x + F_y + F_z = 1$)

The influence of the stereometry can be seen by the fact that
 equation 1 is valid when both phases are continuous, whereas
 equation 2 holds for the case where one phase is dispersed in a
 continuous matrix of the other.

The texture factor ($\cos^2 \alpha_i$) takes into account the orientation
 of the phases to the field and the form factor (F) the particle
 shape. A factor for the size of the particles does not occur in
 these equations. Experimental data show [10,11] that particle
 size does not influence the resistivity. Whereas particle size is
 considered in the derivation of the equations, but cancels out in
 the final result, a factor for the distribution is not included
 because statistical distribution is assumed.

Since our comparison with experimental data will deal with cermets
 having a matrix structure and porous materials with non-inter-
 connected porosity, we shall restrict our discussion to equation
 2 only. This equation was originally derived for the dielectric
 constant [9] and was later adapted for the electrical resistivi-
 ty [8].

In the case of rotational ellipsoid (spheroids $x = y = z$) it
 reduces to the simpler form:

$$\int_0^{V_D} \frac{dv}{1-v} = - \int_{\rho_M}^{\rho_C} \frac{d\rho}{\rho \left[\frac{1}{\rho_D} - \frac{1}{\rho} \right] \left[\frac{\cos^2 \alpha_{xD} + \cos^2 \alpha_{yD} + \cos^2 \alpha_{zD}}{\frac{1}{\rho} + \left(\frac{1}{\rho_D} - \frac{1}{\rho} \right) F} + \frac{1}{\rho + \left(\frac{1}{\rho_D} - \frac{1}{\rho} \right) (1-2F)} \right]} \quad (3)$$

The above equations (1,2 and 3) are derived by considering that in an initially homogeneous field, a stray field is created when a very dissimilar substance is introduced. The stray field is dependent on the shape of the material, which is related to the dielectrization factor in the field equations. In our case it becomes the form factor (F). It can be calculated for the rotational ellipsoids with the following equation [6]:

$$F = \frac{x^2 z}{2} \int_0^{\infty} \frac{du}{|x^2+u|z\sqrt{z^2+u}} \quad (4)$$

and is shown in fig.3 for various ratios of the three axes. The mean axial ratio of the dispersed phase or pores can be determined

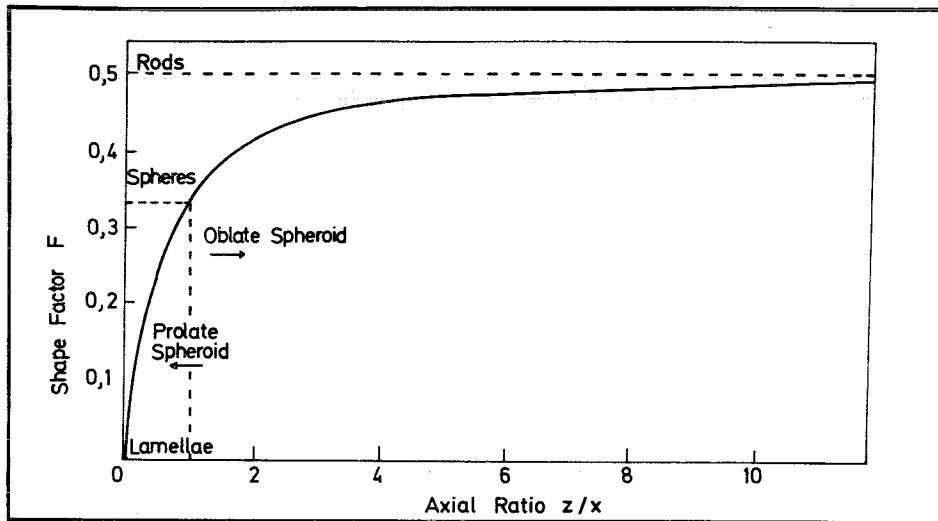


Fig. 3: Variation of the form factor for various ratios of the ellipsoid axes [6]

by metallographic procedures, and the form factor (F) can then be directly obtained from fig. 3.

The use of equation 2 which is implicit and has to be integrated is somewhat cumbersome for practical purposes. An approximate, explicit solution of this equation is however available for texture-free material. It is valid for the cases [12] where:

$$\frac{\rho_M}{\rho_D} \gg 1 \text{ and } \frac{\rho_M}{\rho_D} \ll 1$$

If the texture factor is introduced in these equations we obtain in the case of the electrical resistivity the following approximate equations for a spheroidal dispersed phase.

When $\frac{\rho_M}{\rho_D} \gg 1$ we have:

$$\rho_c = \rho_M \left(1 - v_D\right) \frac{2 \cos^2 \alpha_{xD} + \frac{\cos^2 \alpha_{zD}}{1-2F}}{F} \quad (5)$$

and when $\frac{\rho_M}{\rho_D} \ll 1$ and $\frac{\rho_C}{\rho_D} \ll 1$ we obtain:

$$\rho_c = \rho_M \left(1 - v_D\right) \frac{2 \cos^2 \alpha_{xD}}{F-1} - \frac{\cos^2 \alpha_{xD}}{2F} \quad (6)$$

Exact solutions of the general equation (eq. 3) can be obtained for the case of texture-free material (statistical distribution of the dispersed phase or pores; $\cos^2 \alpha_{iD} = \frac{1}{3}$) in three special cases:

a) spherical dispersed phase or pores [9, 13]

$$x = y = z; F = \frac{1}{3}; \cos^2 \alpha_{xD} = \cos^2 \alpha_{zD} = \frac{1}{3}$$

$$1 - v_D = \frac{\rho_c - \rho_D}{\rho_M - \rho_D} \sqrt[3]{\left(\frac{\rho_M}{\rho_c}\right)^2} \quad (7)$$

b) lamellar dispersed phase or pores [9, 13]

$$x = y \gg z; F = 0; \cos^2 \alpha_{xD} = \cos^2 \alpha_{zD} = \frac{1}{3}$$

$$\rho_c = \rho_M \frac{3 - v_D \left(1 - \frac{\rho_D}{\rho_M}\right)}{3 - v_D \left(1 - \frac{\rho_M}{\rho_D}\right)} \quad (8)$$

c) cylindrical dispersed phase or pores [9]

$$x = y \ll z; F = \frac{1}{2}; \cos^2 \alpha_{xD} = \cos^2 \alpha_{zD} = \frac{1}{3}$$

$$1 - v_D = \frac{\rho_M |\rho_c - \rho_D|}{\rho_c |\rho_M - \rho_D|} \left[\frac{\rho_c |\rho_M + 5\rho_D|}{\rho_M |\rho_c + 5\rho_D|} \right]^{\frac{2}{5}} \quad (9)$$

The implicit solutions (7 and 9) can be used in practice in the following way: The resistivity of the cermet or the porous material is calculated for various concentrations of the dispersed phase or pores by using the known values of the resistivity of the two phases.

In fig. 4 the theoretical relation is compared with the experimental values for cermets. In this particular case a single theoretical curve is justified since the conductivities of the metals considered and the ceramic UO_2 differ very much. The plotted relation represents the electrical conductivity relative to the compact matrix material. The agreement is good, when the experimental accuracy is considered. The stereometric assumptions like e.g. spherical particle shape and as a result statistical orientation of the dispersed phase were approximately fulfilled in this case. These cermets were mostly prepared by using metal coated spherical UO_2 -particles which were subsequently hot pressed isostatically. To check the validity of the stereometric effect on thermal conductivity, UO_2 -Cu-Cermets (5 vol.-% Cu) were prepared. In one case the embedded phase consisted of platelets, in the other case of cylinders. The thermal conductivity was measured at three tem-

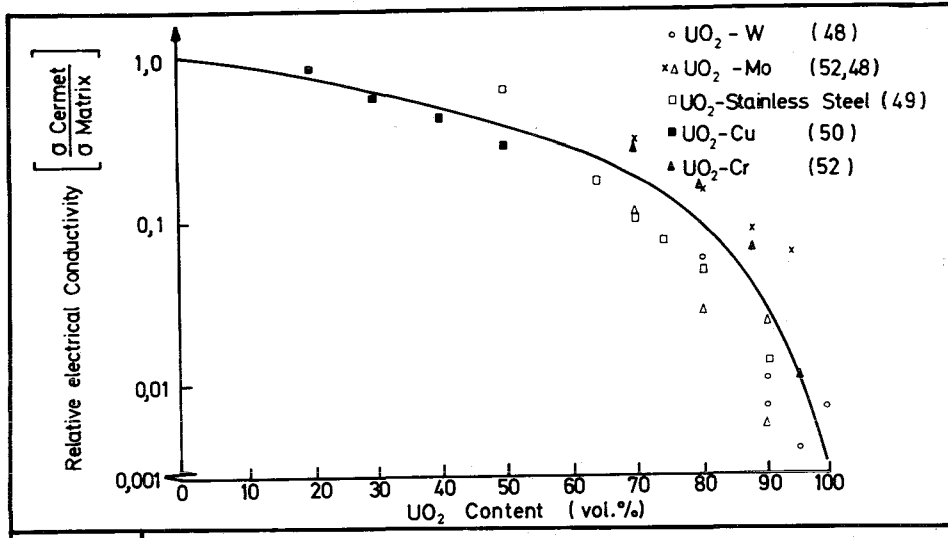


Fig. 4: Relative electrical conductivity of cermets

peratures (40, 93.75, 163°C Colora apparatus). In fig.5 the preliminary results are given. Up to now no test was done to confirm their reproducibility. But they seem to indicate, that in agreement with the theoretical analysis the conductivity of cermets strongly depends on the stereometric structure.

To show the validity of the equations discussed previously the case of spherical geometry of the inclusions shall now be considered more in detail by using porous material as an example. The theoretical relation in fig. 6 for porous materials is also calculated for spherical pores (statistical orientation). The experimental data show deviations from the theory because the

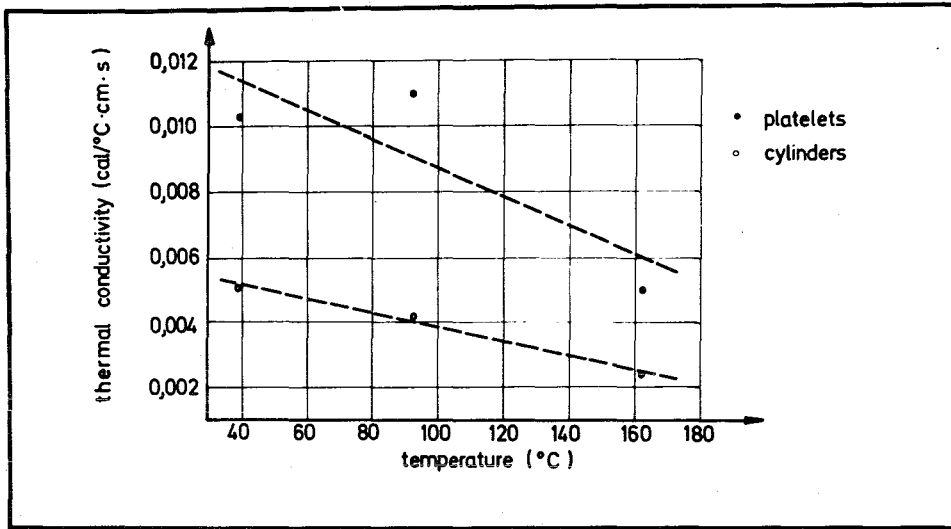


Fig.5: Preliminary results about the effect of dispersed particle shape on the thermal conductivity of UO_2 -Cu cermet (5 vol.-% Cu)

- platelets
- cylinders

stereometric structure does not fully conform with the assumption made.

Finally we shall deal in short with other cermet properties. As a result of the mathematical analogy in the relations for the electrostatic field:

$$\vec{D} = \epsilon \cdot \vec{E} \tag{10}$$

the magnetostatic field:

$$\vec{B} = \mu \cdot \vec{H} \tag{11}$$

the electric current in the steady state:

$$\vec{i} = \sigma \cdot \vec{E} = \frac{1}{\rho} \vec{E} \quad (12)$$

the heat flow in the steady state:

$$\vec{q} = -\lambda \text{grad } T \quad (13)$$

(The symbols mean:

\vec{D} = dielectric deviation; ϵ = dielectric constant; \vec{E} = electrical field strength; \vec{B} = magnetic induction; μ = magnetic permeability; H = magnetic field strength; \vec{i} = electrical current density; σ = electrical conductivity; ρ = electrical resistivity; λ = thermal conductivity; T = temperature)

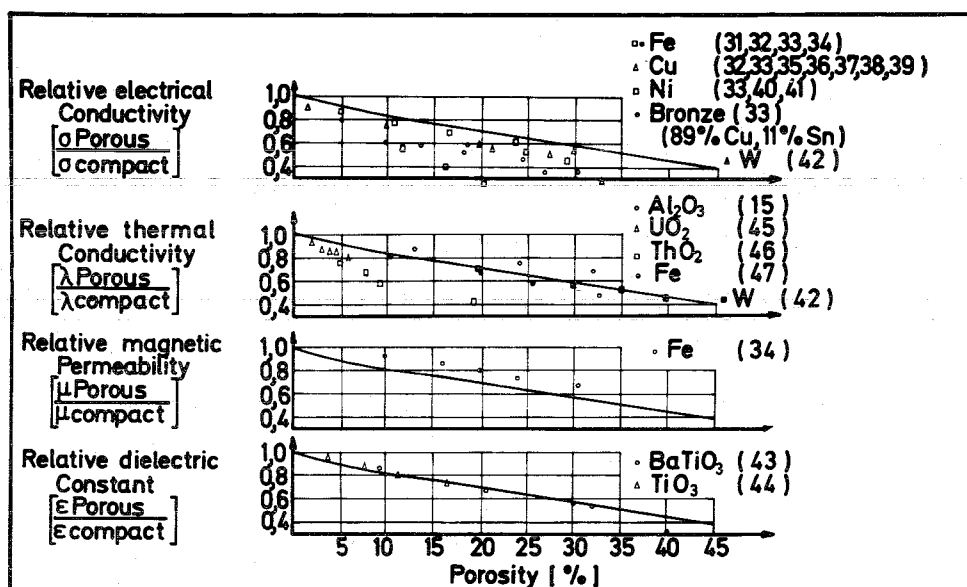


Fig.6: Relative electrical and thermal conductivity, magnetic permeability and dielectric constant of porous materials

———— theoretical curves

The relations which have been derived for the electrical resistivity can be adapted for: the thermal conductivity, the magnetic permeability, the dielectric constant.

The transformation of equation 6 for the thermal conductivity of porous materials (λ_p) yields:

$$\lambda_p = \frac{\lambda_o}{(1-P)^n} \quad (14)$$

With λ_o = thermal conductivity of the compact material

P = porosity and

$$n = \frac{2 \cos^2 \alpha_{xD}}{F - 1} - \frac{\cos^2 \alpha_{zD}}{2 F}$$

For spherical porosity ($\cos^2 \alpha_{iD} = \frac{1}{3}$; $F = \frac{1}{3}$)

we have:

$$\lambda_p = \lambda_o (1-P)^{4.5} \quad (15)$$

The above relation is similar to the simplified form of an equation derived for the thermal conductivity with a different approach [14, 15, 16]. The comparison with the available experimental data of porous materials yields again fair agreement considering the fact that the porosity in the specimens could possibly be neither spherical nor statistically oriented.

When the electrical resistivity in equation 7 is replaced by the reciprocal of the magnetic permeability we obtain the results shown also in fig.6. The same considerations are obviously valid in this case as well in the case of the dielectric constant.

The equations considered above are therefore well suited to explain experimental data, by taking into account stereometric factors like particle or pore shape and orientation. For this purpose the stereometric structure must be known as well as the properties of the pure phases. The validity of the equations restricted to the case where the distribution is statistical. Furthermore they are

only valid for stable cermet combinations and isotropic phases. They do not take into account the degree of bonding at the interfaces.

Acknowledgement: The authors would like to thank Mr. E.von Staden for supplying some of the literature data. Thanks are also due to Miss B.Schulz for her cooperation.

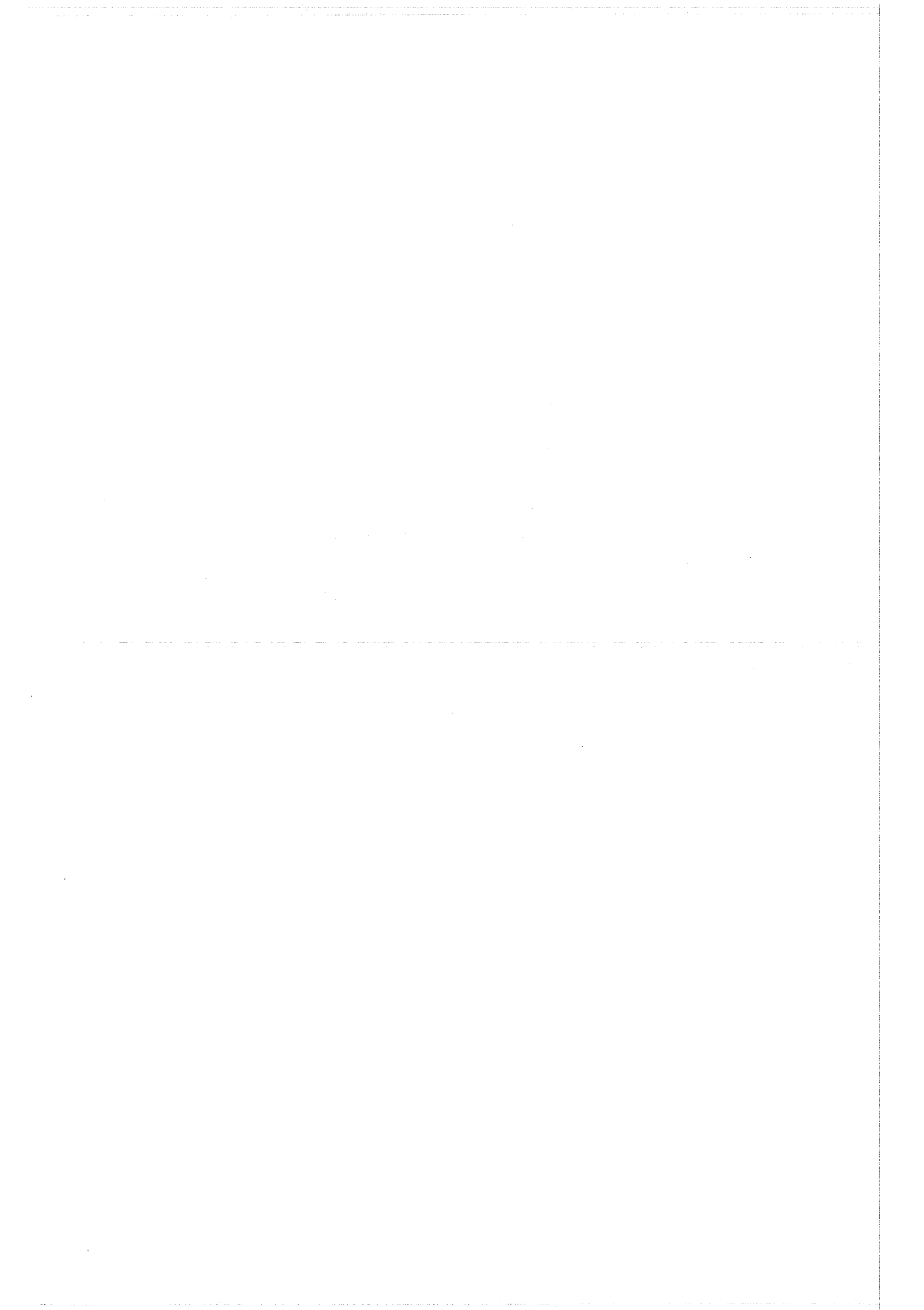
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Supplement: It should be mentioned, that the simplified equations 5 und 6 only apply for the presupposition, that the conductivity of one phase can be neglected compared with the one of the other phase. In the case of pores this is true at all temperatures for the electrical conductivity, but not so for the thermal conductivity. The thermal conductivity of pores may become essential at higher temperatures because of the heat transfer by radiation. In this case the exact equations 1, 2, 3 or 7, 8, 9 have to be used inserting that thermal conductivity for the second phase, which the pores actually have by radiation heat transfer.



Corrections to

S.Nazaré, G.Ondracek, F.Thümmler

"Relations between Stereometric Microstructure and Properties
of Cermets and Porous Materials" (KFK 1236, 1970)

1) In equation 1, second term it has to be

$$\begin{array}{ccc} z & & c \\ \Sigma & \text{instead of} & \Sigma \\ i=x & & i=a \end{array}$$

2) In equation 5, exponent, it has to be

$$\frac{\cos^2 \alpha_{xD} + \cos^2 \alpha_{yD}}{F} \quad \text{instead of} \quad \frac{2 \cos^2 \alpha_{xD}}{F}$$

3) In equation 6, exponent, it has to be

$$\frac{\cos^2 \alpha_{xD} + \cos^2 \alpha_{yD}}{F - 1} - \frac{\cos^2 \alpha_{zD}}{2F}$$

instead of $\frac{2 \cos^2 \alpha_{xD}}{F - 1} - \frac{\cos^2 \alpha_{xD}}{2F}$

4) in equation 8, the factor 2 has to be inserted:

$$\rho_C = \rho_M \frac{3 - V_D \left(1 - \frac{\rho_D}{\rho_M} \right)}{3 - \underset{\uparrow}{2V_D} \left(1 - \frac{\rho_M}{\rho_D} \right)}$$

