

KfK 4296
Juli 1987

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THE INFLUENCE OF EUTECTIC COMPOSITIONS ON THE SINTERING
TEMPERATURE OF ALUMINA-TITANIA CERAMICS

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Kernforschungszentrum Karlsruhe GmbH
Postfach 3640, 7500 Karlsruhe 1

ISSN 0303-4003

DER EINFLUß EUTEKTISCHER ZUSAMMENSETZUNGEN AUF DIE SINTERTEMPERATUR VON Al_2O_3 - TiO_2 -KERAMIK

Zusammenfassung

An Al_2O_3 - TiO_2 -Eutektika wird untersucht, ob und in welchem Ausmaß sich eutektische Mischungen sinterfördernd im Vergleich mit den Komponenten auswirken. Es wurden sowohl dilatometrische wie Dichte-Messungen durchgeführt. In allen eutektischen Zusammensetzungen beginnt der Schrumpfungsprozeß - wie bei den reinen Komponenten - bei etwa zwei Drittel der eutektischen Temperatur, führt aber in der Regel zu höheren Enddichten als bei den reinen Komponenten.

Die Untersuchungen wurden im Rahmen der zentral koordinierten internationalen Zusammenarbeit zwischen Jugoslawien und Deutschland durchgeführt.

The Influence of Eutectic Compositions on the Sintering Temperature of Alumina-Titania Ceramics

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The effect of sintering aids on the sintering temperature of two eutectic alumina-titania ceramics with different compositions is studied in comparison with their pure components. High purity alumina and titania powders are used to obtain starting temperatures of sintering with dilatometric and density measurements. Sintering of Al_2O_3 - TiO_2 -pellets starts at 0.61 of eutectic temperatures in K, and their densification behaviour is improved compared to the pure components.

1. Introduction

The world energy crisis, which started in the early seventies, especially burdened all branches of the ceramic industry. Brick, glass, cement, tile and refractory producers had to solve a huge number of plant problems connected with energy consumption. The sevenfold price increase of crude oil has had a devastating impact on hundreds of ceramic producers [1].

Bearing in mind the energy consumption in a ceramic plant [2], i.e. with 70 % of total energy use being dedicated to drying and sintering, it appears to be very attractive to reduce the firing temperatures to achieve substantial energy savings [3]. The numerous scientific approaches to altering the basic sintering route and to permitting the reduction of sintering temperature/time while maintaining and/or improving product characteristics directly coincide with this line. Taking into account but modifying an earlier proposal [4], this could be done in the following manners:

- Optimizing process conditions via correlation between sintering temperature/time, pressure and atmosphere and/or introducing procedures of hot pressing and hot isostatic pressing
- Change of powders by
 - either mechanical measures (deformation, particle size modification)
 - or thermochemical treatment (sintering aids, prealloying, providing short circuit diffusion paths through second phases as liquid phase or activated sintering).

The present work has been focussed on the role of sintering aids and attempts to explain their effect on the sintering temperature on the basis of the phase diagram.

Considering phase diagram of two components that are mutually insoluble in each other, the first question would be, whether an eutectic composition of the components lowers its sintering temperature in the same relation to the eutectic temperature as the components are related to their melting points. With respect to the

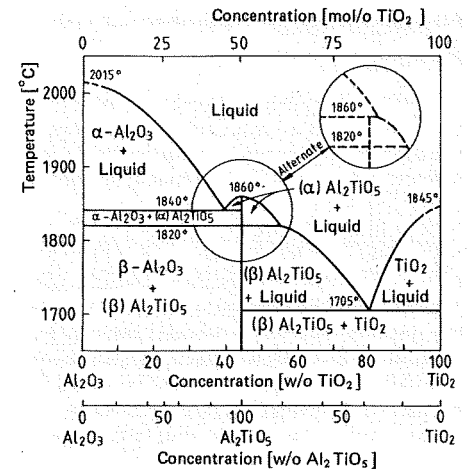


Fig. 1: Al_2O_3 - TiO_2 phase diagram [11, 12]

free energy of the sintered eutectic materials ($\Delta G_{\alpha\beta}$), which is additively composed by the free energies of its phases (ΔG_{α} , ΔG_{β}) and the free energies of its interfaces (grain boundaries: $\Delta G_{\alpha\alpha}^{\text{if}}$, $\Delta G_{\alpha\beta}^{\text{if}}$, phase boundary: $\Delta G_{\beta\beta}^{\text{if}}$)

$$\Delta G_{\alpha\beta} = \Delta G_{\alpha} + \Delta G_{\beta} + \Delta G_{\alpha\alpha}^{\text{if}} + \Delta G_{\beta\beta}^{\text{if}} + \Delta G_{\alpha\beta}^{\text{if}} \quad (1)$$

where usually holds

$$\Delta G_{\alpha\beta}^{\text{if}} \ll \Delta G_{\alpha} \quad (2)$$

for the phase boundary term ($\Delta G_{\alpha\beta}^{\text{if}}$), equ. 2 in the present case of an intimate eutectic mixture of α and β phases [6] should not be valid. If so, the phase boundary energy could play a key role in the case of eutectic mixtures sintering at considerably lower temperature than the components. There are two ways to investigate quantitatively the interface energy of phase boundaries [7] as well as their configuration: one is stereological microstructural analysis [8], and the other is measurement of heat of fusions. — At first, however the more practical aspect of sintering aids will be studied here, which concerns experimental data on the comparison between the sintering temperatures of eutectic compositions and their pure components.

Table 1: Powder characteristics

characteristics	TiO_2	Al_2O_3	premolten eutectic II (VR3)
X-ray structure	rutile	corundum	Al_2TiO_5 + rutile
surface area (m^2/g)	3.6	1.2	3.5
particle dia (μm)	0.4	2.3	0.4
green density (g/cm^3)	2.31	2.00	2.54

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Der Einfluß eutektischer Zusammensetzungen auf die Sintertemperatur von Aluminiumoxid-Titanoxid-Keramiken

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Der Einfluß von Sinterhilfen auf die Sintertemperatur von zwei eutektischen Al_2O_3 - TiO_2 -Keramiken unterschiedlicher Zusammensetzung wird im Vergleich zu den reinen Komponenten untersucht. Reinste Aluminiumoxid- und Titanoxidpulver werden verwendet um Sinterstarttemperaturen mit dilatometrischen und Dichtemessungen zu gewinnen. Das Sintern von Al_2O_3 - TiO_2 -Pellets beginnt bei 0,61 der eutektischen Temperatur in K und ihr Verdichtungsverhalten ist dem der reinen Komponenten überlegen.

Table 2: Pellet compositions and green densities

sample	alumina, wt. %	titania, wt. %	composition corresponds to:	prepared by:	green density g/cm ³
VR-1	61.46	38.54	eutectic I	mixing	2.07
VR-2	20.33	79.67	eutectic II	mixing	2.23
VR-3	20.33	79.67	eutectic II	premelting	2.54

2. Experimental work

The present experimental work was done with eutectics existing in the alumina titania system [5] which shows one single compound of equimolar Al₂O₃/TiO₂ ratio, two eutectics having alumina: titania molar ratios of 5 : 4 (eutectic I) and 1 : 5 (eutectic II), and no solid solubilities in the limiting regions, as shown in fig. 1. In order to follow the changes of starting temperature of sintering high purity, (reagent grade) titania and alumina powders were used in the experimental work. The structural characteristics of the used powders are given in table 1. Powders mixtures corresponding to the eutectics I and II were prepared in ethyl alcohol while eutectic II VR-3 was molten in an induction furnace and milled to produce fine powder [5] (table 2).

For sintering experiments the pellets of different geometries were cold pressed at 110 MPa.

The shrinkage curves obtained by dilatometric measurements are shown in fig. 2. As demonstrated in Table 3, shrinkage of all samples was noticed at the temperatures of about two thirds of eutectic temperature, i.e. of the melting points.

To compensate for measuring uncertainties, which are unavoidable if dynamic procedures like dilatometry are used, a series of more orthodox sintering tests were also conducted.

The green pellets obtained from pure and mixed powders were sintered in air as before at various temperatures. The heating rate was 300 °C/h, the cooling rate 250 °C/h, and the time at maximum temperature was 3 hours.

In fig. 3 the densities of the eutectic compositions at different sintering temperatures are compared with those of the pure components (Al₂O₃, TiO₂). In fig. 4 the density increase in comparison with green pellets is shown for the investigated samples. Considering the differential increase of sintered sample density intercepts of extrapolated curves with temperature axis, the temperatures of sintering starts are determined and given in Table 3 confirm that sinter $\sim \frac{2}{3} T_{\text{eutectic}}$ or T_{mp} [K].

Since the densities of Al₂O₃ ($\rho_{\text{th}} = 3.99 \text{ g/cm}^3$), Al₂TiO₅ ($\rho_{\text{th}} = 3.71 \text{ g/cm}^3$) and TiO₂ ($\rho_{\text{th}} = 4.26 \text{ g/cm}^3$) [13, 14, 15] are known, one can recalculate the eutectic compositions in fig. 1 in terms of volume percent.

$$\text{vol. \% } (\alpha) = \frac{100}{1 + \frac{\text{weight \% } (\beta) \times \rho_{\text{th}} (\alpha)}{\text{weight \% } (\alpha) \times \rho_{\text{th}} (\beta)}} \quad (3)$$

The calculation results in

92.6 Vol.% Al₂TiO₅ and 7.4 Vol.% Al₂O₃ for eutectic I: sample VR1
42.5 Vol.% Al₂TiO₅ and 57.5 Vol.% TiO₂ for eutectic II: samples

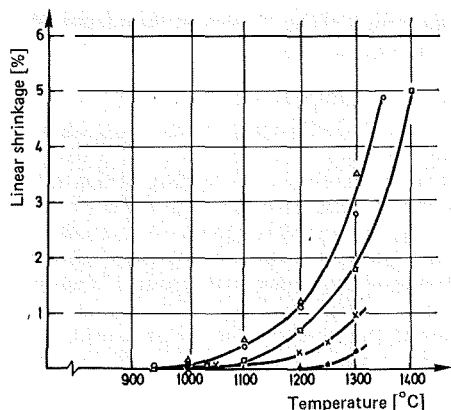


Fig. 2: Shrinkage curves of alumina-titania powders. (dilatometric measurements)
sample VR-1 □ sample TiO₂ ×
sample VR-2 △ sample Al₂O₃ ●
sample VR-3 ○

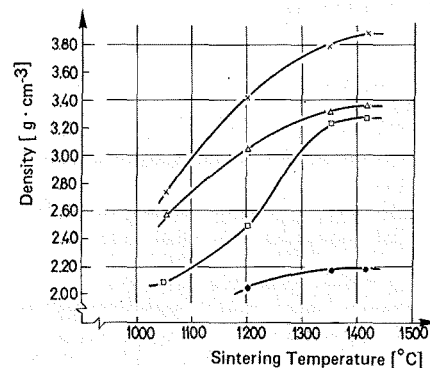


Fig. 3: Sintering density versus sintering temperature
sample VR-1 □ sample TiO₂ ×
sample VR-2 △ sample Al₂O₃ ●

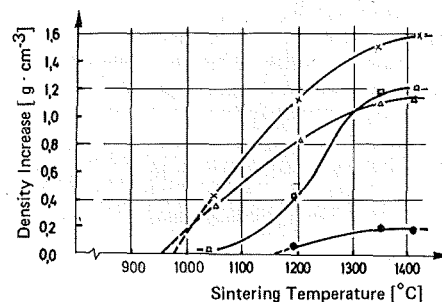


Fig. 4: Sintering density increase in comparison with green pellet density ("densification")
sample VR-1 □ sample TiO₂ ×
sample VR-2 △ sample Al₂O₃ ●

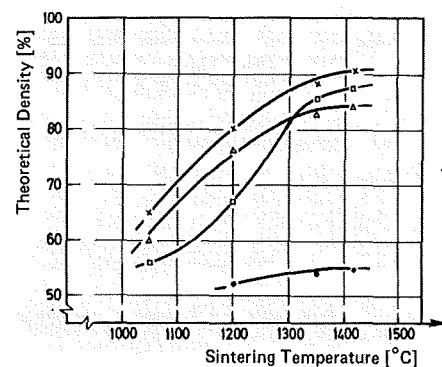


Fig. 5: Relative densities of alumina-titania obtained via sintering tests.
sample VR-1 □ sample TiO₂ ×
sample VR-2 △ sample Al₂O₃ ●

VR2, VR3.

With these quantities one can calculate the theoretical densities for those eutectics the systems of which show no limiting solid solution (cf. fig. 1):

$$\rho (\text{eutectic}) = (\text{Vol.}\%)_{\alpha} \cdot \rho_{\alpha} + (\text{Vol.}\%)_{\beta} P_{\beta} \quad (4)$$

Hence the theoretical densities of the present eutectics follow as:

$$\rho (\text{eutectic I}) \text{ VR1} = 3.73 \text{ g/cm}^3$$

$$\rho (\text{eutectic II}) \text{ VR1/VR2} = 4.02 \text{ g/cm}^3$$

With them, the densities in fig. 3 may be transformed into those related to the respective theoretical densities of each material. In fig. 5 the related densities are plotted versus the sintering temperatures. From fig. 2 and fig. 5, the following preliminary but major conclusions may be drawn:

3. Conclusions

- 1) Sintering of Al_2O_3 - TiO_2 -pellets, either from simple powder mixtures of the components or produced by premolten and milled material, starts at $\sim \frac{2}{3}$ of eutectic temperature [K] or melting point [K].
- 2) The densification behaviour of the Al_2O_3 - TiO_2 -eutectics is much improved compared to Al_2O_3 and is at least comparable to or even better than that of TiO_2 at elevated sintering temperatures.
- 3) The results give reason to assume that the correlation between sintering aids and the respective eutectic phase diagrams makes sense for technical uses.

4. References

- [1] Stamenković, I., "Heat insulating ceramics", Workshop on thermal electrical and magnetic properties of ceramics, Soverato, Sept. 1984, Italy
- [2] Holmes, W., "Energy use and conservation in the pottery industry" Brit. Ceram. Rev., No. 7 (1979) p. 10
- [3] German, R. M., "A quantitative theory of diffusional activated sintering", Sci. Sinter. 15, No. 1 (1983) p. 27
- [4] German, R. M., Robin, "Enhanced sintering", Powder metallurgy, 28, No. 1 (1985) p. 7
- [5] Stamenković, I., G. Ondracek and M. Gašić, "Sintering behaviour of titania and alumina intermixed and premolten powders" VII German Yugoslav Meeting on Materials Sciences and Development, Karlsruhe, April 1985.
- [6] "Phase diagrams", Ed. A. M. Alper, Academic Press 1970, pp. 175, Vol. I and p. 275, Vol. II
- [7] Nikolopoulos, P., G. Ondracek, "Interfacial energies between Uranium dioxide and Liquid Metals", J. Nucl. Mat. 98 (1981) 306
- [8] Ondracek, G., "The key position of stereology in quantitative microstructure correlations of multiphase materials" ACTA STEREOLOGICA I/1 (1982) 5
- [9] Krauth, A., "Keramische Werkstoffe", Umschau 8/11 (1983) 335
- [10] Ondracek, G., Werkstoffkunde — Leitfaden für Studium und Praxis, expert-Verlag Sindelfingen-Grafenau (1979/1985)

Table 3: Starting temperatures of sintering

Sample	T_e	Dilatometric measurement		Sintering test	
	Eutectic temperature or melting point, K	T_s starting temp. of sintering, K	$\frac{T_s}{T_e}$	T_s starting temp. of sintering, K	$\frac{T_s}{T_e}$
VR-1	2133	1308	0.61	1303	0.61
VR-2	1978	1208	0.61	1228	0.62
VR-3	1978	1208	0.61	—	—
TiO_2	2118	1273	0.60	1250	0.59
Al_2O_3	2288	1473	0.64	1453	0.63

- [11] Barczak, V. J. and R. H. Insley, J. Am. Ceram. Soc. 45-3 (1962) 144
- [12] Lejns, A. M., D. Goldberg, A. Revcolevski, C. R. Acad. Sci. Sr. C 263-20 (1966) 1223
- [13] Vogel, H. U. von, W. Bubam, H. Nahme, Chemikerkalender, Springer-Verlag Berlin (1966)
- [14] "Powder diffraction file" sets 6-10, Publ. Joint Committee on powder diffraction standards 1967, p. 484
- [15] "Engineering properties of selected ceramic materials" Publ. Am. Cer. Soc., Columbus (1966) p. 5.5.4-1

Received: May 23rd, 1986

Acknowledgement

The authors gratefully appreciate various valuable comments to the manuscript given by Dr. Brigitte Schulz

DEC D 44 d: A 23
cfi/Ber. DKG 64 (1987) Nr. 5

Bestimmung der Festigkeit keramischer Bauteile aus den mechanischen Daten des Werkstoffes

Determining the strength of ceramic components on the basis of material property data

Berichterstatter / Expositor: H. A. Lindner

Teil 2 / Part 2

5. Weibullstatistische Auswertung der an den Prüfkörpern A und den Bauteilen B, C und D gemessenen Daten:

5.1 Ermittlung der Weibullparameter: $\hat{\sigma}_0$, \hat{m}

Wertet man die an den Prüfkörpern und Bauteilen bestimmten Bruchspannungen bzw. Nennbruchspannungen nach dem statistischen Verfahren: Maximum-Likelihood (MLH) aus, so erhält man die Weibullparameter $\hat{\sigma}_0$ und \hat{m} , mit denen die gemessenen Einzeldaten bestmöglich beschrieben werden können. In der Abb. 5/1 ist das Ergebnis der weibullstatistischen Auswertung der Meßdaten der AK-Gruppe 1 tabellarisch und grafisch wiedergegeben. Die Meßdaten sind zusammen mit den durch die Weibullparameter bestimmten Weibullfunktionen in der Darstellung: Bruchwahrscheinlichkeit als Funktion der Bruchspannung σ sowie in

5. Weibull-statistical evaluation of the measured data from test specimens A and components B, C and D

5.1 Determining the Weibull parameters: $\hat{\sigma}_0$, \hat{m}

The Weibull parameters $\hat{\sigma}_0$ and \hat{m} , which yield the best description of the individual measured data, can be arrived at by performing a statistical maximum-likelihood evaluation of the breaking stresses and nominal breaking stresses determined for the test specimens and components, respectively. Figure 5/1 shows the plotted results of Weibull-statistical evaluation of the tabulated measured data obtained by working-committee group 1. The measured data are shown together with the Weibull functions determined by way of the Weibull parameters: failure probability as a function of breaking stress, σ , and, in the so-called Weibull ren-

Fortsetzung aus cfi/Ber. DKG 3/4-87, S. 74 ff

DKG/DVM-Arbeitskreis „Festigkeit keramischer Werkstoffe“
(K. Berroth, H. Bretfeld, A. Brückner, H. Dannheim, W. Grellner, A. Hesse, H. Kolaska, H. A. Lindner, H. Müller, D. Munz, H. Richter, O. Rosenfelder, D. Rothermund, H. Ruf, C. Sonsino, W. Storch, H. J. Thoma)

Continuation from cfi/Ber. DKG 3/4-87, p. 74 ff.

DKG/DVM working committee "strength of ceramic components"
K. Berroth, H. Bretfeld, A. Brückner, A. Dannheim, W. Grellner, A. Hesse, H. Kolaska, H. A. Lindner, H. Müller, D. Munz, H. Richter, O. Rosenfelder, D. Rothermund, H. Ruf, C. Sonsino, W. Storch, H. J. Thoma