THE STABILITY OF SIC-BASED CERAMICS CONTAINING ZrO, AND OTHER OXIDES

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ABSTRACT. Calculations of thermochemical equilibria, using the program SOLGASMIX, have defined the conditions and compositions of SiC-based ceramics in which stable ZrO₂ particles can be obtained. The results are compared with experiments. The calculation method offers the possibility of evaluating compositions and fabrication conditions for SiC-ZrO₂ and SiC-ZrO₂-Al₂O₃-SiO₂ composites.

1. Introduction

The thermochemical behaviour of ceramic compounds is difficult to predict because of their strong interaction with the processing environment and trace impurities. In the carbide-oxide system considered here the ratio, C/O , of excess carbon to oxygen considerably affects the thermochemical equilibrium. Excess oxygen may be caused by the presence of an SiO_2 coating on the SiC powder, whereas excess carbon is normally used as a sintering additive for SiC , furthermore, carbon dies may supply carbon at high temperatures.

Different kinds of environments, including variations in furnace hot zone size and flow rates of inert gas, cause various mass losses from the solid to the gas phase. The amount of mass loss itself affects the equilibrium of the solid phases since it alters the overall composition of the remaining solid. In this paper the influence of the environment, especially of the equilibrium gas phase, will be discussed.

In complex systems (like the carbide-oxide system) computer calculations of the equilibria are helpful to select reasonable experiments and to understand the process occurring during manufacture.

Calculations are presented for thermochemical equilibria and compared with experimental results in the systems: SiC-ZrO2 and SiC-ZrO2+Al2O3-SiO2. The following aspects will be discussed:

A. The utility of the calculation of thermochemical equilibria for the Received 1 April 1983

development of ceramic materials.

B. The importance of the mass loss from the solid to the gas phase.

C. Presentation of the calculated values as function of temperature and mass

loss from the solid phases to the gas phase. D. The conditions of hot pressing $SiC-ZrO_2$ and SiC-7rO2-Al2O3-SiO2 composites without reduction of the oxides to carbides.

The composites with $2r0_2$ are of interest, because such dispersions of $2r0_2$ may yield greatly enhanced fracture toughness due to a mechanism which is based on the transformation tetragonal-monoclinic and which has already been verified with ZrO₂ dispersions in Al₂O₃ /1/ and in Si₃N₄ /2/. Fracture toughness and hardness of SiC-ZrO₂ and SiC-ZrO₂-Al₂O₃-SiO₂ composites, as developed in this investigation, are reported in /3/.

2. Calculation Method and Experimental Procedure

2.1. The Computer Program and the Presentation of the Results

For these calculations the computer program SOLGASMIX developed by Eriksson /4-6/ was used. The introduction of ionic species into this program has been described earlier /7/. For a given composition it calculates which phases are in stable equilibrium and the amounts n_i of species present, by minimizing the Gibbs free energy, given by equation (1):

$$G/RT = \sum_{i} n_{i} (G_{i}/RT + ln a_{i})$$
 (1)

= Gibbs free energy of the entire system

gas constant

temperature (Kelvin)

Gibbs free energy of formation of species i

amount of species i

activity of species i in solution index of species

To transform concentrations into activities the activity coefficients of the regular solution phases were calculated in a subroutine as described earlier /7/.

The calculation includes the elements ${ t Zr}$, ${ t Al}$, ${ t C}$, ${ t Si}$, ${ t O}$, and ${ t Ar}$ and ${ t all}$ the known compounds formed between them. The thermodynamic data were gathered from the tables of Barin and Knacke /8/ or from the JANAF-tables /9/. In table 1 the species considered are listed. The C $_{\rm p}$ -values between 1000 K and 3000 K given by the JANAF-tables were expanded into the approximation formula:

$$C_p = C + D * T + E * T^{-2} + F * T^2$$
 (2)

by a least squares calculation. The number of terms used is given in table 1. The phases $\mathrm{Zr}_4\mathrm{Al}_3$, $\mathrm{Zr}_2\mathrm{Al}_3$ and ZrAl_2 are tabulated neither by Barin and Knacke nor by the JANAF-tables. G-values at 1023 K are reported by Hultgren et al 100. To estimate the temperature dependence of G a constant specific heat of 29 J/K*mol and an entropy of formation of 1 J/K*mol at 1023 K, referred to 1 mole of atoms was assumed. These values correspond to the mean values given for the Zr-Si phases.

To reproduce approximately the melting temperatures of the Zr-Si and Zr-Al phases reported by Hansen and Anderko /11/ the Zr-Si and Zr-Al melts were described as regular solutions with the same solution parameter in both systems of -175000 J/mol. Similarly the melts of the systems Al-C, Si-C and Al-Si were described as regular solutions with the parameters -55000, -25000 and -10836 J/mol respectively.

The oxide melt is described as a solution of the ions ${\rm Zr}^{4+}$, ${\rm Al}^{3+}$, ${\rm Si}^{4+}$. The G-value of the species ${\rm O}^2$ was given the arbitrary expression:

TABLE 1
Species and Source of Data used in the Calculations.

Terms for the description of G after the formula: $G = A/T + B + C*T + D*T^2 + E*T^3 + F*T*log(T)$

Gaseous Species

species	ref.	terms	species	ref.	terms	species	ref.	terms
Ar	-	0	SiC ₂	9	A,B,C,D,F	SiO	8	A,B,C,D,E,F
Zr	9	B,C,F	SiC	9	B,C,D,F	SiO2	9	A, B, C, D, E, F
Al	8	B,C,D,F	Si ₂ C	9	A,B,C,D,F	electron	9	B,C,D,F
C	8	B,C,D,F	ZrŌ	8	B,C,D,F	Zr+	9	B,C,D,F
c ₂	8	A,B,C,D,E,F	Zr02	9	A,B,C,D,F	Al+	9	в,с,ғ
C ₃	8	A,B,C,D,E,F	Al ₂ Ō	8	A,B,C,D,E	0-	9	B,C,D,E,F
Sí	8	A,B,C,D,F	Alo	8	A,B,C,D,F	02-	9	A,B,C,D,F
Si ₂	8	A,B,C,D,E,F	A1202	8	A,B,C,D,E,F	AlO+	9	A,B,C,D,E,F
Si ₃	8	A,B,C,D,F	A102	9	A,B,C,D,E,F	A10-	9	A,B,C,D,F
0	8	B,C,F	C ₂ 0 rad.	9	A,B,C,D,E,F	A102-	9	A,B,C,D,E,F
02	8	A,B,C,D,F	cō	8	A,B,C,D,F	Al ₂ 0+	9	A,B,C,D,E,F
Alc	9	A,B,C,D,F	co ²	8	A,B,C,D,F	A1 ₂ 0 ₂ +	9	A, B, C, D, E, F

Solid Stoichiometric Phases

phase	ref.	terms	phase	ref.	terms	phase	ref.	terms
Zr(r)	8	B,C,D,F	ZrC	8	A,B,C,D,F	Zr0 ₂ (r)	8	A,B,C,D,P
Zr(h)	8	B,C,D,F	Zr ₂ Si	8	A,B,C,D,F	$2r0_{2}(h)$	8	B,C,F
Al	8	A,B,C,D,E,F	Zr ₅ Si ₃	8	A,B,C,D,F	Al ₂ 0 ₃	8	A,B,C,D,F
graphite	8	A,B,C,D,F	ZrŠi	8	A,B,C,D,F	Sio (Qu)	8	B,C,D,F
Si	8	A,B,C,D,F	ZrSi	8	A,B,C,D,F	$Si0_{2}^{-}(Cr)$	8	A,B,C,D,F
Zr ₄ Al ₃	10	B,C,F	Al ₄ C ₃	8	A,B,C,D,F	ZrSiO _A	8	B,C,F
Zr Al3	10	В,С,Е	SiČ	8	A,B,C,D,E,F	mullite	8	A,B,C,D,E,F
ZrĀl ₂	10	В,С, F						

Liquid Species

species	ref.	terms	species	ref.	terms	species	ref.	terms
2r0 ₂	8	в,с, г	Zr	8	B,C,F	C	7	B,C,F
		В,С,Е	Al	8	B,C,F	Si	8	₿,ሮ,፻
	8	В,С,Р						

G = -300000.0 + 180.0 * T - 30.0 * T * log(T) J/mol (3) The G-expressions for Zr^{4+} , Al^{3+} , and Si^{4+} were adjusted to fit the values of liquid $Zr0_2$, Al_20_3 and $Si0_2$ given by Barin and Knacke by the formula (for 3 moles of atoms of $Zr0_2$):

$$g_{Zr0_2} = g_{Zr4+} + 2 g_{02-} + RT * (log(1/3) + 2 log(2/3))$$
 (4)

Similar formulas were used for Al_2O_3 and SiO_2 respectively. The quasibinary liquid of the system Al_2O_3 - SiO_2 was described by an additional regular term, formulated as the product of the concentrations of Al_2^{2+} and Si_4^{2+} with a value of 90000 J/mol, in order to correspond with a description given earlier /7/.

The program calculates equilibrium conditions, which are not always achieved during processing. Considerable attention must be given to the fact that variations in mass loss from the solid to the gas phase may yield different compositions of the solid phases. A particular mass loss depends on processing, i. e., densification rate, particle size, gas flow. Low densification rate, coarse particles, large furnace and rapid gas flow favor high mass loss while high densification rate and high density cause a smaller mass loss. A translation of these processing conditions into thermodynamic quantities is made using argon as one gas phase component. Daltons law of partial pressures then can be written:

$$p_{\text{total}} = n_{\text{Ar}} * RT/V_{\text{gas}} + \sum_{i} p_{i}$$
 (5)

ptotal = total pressure of the system
pi = partial pressure of species i
nAr = moles of argon
Var = total volume of gas
i, R, T as in equ. (1)

At constant total pressure the variations of the amount of argon yield variations of the total gas volume. The total gas volume determines the mass loss from the solid phases to the gas phase:

$$n_i = p_i * V_{gas} / RT$$
 (6)

i.e. larger gas volume yields higher mass loss. The following strategy is used in the computer programs: The total pressure is specified and by changing the amount of argon various amounts of mass are transported from the solid to the gas phase. This corresponds to the establishment of the thermochemical equilibrium in closed furnaces of various sizes. As a rough approximation this may also be taken as a simulation of transport of mass out of the system due to open furnace, argon streams and temperature gradients between the reaction zone and the cooler outer walls.

As the presentation of the results is limited to three dimensions, the most interesting variables must be selected. Using the calculations to determine the fabrication conditions of new materials, usually the dependence of the composition of the sample on fabrication temperature is very interesting. Further the amount of mass loss influences the composition of the mixture of solid phases and has to be considered. Consequently a diagram showing the composition of the material as a function of temperature and mass loss will be a valuable instrument for rationalising the experimental procedure.

2.2. Experimental Procedure and Results

The X-ray phase analysis and specific surface areas of the powders used are listed in table 2. Mixtures of these powders were milled with Al₂O₃ balls in an attritor mill for 4 hours. Subsequently the powder mixtures were hot pressed in graphite dies of 20 mm diameter at pressures of 27.5 MPa for 60 min. Flowing argon, yielding approximately 0.1 MPa gas pressure was used as inert atmosphere.

MABLE 2
Powders Used

Powder	Manufacturer	Spec. Surface Area	Y-ray phase analysis
SiC	H.C. Starck	12 - 20 m ² /g	cubic SiC
ZrO ₂	Ugine Kuhlmann	$6 m^2/g$	monoclinic 67 %
_		own measurements $9.7 \text{ m}^2/\text{g}$	tetragonal 33 %
Hf0 ₂	Serva	milled with WC-balls $17.9 \text{ m}^2/\text{g}$	monoclinic
A1 ₂ 0 ₃	Alcoa	$8.7 \text{ m}^2/\text{g}$	
SiO ₂	Heraeus		🗙 - cristobalite

TABLE 3
Selected Experimental Results

composition / wt%	hot press. temp. / °C	X-ray phase analysis
90 SiC + 10 ZrO ₂	2250 - 2000	∝-SiC, G-SiC, ZrC, Zr ₅ Si ₃
	1900 - 1800	ß-SiC, ZrC, Zr ₅ Si ₃
70 SiC + 10 ZrO ₂ + 10 Al ₂ O ₃ + 10 SiO ₂	1950	8-SiC, Zr_5Si_3 , ZrO_2 (ca 50% remained) monocl. / tetr. = ca. 2 / 1
	1850	S-SiC, mullite, ZrO ₂ (> 90% remained) monocl. / tetr. = ca. 2 / 1
83 SiC + 15 HfO ₂ + 2 Al ₂ O ₃	1850	8-SiC, HfC, Hf5Si3
77 SiC + 15 HfO ₂ + 4 Al ₂ O ₃ + 4 SiO ₂	2000	S-SiC, HfO ₂ (monoclinic) Hf ₅ Si ₃ (trace)

Mixtures of SiC and 10 wt.-% ZrO, were hot pressed at 2250°C, which was found to be the temperature of best densification of the B- and C-doped SiC powder (98.5 - 99 % of theoretical density (th. D.)). The phase analysis, made by X-ray diffraction measurements, showed that ZrO, reacts completely to ZrC and carbon stabilized Zr $_5$ Si $_3$, even if the hot pressing time was reduced to 10 min (table 3).

The density of the hot pressed bodies decreased with lower hot pressing temperatures to less than 90 % of th. D. for temperatures below 2000°C. The phase analysis still yielded SiC, ZrC and $\rm Zr_5Si_3$, but no $\rm ZrO_2$. Various amounts of $\rm Al_2O_3$ and $\rm SiO_2$ were added to the mixture considered above in order to enhance the densification at temperatures below 2000°C and to thermochemically stabilize $\rm ZrO_2$. The detailed results are described in /12/. Additions of 10 wt.-% $\rm Al_2O_3$ and 10 wt.-% $\rm SiO_2$ respectively, were needed to get dense samples (> 98 % of th. D.) at 1850°C and to prevent the reaction:

$$ZrO_2 + 3 SiC = ZrC + 3 Si(liquid) + 2 CO(gas)$$
 (7)

From comparisons of the X-ray peak heights of the starting powders and the powdered samples (the same area was irradiated) it was concluded that more than 90 % of the starting amount of $\rm ZrO_2$ remained unreacted after hot pressing at 1800 $^{\circ}$ C. This amount decreases rapidly with increasing hot pressing temperature, as shown in table 3.

 $\rm ^{Hf0}_2$ is more stable in a reducing atmosphere than $\rm ^{Zr0}_2$. Experiments showed that an addition of 4 wt-% $\rm ^{Al}_2O_3$ and 4 wt-% $\rm ^{Si0}_2$ respectively, was enough to effect an equilibrium, where $\rm ^{SiC}$, $\rm ^{Hf0}_2$ and a small amount of $\rm ^{Hf}_5Si_3$ were present up to the hot pressing temperature of 2000 $\rm ^{C}$.

3. Discussion of the Development of the Composites

3.1. Range of Stability of SiC + ZrO2

Relatively simple thermochemical equilibrium considerations allow the construction of fig. 1, which shows that only a very restricted region of activities of Si, Zr, O and C exists, where SiC and ZrO $_2$ are stable without other phases than gas at 2250°C. In equilibrium with SiC the activities $a_{\rm Si}$ and $a_{\rm C}$ are connected by:

$$\log(a_{Si}) + \log(a_{C}) = G_{SiC}/RT$$
 (8)

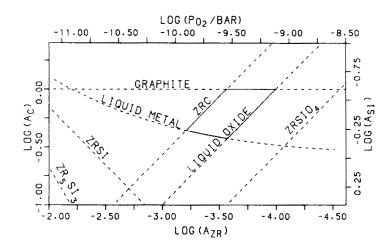
in equilibrium with ZrO2, analogously:

$$\log(a_{Zr}) + \log(p_{O_2}) = G_{ZrO_2}/RT$$
 (9)

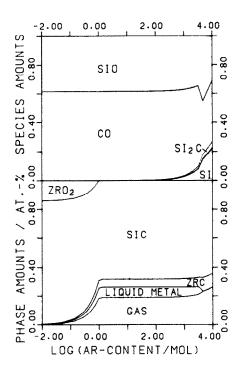
Therefore the logarithms of the activities of Si and C, respectively of Zr and O_2 , can be plotted along the same axis of the diagram but on opposite directions.

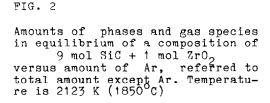
Simultaneous equilibrium with an additional phase gives another condition between activities. Therfore the 4-phase equilibria (SiC + $\rm ZrO_2$ + gas + another phase) are lines in the diagram. Such ones are straight for phases of fixed composition and curved for phases of variable composition. The full lines in fig. 1 show the stable 4-phase equilibria of SiC + $\rm ZrO_2$ + gas with graphite, ZrC, liquid metal (mainly Si) and liquid oxide (mainly SiO₂). The crossing points of these lines are found by calculating with SOLGASMIX the equilibria of compositions of nearly equal amounts of the involved 4 solid phases with a small amount of Ar. The area between the full lines is the range, where SiC + $\rm ZrO_2$ + gas exist without other phases. If the pressure is not sufficient, one of the two solid phases may disappear and react to gaseous species. Four-phase equilibria of SiC + $\rm ZrO_2$ + gas with other phases are metastable at 2523 K and given by dashed lines in fig. 1. They are found by SOLGASMIX by omitting the more stable phases from the table of G-values.

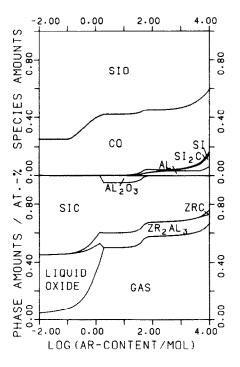
The gas pressures at 2250°C of the equilibria within the allowed range are



Stable and metastable equilibria of SiC + 7r0, with other phases at 2523 K (2250°C)







Amounts of phases and gas species in equilibrium of a composition of 7 mol SiC + 1 mol ZrO₂ + 1 mol Al₂O₃ + 1 mol²SiO₂ versus amount of Ar, referred to total amount except Ar. Temperature is 2123 K (1850°C)

FIG. 3

very high and cannot be conveniently achieved even in a hot press. shows the calculated pressures of the major constituents CO and SiO at the corners of the range of stability given in fig. 1.

Indeed, SiC-ZrO₂ samples hot pressed at 2250° C showed no remaining $7rO_2$. They showed SiC, ZrC and a third phase identified as carbon stabilized $2r_5Si_3^2$. The latter may have been formed from liquid metal Si-Zr during cooling.

At lower temperatures the total gas pressure required for equilibrium in the region where SiC and $2r0_2$ are stable without other condensed phases, are much smaller than at $2250^{\circ}C$. The values at $1850^{\circ}C$ (table 4) show a possibility for the SiC-ZrO₂ composite to be stable. Nevertheless the experimental results showed the same phases as before: SiC, ZrC and $\rm Zr_5Si_3$.

TABLE 4 Pressure of CO and SiO in the Stable Four Phase Equilibria Containing SiC and ZrO2

Temperature / OC	2250		1850		
	pressure /	bar	pressure /	bar	
Additional phases	CO	SiO	CO	SiO	
liquid metal, liquid oxide	41.5	7.3	0.9	0.7	
graphite, liquid oxide	181.4	4.4	16.1	0.3	
liquid metal, ZrC	32.1	4.1	0.5	0.2	
graphite, ZrC	110.1	2.7	6.2	0.1	

3.2. Calculations with Variable Gas Amount

The experimental result is easily understood from a thermochemical calculation simulating the mass loss from the solid phases to the gas phase, as described in section 2.1. Fig. 2 shows the mole fractions of the phases plotted against the total volume of gas, referred to the total amount except Ar, and the relative amounts of the gas species except Ar for the starting composition of 9 moles SiC and 1 mole ZrO₂ at 1850°C. ZrO₂ is stable only at low amounts of argon, which corresponds to low volumes of gas and low mass low amounts of argon, which corresponds to low volumes of gas and low mass loss from the condensed phases to the gas, or high densification rate. However, hot pressing of SiC at the relatively low temperature of 1850°C yields a very low densification rate coupled with high mass loss and the experimental conditions are located at the right hand side of the diagram in fig. 2, where ZrO is not stable. As expected, the experimental result (table 3) matches very well with calculated values of large gas volumes (10 -10 moles). Here in both cases SiC, ZrC and has given a present. In the experiments $\mathrm{Zr}_{5}\mathrm{Si}_{3}$ may be formed from this melt during cooling.

At the left hand side of fig. 2 there is a region of low mass loss, where ZrO2 is stable. This demonstrates, that a better densification behavior of SiC would yield stable Zro. Therefore additional oxides were sought to reach higher densities and prevent mass loss at hot pressing temperatures below 2000°C. These oxides must satisfy the following criteria:

1. the oxide must form a liquid phase in the temperature range between 1800-2000°C, in order to get rapid and extensive densification,

- 2. the oxide must not stabilize the cubic structure of ZrO2, otherwise the toughening effect would be lost,

3. the oxide should not yield an oxygen partial pressure so low that $2r0_2$ can not be brought into chemical equilibrium. The first two criteria will be satisfied by Al_20_3 , the second and third by $Si0_2$, so a combination of them should be an useful additive to the $SiC-Zr0_2$ composite.

Replacing two moles of SiC by one mole each of Al_2O_7 and SiO_2 in the mixture considered in fig. 2, the calculation yields the phase amounts shown in fig. 3 vs. argon content. At low volumes of gas, SiC is stable together with a liquid oxide. The ZrO_2 is totally dissolved in liquid oxide. At higher gas volumes the SiO_2 content of the liquid oxide evaporates to SiO_3 whereas the ZrO_2 content and part of the Al_2O_3 content is reduced to a Zr-Al intermetallic compound with formation of CO. The remaining Al_2O_3 content crystallizes at medium gas volumes to corundum, which evaporates at very high gas volumes.

Experimentally a smaller mass loss was observed than without ${\rm SiO_2}$ and ${\rm Al_2O_3}.$ In addition SiC, ${\rm ZrO_2},$ mullite, and a glass phase were found.

Fig. 4 shows the mole fractions of the equilibrium phases of the above mixture with one mole of argon vs. temperature in the range between 1700 and 2000°C. Lowering the temperature from 1850°C, which corresponds to fig. 3, first causes the gaseous species CO and SiO to react with the intermetallic compound forming SiC and oxide melt. On further cooling ZrO₂ and mullite crystallize from the oxide melt which disappears completely between 1770 and 1740°C. At lower temperatures an SiO₂ rich oxide melt is formed again by further condensation of SiO and CO. Above 1850°C the SiO₂ content of the liquid oxide reacts with SiC to gaseous SiO and CO leaving solid Al₂O₃. At higher temperatures there appears a metallic melt with about 80 % Si, 15 % Al and smaller amounts of Zr and C. Above 1970°C Al₂O₃ disappears and the whole oxygen content is bound to gaseous species.

Because of the uncertain thermodynamic values of the nonideal solution phase liquid oxide, the temperature of appearance of mullite and ZrO, cannot be calculated precisely. Therefore two possibilities must be considered to explain the presence of mullite and ZrO, in the samples hot pressed at 1850°C:

1. mullite and ZrO, are stable at 1850°C though the calculation does not show them

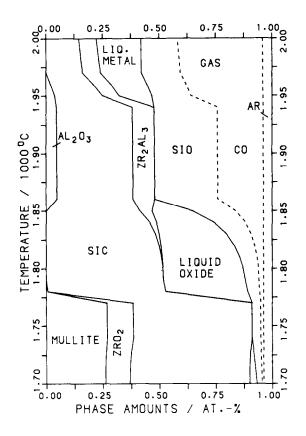
2. mullite and ZrO₂ are precipitated from the oxide melt during cooling of the sample after hot pressing. The remainig oxide melt forms a glass phase not detected by X-rays.

Fig. 4 shows $\rm Zr_2Al_3$ to be stable above $\rm 1800^{\circ}C$. Experimentally $\rm Zr_2Si_3$ and $\rm ZrC$ were found. The appearance of the intermetallic compound $\rm Zr_2Al_3$ instead of $\rm Zr_2Si_3$ in the calculation may be due to the uncertain thermodynamic data of the $\rm Zr_2Al_3$ intermetallic compounds. The appearance of $\rm ZrC$ in the calculation is strongly dependent on the ratio of excess carbon to oxygen. Excess carbon yields $\rm ZrC$ and excess oxygen favours the intermetallic compounds. In order to obtain stable $\rm SiC_2ZrO_2$ composites without intermetallic compounds or $\rm ZrC$ it can be concluded from fig. 4 that the hot pressing temperature must not be much higher than $\rm 1800^{\circ}C$, if $\rm SiO_2$ and $\rm Al_2O_3$ are present.

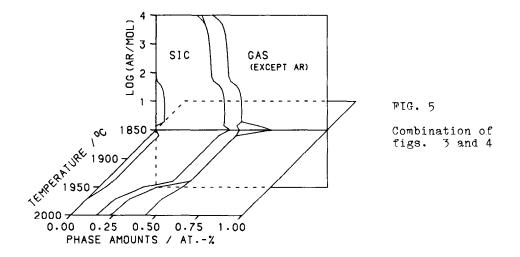
This $SiC-ZrO_2$ composite with small amounts of mullite and glass satisfies the goals expressed in the introduction.

4. Conclusions

Calculated results, presented as the dependence of equilibrium phases on temperature and mass loss to the gas phase, as indicated by fig. 5, are a powerful tool for the development of new ceramic materials, especially in very complex systems. The calculations help the selection reasonable experiments and the understanding of the process occurring during manufacture. In the particular case of the ${\rm SiC-ZrO_2}$ composites these calculations have led to the development of ceramics that show greatly enhanced fracture toughness in comparison to other SiC based materials.



Amounts of phases and gas species in equilibrium of a composition of 7 mol SiC + 1 mol $\frac{7}{2}$ + 1 mol $\frac{1}{2}$ versus temperature, referred to total amount



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