

Thermal Conductivity of SiC–AlN Ceramic Materials

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Abstract

The thermal conductivity of monophased and multiphased SiC–AlN materials was measured at room temperature. Thermal resistance of monophased 2H solid solution samples was studied in the whole range of SiC content. Comparisons of thermal conductivities of four different samples with 10, 30, 50 and 75 wt% SiC according to the hot-pressing cycles (temperatures and soaking times) were undertaken. A minimal value of $40 \text{ W m}^{-1} \text{ K}^{-1}$ was obtained for the monophased equimolar composition when sintering was carried out at 2150°C for 45 min. A maximal value of $73 \text{ W m}^{-1} \text{ K}^{-1}$ was reached for the two compounds with 50 and 75 wt% SiC when the sintering temperature was lower than 2150°C . Thermal behavior was correlated with the formation of SiC polytypes and with the phase transformations.

Die Wärmeleitfähigkeit einphasiger und mehrphasiger SiC–AlN-Werkstoffe wurde bei Raumtemperatur gemessen. Die Wärmeleitfähigkeitsmessungen einphasiger 2H-Mischkristallproben wurden über den gesamten Variationsbereich des SiC-Anteils gemessen. Die Wärmeleitfähigkeit vier verschiedener Proben mit 10, 30, 50 und 75 Gew.% SiC wurde zu den Heipreparametern (Temperatur und Haltezeit) in Bezug gesetzt. Fr die einphasige äquimolare Zusammensetzung ergab sich bei einer Sintertemperatur von 2150°C und bei einer Haltezeit von 45 min ein minimaler Wert von $40 \text{ W m}^{-1} \text{ K}^{-1}$. Fr die zwei Verbindungen mit 50 und 75 Gew.% SiC konnte bei einer Sintertemperatur von weniger als 2150°C ein maximaler Wert von $73 \text{ W m}^{-1} \text{ K}^{-1}$ erreicht werden. Die Wärmeleitfähigkeit konnte mit der Bildung von SiC-Polytypen und mit Phasenumwandlungen korreliert werden.

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La conduction thermique des matériaux à base de SiC et d'AlN se présentant sous forme de solution solide 2H ou polyphasés a été mesurée à température ambiante. La conduction thermique des matériaux monophasés 2H a été étudiée en fonction de la teneur initiale en carbure de silicium dans le mélange SiC–AlN. Les valeurs de conduction thermique de quatre échantillons à teneurs différentes en SiC en fonction des paramètres de compression à chaud ont été comparées. Une valeur minimale de $40 \text{ W m}^{-1} \text{ K}^{-1}$ a été observée pour la composition équimolaire se présentant sous forme de solution solide 2H et obtenue par compression à chaud à 2150°C pendant 45 min. Une valeur maximale de $73 \text{ W m}^{-1} \text{ K}^{-1}$ a été mesurée pour les deux compositions 50% et 75% SiC, comprimées à chaud à des températures inférieures à 2150°C . Le comportement thermique des échantillons a pu être corrélé à la formation des polytypes de carbure de silicium et aux transformations de phases.

1 Introduction

In the last decade, thermal conductivity studies of AlN and SiC ceramic materials have been investigated because of their potential applications in the electronic field: AlN as a substrate because of its high theoretical thermal conductivity and SiC because of its thermal expansion close to that of silicon.

The use of integrated circuits and VLSI (very large scale of integration) systems generate a large amount of heat. High conductivity is required to remove heat built up by electronic components and substrates must have a thermal conductivity higher than $100 \text{ W m}^{-1} \text{ K}^{-1}$; nowadays a thermal conductivity of 20 to $35 \text{ W m}^{-1} \text{ K}^{-1}$ is reached when alumina is used as substrate. So in order to dissipate this energy a new

type of substrate needs to be found. AlN and SiC single or polycrystals are both well known for their high thermal conductivity.^{1,2} Because of the covalent atomic bonds, electrons are not free and phonons ensure the heat transport. The mean free path of the lattice waves is strongly affected by crystalline defects, impurities such as oxygen, carbon and metallic elements, even in small amounts, and also by the form and size of samples.

2 Experimental Procedure

2.1 Powders

Only commercial powders from Starck (Berlin) were used (Table 1). SiC B10 (cubic) and AlN grade B were mixed to obtain an homogeneous slurry.

Separate SiC and AlN slurries were prepared. SiC powder was added to an anhydrous ethyl alcohol solvent containing the dissolved phosphoric ester deflocculant.

Magnetic stirring and ultrasonic apparatus enabled the breaking up of agglomerates. The AlN slurry was prepared in the same manner. These two slurries were then mixed. Once again ultrasonic apparatus was used to obtain a well-dispersed mixture which was finally ball milled for 3 days, then dried and sieved.³⁻⁵

2.2 Hot-pressing cycles

Hot-pressing temperatures of 1850°C, 1950°C and 2050°C were maintained for 30 min. The cycles are called 1, 2 and 3. Figure 1 describes cycle 1. The heating rate was 30°C min⁻¹.

Three other sintering cycles were computed (cycles 5, 6, 7): temperatures of 2050°C for 5 min (cycle 7), 2150°C for 15 min (cycle 6) and 2150°C for 45 min (cycle 5). Their heating rate from the room temperature to 1800°C was 30°C min⁻¹, then reduced to 15°C min⁻¹. Figure 2 describes cycle 5. A pressure of 40 MPa was applied as soon as a temperature of 1200°C was reached (in cycles 5, 6, 7).

Table 1. Commercial powders

	Composition (wt%)	Specific area (m ² g ⁻¹)	Particle size (μm)
Aluminum nitride grade B (Starck)	Al, 64.5% N, 30% O, 2% C, 0.08% Fe, 0.15%	5-8	0.8-1.3
Silicon carbide grade B10 (Starck)	C, 30-30.5% N, 0.04% O, 0.6% Fe, 0.05%	13-17	max. 0.8

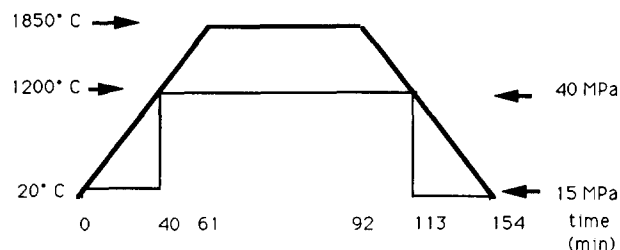


Fig. 1. Hot-pressing cycle 1.

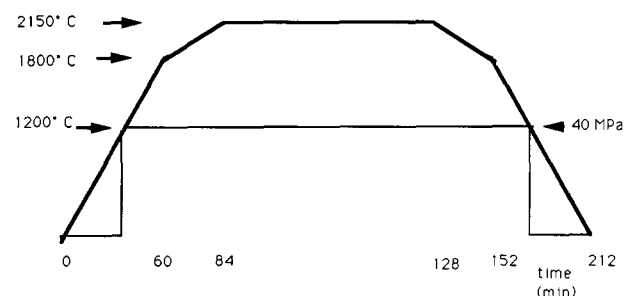


Fig. 2. Hot-pressing cycle 5.

2.3 Density

Density measurements were made using the Archimedes method in water.

2.4 X-Ray diffraction

The phase study was investigated using a Siemens apparatus. The recording was made in the range $2\theta = 25-100^\circ$ with a low speed (0.5° min⁻¹), using an Elphyse linear detector (window width 12 mm) at room temperature. Cu $K_\alpha = 1.5418 \text{ \AA}$ and a nickel filter were used. Before each recording a calibration of the apparatus was made using a gold sheet.

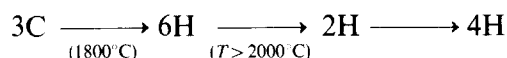
SiC polytypes will be described in Section 3.

2.5 Thermal conductivity measurements

Thermal conductivity determination was carried out on pellets (3 mm thick and 20 mm in diameter). An unbalanced temperature was applied between the faces of the ceramic sample in order to produce a heat flux traveling through its thickness. The heat flux was measured by a thermopile located between the ceramic sample and the cold sheet. The calibration of the thermopile was previously made using an iron sample (Armco, Middleton, Ohio), the sizes of which were close to those of the ceramic samples. In order to compare the heat flow measurements the same heat power levels were delivered by the hot sheet. Knowledge of parameters such as the heat flow, the temperature gradient between the hot and cold faces of the sample, the thickness and area of the specimens allowed the calculation of the thermal conductivity at room temperature. Standard deviations are about $\pm 5\%$.

3 Crystalline Phases

An XRD analysis shows the SiC powder exists in the cubic 3C form at room temperature. With higher temperatures ($T > 1800^\circ\text{C}$) allotropic transformations of SiC structure occur, and hexagonal forms as 6H, 4H, 2H or 15R, 21R, 33R appear, called SiC polytypes. The general agreement regarding the SiC transformations is:^{6–11}



(results also observed in previous experiments^{4,5,12}). The 4H SiC polytype is only observed in very rich SiC solution.¹³

When SiC and AlN powders are mixed and processed under specific sintering conditions the 2H solid solution is created.¹³ The nucleation of the 2H solid solution occurs by diffusion mechanisms. As previously mentioned, diffusion coefficients, because of the covalent bonds,¹⁴ are low and a hot-pressing temperature higher than 2100°C is needed to form the 2H phase. When the local concentration of AlN is poor, the remaining SiC grains which are not close to AlN grains are transformed to the 6H or 4H or R polytypes.^{5,12}

4 Results

4.1 Influence of SiC content

TEM analysis shows that 2H solid solution is formed between AlN and SiC when the cycle is carried out at 2150°C for 45 min.^{5,12} Lattice parameters (a and c hexagonal) of the 2H solution follow Vegard's law (Fig. 3).^{4,5}

Samples hot-pressed according to the sintering cycle 5 are highly densified except those with 99.5 and 90 wt% SiC (Table 2). Most of those compounds are monophased and crystallized in the 2H solid solution phase. Figure 4 indicates the evolution of the thermal conduction K of samples versus the SiC content in mixture. A decrease of values is observed with the increasing content of SiC in mixture until a 50% composition is reached, then an increase of thermal conductivity measurements is again observed. The minimum value of $40 \text{ W m}^{-1} \text{ K}^{-1}$ is

Table 2. Density of monophased samples

Composition	99.5	90	75	60	30	10	0.5
β -SiC (wt%)	99.5	90	75	60	30	10	0.5
Density (%)	98.5	97.7	99.1	99.3	99.6	99.2	100

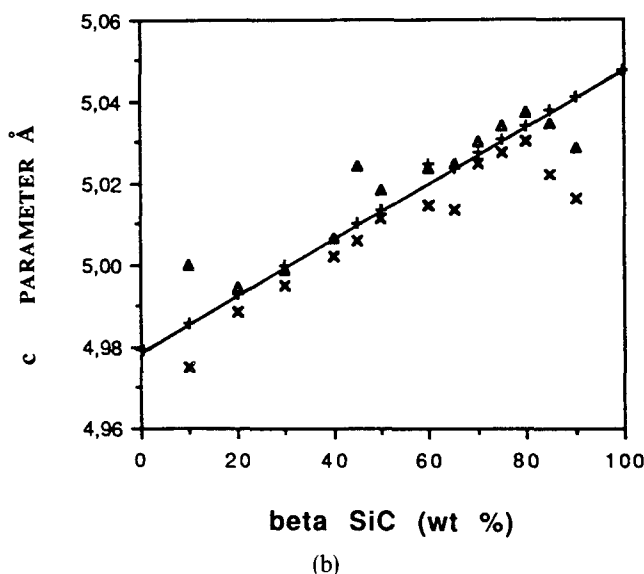
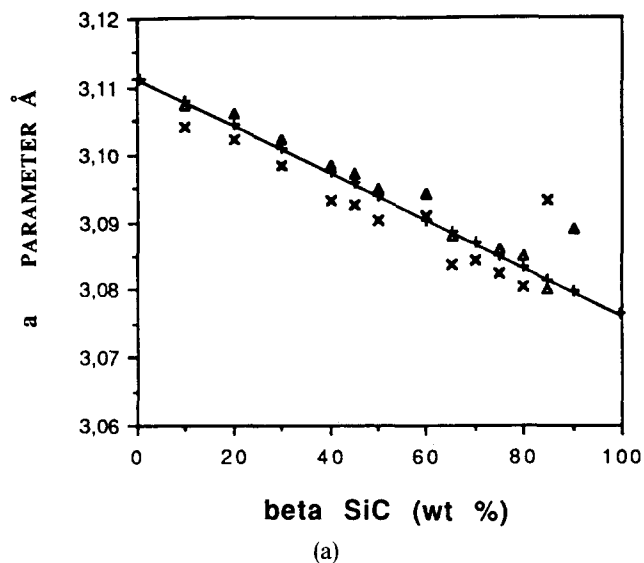


Fig. 3. Lattice parameters (a) a and (b) c of the 2H solid solution calculated according to the least squares method for powdered materials. +, theoretical values; x, small angles; \blacktriangle , large angles.

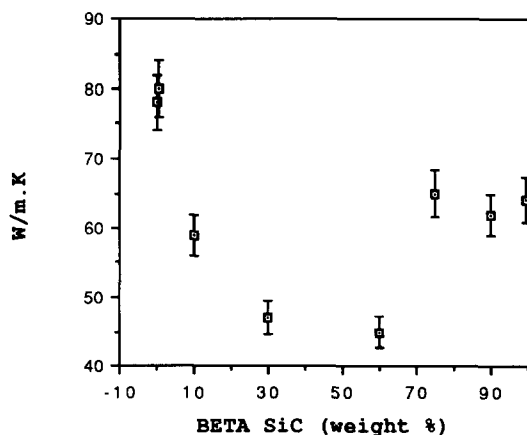


Fig. 4. Influence of the SiC content on the thermal conductivity of SiC–AlN materials.

shown for the equimolar composition. A relationship between the general evolution of $K=f(\text{wt}\% \text{SiC})$ and the solid solution formation can be established. With the introduction of an increasing number of Si and C atoms in the AlN structure, to form the 2H solid solution, locally an electrical lack of balance and slight weight differences (between Si–C–Al–N atoms) appear. These phenomena are considered as lattice defects resulting in lattice distortions. The mean free path of waves (phonons) decreases and subsequently the thermal conduction decreases too. The maximum of extraneous atoms in the AlN structure is reached for the equimolar composition. Thermal conductivity values are higher on the AlN-rich side than on the SiC-rich side. A value close to $65 \text{ W m}^{-1} \text{ K}^{-1}$ is measured for samples containing 75, 90 and 99.5 wt% SiC. These values can be compared to the data obtained by Rafaniello *et al.*¹⁵ and Shimada *et al.*¹⁶ who respectively obtained a minimum value of $10 \text{ W m}^{-1} \text{ K}^{-1}$ for 50 wt% SiC and $5 \text{ W m}^{-1} \text{ K}^{-1}$ for 40 wt% SiC.

It is difficult to compare these different results because

- (i) the technique may be different: flash laser,¹⁶ so-called ‘comparator method’;¹⁵
- (ii) the density of samples may be $>99 d_{\text{th}}$ (this work and Ref. 15) or not indicated;¹⁶
- (iii) the presence of a ‘small amount of glassy phase at grain boundary’¹⁶ or of 2.6–4.5 wt% SiO₂ in the starting powders¹⁵ may explain the low values of the thermal conductivities in the literature, where the present materials are free of these glassy phases in SiC-rich materials.^{5,12}

4.2 Influence of hot-pressing parameters

4.2.1 Compositions with high AlN content

Two compositions, 30 and 10 wt% SiC, were hot-pressed according to the sintering cycles 5 and 7. In all cases, materials were densified (Tables 3 and 4). Thermal conductivity values were still higher when

Table 3. Thermal conductivity of 30 wt% SiC sample

	Temperature (°C)	
	2150°C (45 min) cycle 5	2050°C (5 min) cycle 7
Thermal conductivity ($\text{W m}^{-1} \text{ K}^{-1}$)	47	57
Density (%)	99.6	99.3

Table 4. Thermal conductivity of 10 wt% SiC sample

	Temperature (°C)	
	2150°C (45 min) cycle 5	2050°C (5 min) cycle 7
Thermal conductivity ($\text{W m}^{-1} \text{ K}^{-1}$)	59	65
Density (%)	99.2	99.6

the sintering temperature and soaking time were reduced from 2150°C for 45 min to 2050°C for 5 min.

4.2.2 Compositions with high SiC content

Powdered mixtures (50 and 75 wt% SiC) were hot-pressed according to all the types of sintering cycles previously described in Section 2.2. Results are given in Tables 5 and 6. An increase of thermal conductivity for 50 wt% SiC was seen until a temperature of 2150°C was reached for 15 min (cycle 6); a maximum value of $73 \text{ W m}^{-1} \text{ K}^{-1}$ was obtained (Table 5). At 2150°C, with an increasing soaking time (45 min), a strong decrease occurs (Table 5). Nearly the same behavior is seen for the SiC-rich samples (Table 6). This maximum value can not be exceeded for the 75 wt% SiC, but is observed at a lower temperature: 2050°C for 30 min (cycle 3). Above 2050°C, the conductivity variations are inhomogeneous.

4.3 Discussions

Tables 7–9 indicate the different phases obtained according to the sintering cycles (5–7). As no pure standard phases are available, predominant and trace phases are qualitatively indicated.

Table 5. Thermal conductivity of 50 wt% SiC sample hot-pressed from 1850°C to 2150°C

	Temperature (°C)					
	1850 (30 min) cycle 1	1950 (30 min) cycle 2	2050 (30 min) cycle 3	2050 (5 min) cycle 7	2150 (15 min) cycle 6	2150 (45 min) cycle 5
Thermal conductivity ($\text{W m}^{-1} \text{ K}^{-1}$)	55	60	65	69	73	58
Density (%)	93	99.5	99.6	99.4	99.4	99.8

Table 6. Thermal conductivity of 75 wt% SiC sample hot-pressed from 1850°C to 2150°C

	Temperature (°C)					
	1850 (30 min) cycle 1	1950 (30 min) cycle 2	2050 (30 min) cycle 3	2050 (5 min) cycle 7	2150 (15 min) cycle 6	2150 (45 min) cycle 5
Thermal conductivity (W m ⁻¹ K ⁻¹)	69	71	73	63	51	65
Density (%)	89	95.8	99.8	99.8	99.2	99

Table 7. Crystallographic phases formed in composites sintered according to cycle 5 (sintering temperature 2150°C for 45 min; pressure applied at 1200°C)

β -SiC (wt%)	Phases present
99.5	2H ^a
90	6H, 15R, 3C
	2H ^a
75	6H, 3C
	15R traces
60	2H
	2H ^a
50	3C
	2H
	4H, 3C
30	15R traces
	2H ^a
10	6H, R traces
	2H ^a
0.5	6H, R traces
	2H ^a
	15R traces

^a Predominant phase.**Table 8.** Crystallographic phases formed in composites sintered according to cycle 6 (sintering temperature 2150°C for 15 min; pressure applied at 1200°C)

β -SiC (wt%)	Phases present
75	2H ^a
	3C
	6H traces
50	2H ^a
	3C

^a Predominant phase.**Table 9.** Crystallographic phases formed in composites sintered according to cycle 7 (sintering temperature 2050°C for 5 min; pressure applied at 1200°C)

β -SiC (wt%)	Phases present
50	2H ^a
	3C
	6H traces
30	2H
10	2H

^a Predominant phase.

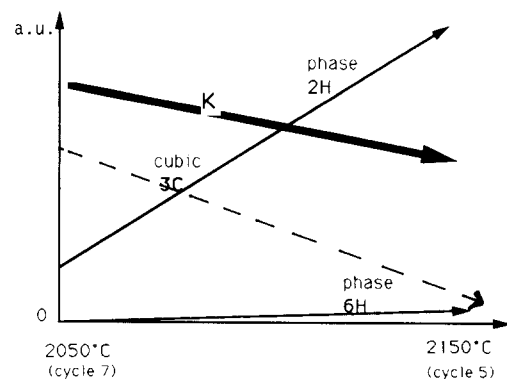
The relative variation of phase contents (in arbitrary units) is related to the thermal conductivity K (Figs 5–10). Sintering temperatures (cycle number) related to polytype content described in Tables 7–9 are also indicated.

4.3.1 Compositions with high AlN content

XRD analysis indicates that the 2H solid solution is not fully formed at 2050°C^{4,5} and some SiC grains remain under original cubic (3C) form. No trace of 6H polytype is seen at 2050°C; but when a higher sintering temperature is applied, the (3C → 2H) SiC transformation occurs, and these SiC grains react with AlN grains, giving the 2H solid solution; but some of the starting SiC grains are partially transformed under 6H phase, whereas a decrease of conductivity is observed. The qualitative results are shown in Figs 5 and 6.

4.3.2 Composition with high SiC content

For the two compositions 50 and 75 wt% SiC an increase of thermal conductivity K is observed when the formation of the 2H solid solution goes on and subsequently the 3C phase disappears (Figs 7 and 8). The 6H polytype seen when sintering is carried out at 1850°C disappears at 1950°C (Fig. 7). If the 2H formation is favorable to thermal conductivity, as compiled results seem to show, a thermal conductivity increase is expected when sintering is conducted

**Fig. 5.** Relations between thermal conductivity K and the crystalline phase formation according to the hot-pressing cycles: samples 10 wt% SiC.

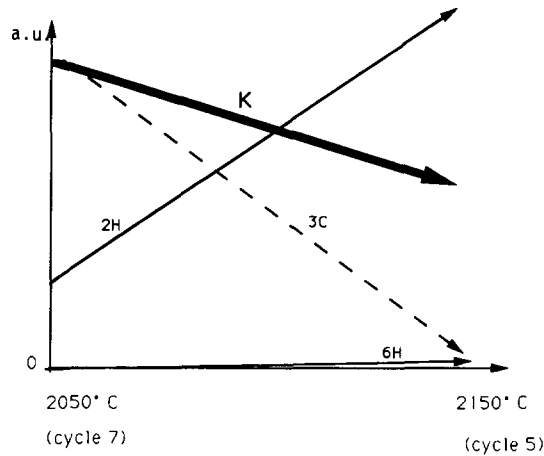


Fig. 6. Relations between thermal conductivity K and the phase formation according to the hot-pressing cycles: sample 30 wt% SiC.

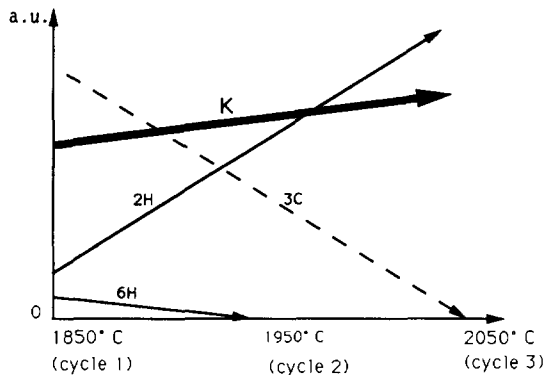


Fig. 7. Thermal conductivity K -phase formation relations. Equimolar sample hot-pressed from 1850 to 2050°C.

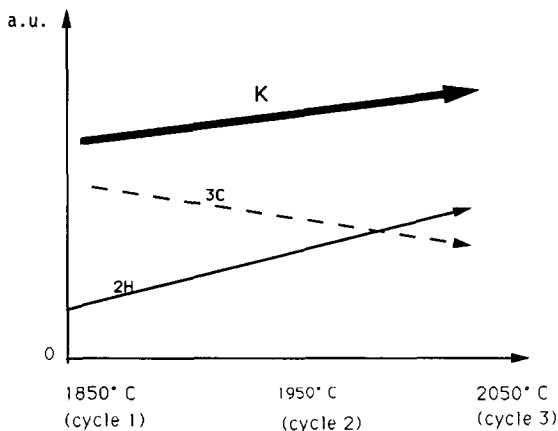


Fig. 8. Thermal conductivity K -phase formation relations. 75 wt% SiC sample hot-pressed from 1850 to 2050°C.

at higher temperature than 2050°C. However, results exhibit an inhomogeneous variation of the thermal resistivity (Figs 9 and 10). Even so, the 2H solid solution formation goes on with increasing sintering temperatures; the phase investigations indicate the presence of 6H SiC polytype. For 75 wt% SiC solution, when the 6H SiC polytype appears, a decrease of K is observed (2050–2150°C range); the

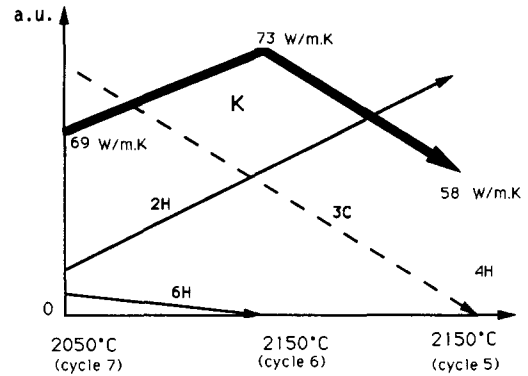


Fig. 9. Thermal conductivity K -phase formation relations. Equimolar sample hot-pressed from 2050 to 2150°C.

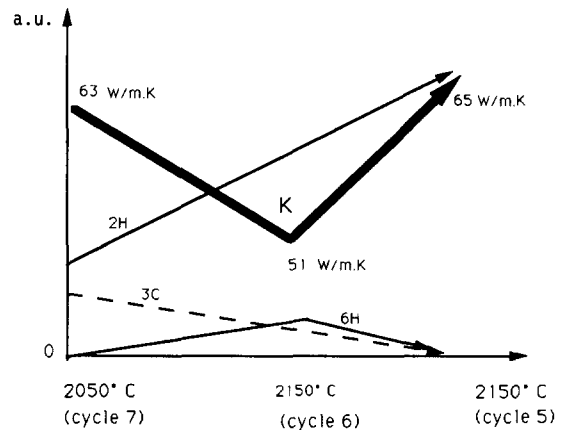


Fig. 10. Thermal conductivity K -phase formation relations. 75 wt% SiC sample hot-pressed from 2050 to 2150°C.

opposite behavior is observed when a longer soaking time is applied (2150°C, 15–45 min; Fig. 10).

For the equimolar composition, when the 6H polytype decreases, increasing K values are seen (2050–2150°C range). A decrease of K is observed when the 2H solid solution is fully formed (2150°C, 45 min; Fig. 9). The maximum of extraneous atoms in the lattice corresponds to the minimum value of K .

5 Conclusions

Solid solutions were obtained by hot-pressing (2150°C, 45 min) commercial SiC and AlN powders mixtures. The minimum of the thermal conductivity K ($40 \text{ W m}^{-1} \text{ K}^{-1}$) was observed for a 50 wt% SiC–AlN mixture. It has been shown, according to the hot-pressing cycles, that a maximum value for the thermal conductivity of $73 \text{ W m}^{-1} \text{ K}^{-1}$ can be obtained. Thermal conduction variations are strongly related to SiC polytypes formation. K decreases when the SiC polytype 6H increases, whereas the 2H phase formation increases following the sintering temperature increase. This polytype 6H can be considered as lattice defects affecting the lattice periodicity as impurities.

Meanwhile substrate applications for SiC–AlN materials are unforeseen because a high electrical resistivity (effectively found for samples with high AlN content) and very low dielectric losses (not pointed out in these experiments) have to be simultaneously observed.⁵

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