

Review article: Silicon Carbide. Structure, Properties and Processing

(Artigo revisão: Carbetto de Silício, Estrutura, Propriedades e Processamento)

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Abstract

In view of considerable interest in the development of liquid phase sintered structural and high-temperature ceramics on the base of silicon carbide, a comprehensive review of the data on structure, properties and the known methods of processing of silicon carbide seems timely. The most striking feature of silicon carbide is its polytypism, i.e. formation of a great number of different structural modifications without any change in composition. Although this feature of silicon carbide was extensively studied, no systematic up to date analysis was done. However, polytypism and the tendency of the polytypes to undergo structural transformations at working temperatures may lead to uncontrollable modification of the materials properties, and therefore needs to be fully understood. Furthermore, the recently developed liquid phase sintering technique for silicon carbide densification is of an undoubtful interest and the overview of the results achieved until present time may provide some guidelines for the ceramists.

Keywords: silicon carbide, polytypism, microstructure, thermal stability, liquid phase sintering.

Resumo

Em vista do considerável interesse no desenvolvimento de cerâmicas estruturais e para aplicações em alta temperatura, é oportuna uma revisão quanto a estrutura, propriedades e métodos conhecidos de processamento de cerâmicas a base de carbetto de silício sinterizados via fase líquida. A característica mais interessante do carbetto de silício é o seu politipismo, isto é, a formação de um grande número de modificações estruturais para uma mesma composição. Embora este fenômeno venha sendo extensivamente estudado, não se tem até o momento, uma análise sistemática do mesmo, o que seria de extrema importância, uma vez que o politipismo e a tendência à transformação estrutural destes politipos em temperaturas típicas de trabalho podem levar a incontáveis modificações nas propriedades do material. Além disso, os recentes avanços obtidos na densificação do carbetto de silício através da técnica de sinterização na presença de fase líquida justificam uma avaliação dos resultados obtidos até o momento, que podem proporcionar alguma orientação aos profissionais da área.

Palavras-chave: carbetto de silício, politipismo, microestrutura, estabilidade térmica, sinterização fase líquida.

INTRODUCTION

As an industrial material silicon carbide (SiC) has been used since last century, the methods of its synthesis being introduced in 1885 by Cowless and Cowless [1] and in 1892 by Acheson [2]. Silicon carbide has been recognized as an important structural ceramic material because of its unique combination of properties, such as excellent oxidation resistance, strength retention to high temperatures, high wear resistance, high thermal conductivity, and good thermal shock resistance. Such a combination of properties is determined by the highly covalent (up to 88%) chemical bonding between silicon and carbon atoms. However, this very same bonding presents a problem in dense SiC bodies production by means of powder technology. Due to extremely low self-diffusion coefficient, densification of the SiC powders alone is possible only at extremely high pressure and/or temperatures exceeding 2100 °C. In order to densify SiC successfully the use of sintering aids is necessary.

Among the methods of dense SiC fabrication developed until present time, the most common ones are pressure-less sintering in solid state (SSiC), infiltration of the reaction bonded (porous) silicon carbide by molten silicon (SiSiC), and hot pressing (HPSiC). However, all of these methods have definite drawbacks. The SSiC materials that are usually densified with the aid of C and B [3] have fine-grained equiaxed microstructure (grain size 1 to 4 μm), show good high-temperature creep and oxidation resistance [4, 5] but at the same time exhibit poor fracture toughness (3 to 4 MPa·m^{1/2}) and have highly flaw-sensitive strength [6] at room temperature. Moreover, due to the high temperatures applied for sintering, and due to relatively prolonged soaking times at these temperatures, abnormal grain growth occurs often resulting in anisotropic α-SiC phase formation. The SiSiC materials are poor candidates for high-temperature applications due to the limit set by the melting point of silicon, and the limitations of hot pressing (HPSiC) as a densification technique are well known.

Further research of the possibilities of SiC densification showed that pressure-less sintering of SiC can be achieved with liquid-phase forming additives, such as Al₂O₃ [7] and Al₂O₃ + Y₂O₃ (or rare-earth oxides) [8-14]. Such an approach enables to sufficiently lower the sintering temperature (to as low as 1850 °C) and still achieve complete densification. The majority of thus sintered materials have equiaxed fine-grained microstructure with secondary phases located at triple joints of SiC grains [12, 14]. This densification technique is quite similar to the one used for silicon nitride (Si₃N₄), and the resulting microstructure consisting of two main phases – crystalline and intergranular non-crystalline – is also similar to the one formed by Si₃N₄ on liquid-phase sintering. Such similarity of the processing routes and of the processes occurring during sintering of both materials opened the possibility to apply in the case of SiC several methods of structure and properties tailoring, such as in-situ toughening, weight loss control by means of controlled atmosphere of sintering or reaction powder beds, sintering aids variation, secondary phase crystallization, etc., that were successfully developed for silicon nitride based ceramics.

In the present paper an overview of the new developments in silicon carbide processing will be presented together with some relevant general information about silicon carbide, such as structure, polytypism, polytype transformations, etc. Due to a vast variety of the information on a relatively new subject of SiC liquid-phase sintering, and due to the fact that information until now was not comprehensively analyzed, such a review might facilitate advances of this subject and allow the areas for further study to be more clearly identified.

Silicon carbide: structure, some properties, and polytypism.

The fundamental structural unit of silicon carbide is a covalently bonded primary co-ordinated tetrahedron, either SiC₄ or CSi₄. The four bonds directed to the neighbors have a nearly purely covalent character and from the difference in electronegativity between the silicon and the carbon atom, an ionic contribution to the bond of about 12% can be estimated from Pauling's formula. This small positive charge on the Si atom resulting in the ionic contribution to the interatomic bonds can be also deduced from the shift of the K_α doublet in the X-ray emission

spectrum of Si in SiC.

However, the most remarkable feature of silicon carbide crystal structure is its polytypism, that is that the crystal structure exhibits a number of different one-dimensional ordering sequences without any variation in stoichiometry. Although a great variety of SiC polytypes is known, it has become accepted practice to refer to the cubic polytype as β -SiC, and to all non-cubic structures (hexagonal and rhombohedral) collectively as α -SiC.

The SiC crystals appear in a number of modifications that have either hexagonal or trigonal symmetry. They can all be described in the usual hexagonal axis system, with one c -axis perpendicular to three equivalent axes a , b , and d having angles 120° with one another. It was shown by Ott [16-19] that all crystallographic modifications of SiC have in fact very similar structures: they all consist of identical layers perpendicular to the hexagonal or trigonal axes. In the direction of these axes, however, each structure has its own repetition distance, resulting from a characteristic variation of the stacking of the identical layers. The SiC₄ or CSi₄ tetrahedra are arranged in such a way that all atoms lie in parallel planes on the nodes of regular hexagonal networks, as presented in Fig. 1 (b) [20]. The distances from the carbon plane to the neighboring silicon planes have a ratio 1:3 in relation to carbon-carbon interplanar distance. This has the effect that the symmetry axis perpendicular to these planes is polar.

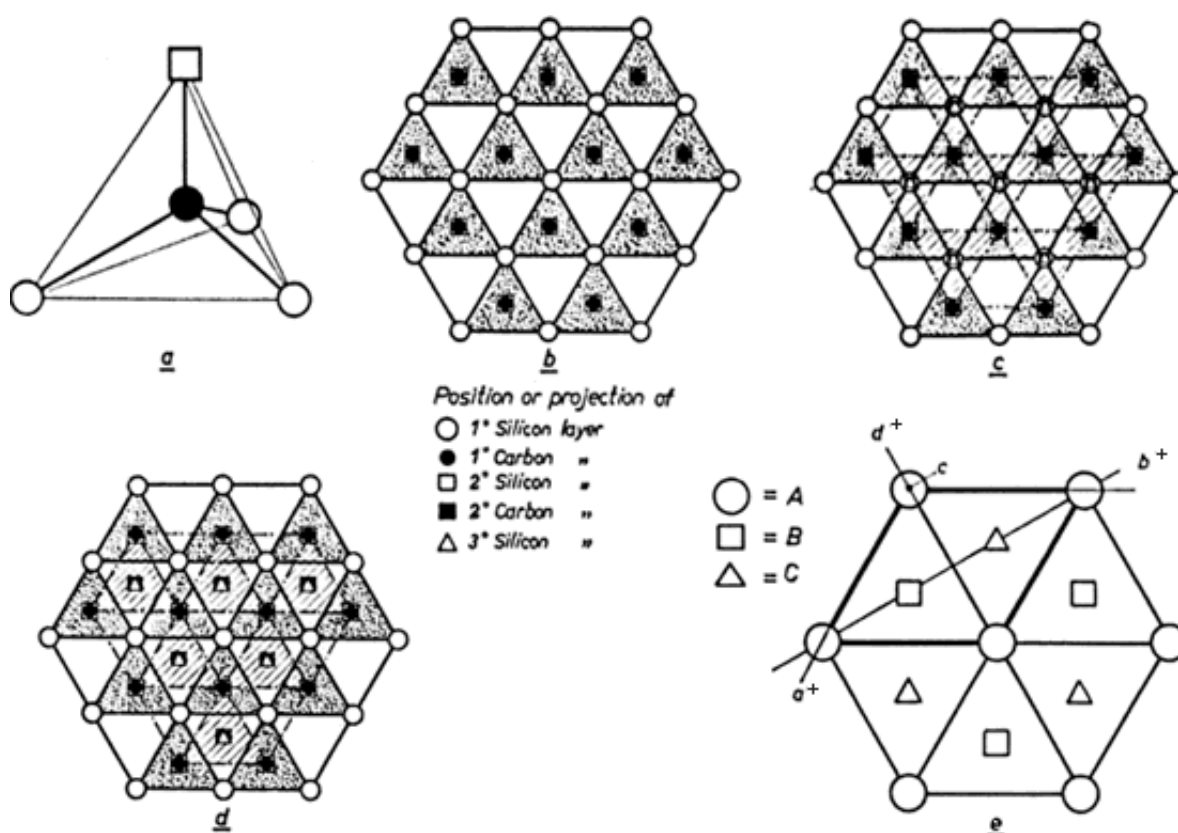


Figure 1: Position or projection of silicon and carbon atoms in SiC [20].

- a) elementary Si-C tetrahedron;
- b) projection of one tetrahedral layer;
- c) projection of two adjacent tetrahedral layers of the cubic configuration;
- a) projection of two adjacent tetrahedral layers of the hexagonal configuration;
- b) Projection of the different positions of the atoms; the axes system and the base of the unit cell are indicated.

A carbon atom lies above the center of a triangle formed by three adhering silicon atoms of such a hexagonal silicon network. The fourth silicon atom, belonging to the second silicon layer, connected to this carbon atom has the same projection as this atom ([Fig. 1\(a\)](#) and [\(b\)](#)). The atoms of the third silicon layer connected also in unilateral positions to the atoms of the second carbon layer may either occupy a position having its projection on the atoms of the first silicon layer ([Fig. 1\(c\)](#)), or on the center of the triangle not covered by the projections of the atoms of the first carbon layer ([Fig. 1\(d\)](#)). Identical successive layers of tetrahedra are oriented either parallel ([Fig. 1\(d\)](#)) or antiparallel ([Fig. 1\(c\)](#)). Different structures arise as a consequence of the fact that by a characteristic succession of alterations of tetrahedral layers, a repeating unit is formed. If every second layer is parallel to the preceding layer, the cubic structure is formed, and if every second layer is antiparallel to the preceding, the hexagonal type is obtained.

Another way of visualizing the structure formation in SiC polytypes was suggested by Page [21]. As it is shown in [Fig. 2](#), different polytype structure can be presented as polar frameworks formed by the layers of SiC_4 or CSi_4 tetrahedra in which all the tetrahedra have one apex out of the layer plane. The tetrahedra are linked through their corners to satisfy the four-fold coordination at any point of the structure and are arranged in the same way as spheres in close-packed structures. Therefore, the stacking sequence can be described by the commonly accepted ABC notation. While both cubic (...ABC...) and simple hexagonal (...ABAB...) stacking sequences are found in SiC, the two stacking types can also occur in more complex, intermixed, forms yielding a wide range of ordered, larger period, stacking structures. Disordered structures are also well described. Following the notation suggested by Jagodzinsky [22] any separate layer in these stacking sequences can be described as having a local cubic (k) or hexagonal (h) environment. However, the acentric nature of the tetrahedral unit requires that in sequences of the type CACA (hhhh), the A and C layers are not only offset, but rotated by π (see [Fig. 2](#)). Thus for SiC two stacking operations exist: layer translation only (yielding ...ABCABC... (kkkkkk)), and layer translation and rotation (yielding ...ABAB... (hhhh)). In order to indicate this rotation of π , dashes can be added to the layer notation, which means that layers designated A and A' have exactly identical spatial arrangement but are rotated by π [23]. For example, the common high-temperature SiC polytype has a hexagonal unit cell and a six-layer repeat in the c-direction (chosen perpendicular to the layers) and can be described as C'ABCBA'A'C'. As it can be seen, the stacking sequence of this polytype results in a structure which may be derived from that of the cubic polytype by the insertion of [111] rotation twin boundaries every three layers (see [Fig. 2](#)).

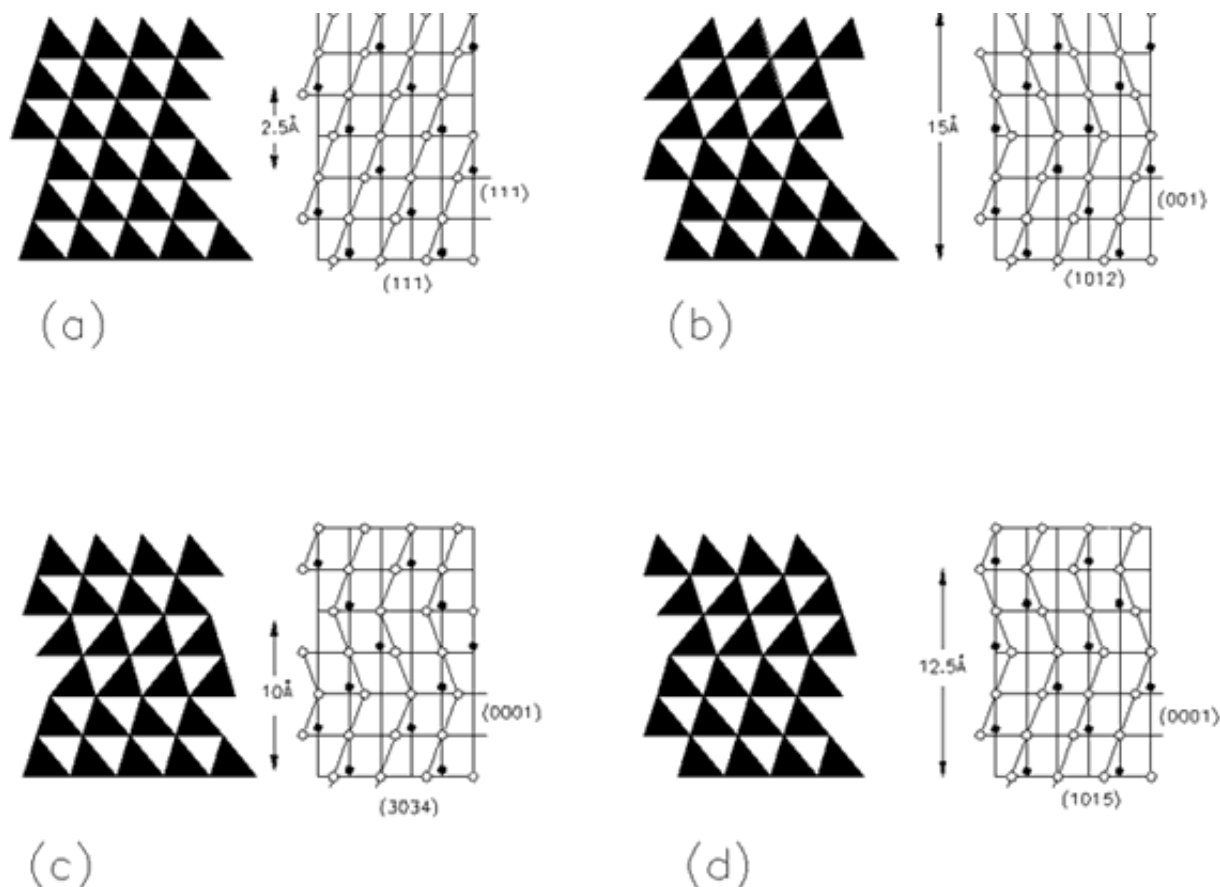


Figure 2: Schematic representation of the four most common SiC polytypes according to Page [21]:

a) 3C; b) 6H; c) 4H; d) 15R.

An alternative description of this six-layer structure according to the notation proposed by Ramsdell [24] is 6H, and specifies both the number of layers in the repeat along the stacking direction, together with Bravais lattice type of the resultant structure (i. e., hexagonal (H), cubic (C), or rhombohedral (R)).

The sequence of tetrahedral layers may be visualized in models, the so-called "tramline" structure diagrams, by considering zig-zag sequence of non-basal tetrahedral planes (see Fig. 2). In order to represent this zig-zag layers, Zhadanov [25] proposed still another notation which specifies the number of consecutive layers without rotation. Thus, the 6H structure is described by the Zhadanov symbol as (33), indicating that the cubic sequence is interrupted by rotation every three layers. Similarly, all other polytypes may be described using this notation: the hexagonal polytype 2H, which has two layers in the unit cell, has a structure described as (11), i. e., each layer is rotated by π with respect to the preceding layer.

Although in principle there may exist an infinite number of possible stacking variants, the structure of even the longest-period polytypes may be considered as sequences of one or more of the smaller-period units 4H (22), 6H (33), 15R (32)₃ and 21R (34)₃, which at the same time are the most common SiC polytypes. For example, the sequence 39H may be represented as (33)₂32(33)₂(32)₂. Certain families of structures were found to exist, for example (33)_n32 sequences with $n = 1, 2, 3, 4, 5, 6, 7, 13, 16, 21$ were identified by Jepps [26]. The "n" in this Zhadanov symbol may be considered as a stacking fault in otherwise unfaulted 6H (33) structure. If the SiC polytype structures are considered from this standpoint, the family of different structures then may be considered as a result of a difference in the separation of stacking faults.

Occurrence and stability of SiC polytypes.

Although a large number of SiC polytypes is known and well documented, very few of them are

considered to be thermodynamically stable. However, there appear to be five small-period polytypes (2H, 3C, 4H, 15R, and 6H) which are considered as basic SiC structures and which are found to occur most frequently [27].

Large number of crystal growth experiments, both from vapors and liquids, have been conducted by various researchers in an attempt to define stability regions for these basic silicon carbide polytypes. In all cases, the resulting polytype was observed to depend on both the rate of growth and the temperature. It was established that under conditions of high supersaturation (i. e., non-equilibrium conditions) the cubic polytype was initially formed in sublimation and growth experiments over the temperature range of 1273-3023 K. However, on some occasions, this polytype was observed to subsequently disappear as a result of transformation and recrystallization processes resulting in α - SiC formation. Under the same growth conditions of temperature and purity, but with lower supersaturations, which leads to lower growth rates, the other basic SiC structures were observed to form. According to these considerations and observations, both Knippenberg [20] and Inomata *et al.* [28] suggested stability diagrams for SiC polytypes as a function of temperature as presented in [Fig. 3](#).

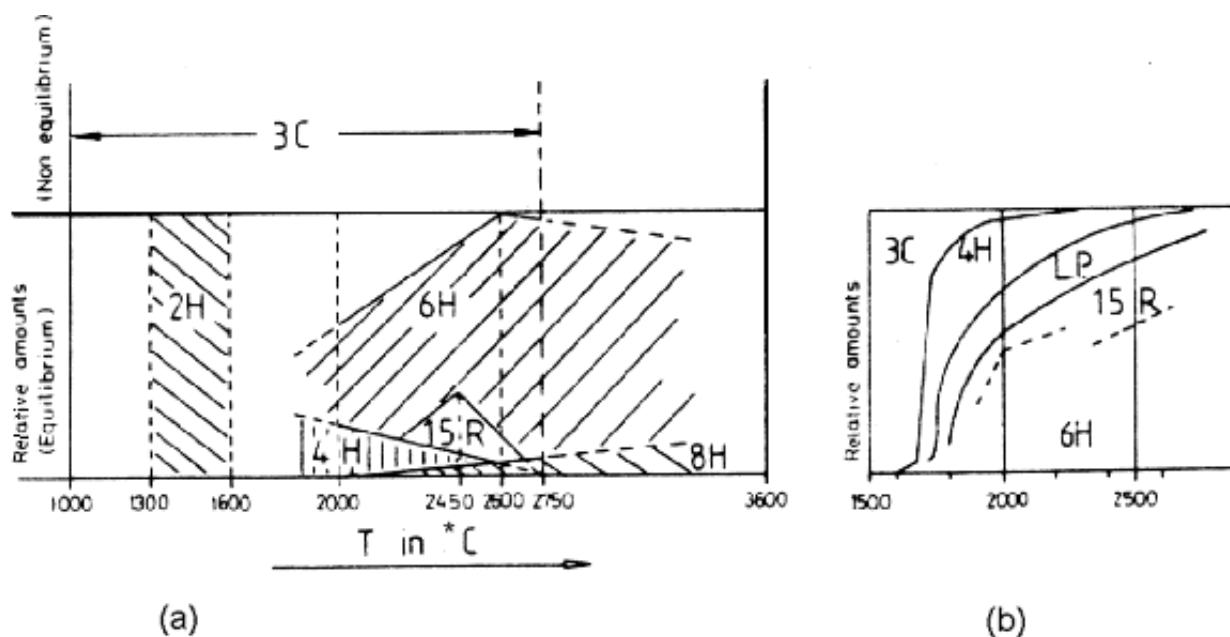


Figure 3: Stability diagrams of SiC polytypes as a function of temperature according (a) to Knippenberg [20] and (b) Inomata et al. [28].

Although these experiments were performed using relatively pure starting materials, the effect of even small quantities of impurities and non-stoichiometry (the partial pressure of silicon vapors is shown to be several times higher than that of carbon [29] under conditions of standard growth experiments), must be taken into account and was actually shown to play a large part in polytype stabilization [26, 30]. The impurity elements that were shown to have the most pronounced influence on polytype formation are those in groups III and V of the periodic table, i.e., electronic acceptors (Al, B, etc.), and electronic donors (N, P) with respect of SiC. Aluminum was first noted to stabilize the 4H structure [30] and, since this primary observation, other investigations have noted the same effect [31, 32]. The same stabilizing effect is also attributed to boron [33]. On the other hand, electron donors, like nitrogen and phosphorus, seem to stabilize cubic SiC [20].

Theories of polytype formation

The first attempt to explain the reason of SiC polytypism was made by Lundqvist [30] who suggested that formation of polytypes was controlled by impurities. As it was discussed in the previous section, there are many experimental results, which support the idea that certain impurities may stabilize some of the common small-period polytypes. However, the existence of

a large number of long-period polytypes leads to a conclusion that impurity stabilization can not be the only effect to be taken into consideration. Many other theories have been proposed for extensive SiC polytypism, and in particular to explain the occurrence of very-long-period polytypes, such as 1560H or 4680R, etc. However, until now no single simple theory from the existing ones can satisfactorily explain all the experimental data.

Existing theories may be divided into two categories: theories based on kinetic and growth considerations, and those resulting from a thermodynamic basis.

Nearly all growth theories may be considered as variations of the theory of spiral growth around a screw dislocation [34, 35] with the repeat of the polytype being determined by the step height of the growth spiral. A number of experimental observations support this theory including the discovery of growth spirals and the measurements of step heights on crystal surfaces. The strong point in favor of this mechanism is that it enables to explain formation of almost any polytype, especially when theory is modified to include spiral growth in faulted structures [36-41]. Other modifications of this spiral growth theory were proposed by Vand and Hanoka [41] who postulated the dislocation to result from epitaxial growth on a foreign body, and by Madrix and Steinberger [42] who proposed that the stacking faults introduced during growth subsequently expand around a screw dislocation to give rise to a regular array of stacking faults and a new polytype. However, there has been no experimental confirmation of identification of the dislocations associated with such spirals in the bulk below the crystal surface. Moreover, there have been few suggestions as to how the necessarily large Burgers vectors for initial dislocation might arise, either individually or as a result of a closely spaced dislocation cluster. Spiral growth theories also seem to be in contradiction with the commonly observed plate-like habit of as-grown crystals where the spirals appear on the largest facets, i. e., the growth direction appears to be parallel to the smallest crystal dimension. The observation of many randomly faulted crystals, and crystals of different polytypes in syntactic coalescence, further indicates that this theory can not explain all of the observed structures. The exact mechanism of various SiC polytypes formation thus seems to remain speculative.

Because of a number of obvious inconsistencies of the spiral growth theory, Jagodzinski [43] proposed a theory based on equilibrium thermodynamic basis. He assumed that the cubic polytype was the most stable, and all others resulted from the ordering of stacking faults within this structure, i. e., transformation after growth. He also assumed that the internal energy of the polytypes would be similar and considered the contribution of the vibrational entropy to the free energy, postulating that this contribution provided the driving force for the ordering of stacking faults and the subsequent occurrence of polytypes. However, although measurements of stacking faults densities by X-ray line broadening showed good agreement with predictions from this theory [44], later X-ray reflection, high-energy electron diffraction and transmission electron microscopy observations have established that the necessary density of faults is not homogeneously distributed [45]. Also using an energy approach, Schner [46] interpreted polytypism as an order-disorder phenomenon. However, such a model associates a specific temperature range with each polytype, although this is not generally observed.

Due to the nature of the structure of SiC polytypes, differences in the internal energies are expected to be small. However, from measurements of bond length and band gaps it becomes obvious that they are not negligible. 2H polytype is found to have a largest band gap, and hence the largest binding energy, and measurements of lattice parameters suggest that it is the most dense structure, while the 3C structure is the most open one [47] (see [Table 1](#)). It may be concluded from these measurements that 2H is the most stable polytype, and the 3C the least stable one [48]. However, the apparent stability of the cubic polytype at intermediate temperatures of 1673-1873 K is seen as a central problem in an otherwise gradual increase in the degree of cubic stacking from 2H through 4H to 6H etc., with increasing temperature.

Table 1 - Variation of the band-gap and lattice parameters for the four most common polytypes of SiC. The ratio (c/na) shows the variation of (c/a) per layer in an n-layer polytype.

| Polytype | Band gap [46] eV | Lattice constants [46] | | |
|----------|---------------------|------------------------|---------|--------|
| | | a | c | c/na |
| 2H | 3.300 | 3.076 | 5.048 | 0.8205 |
| 4H | 3.263 | | | |
| 6H | 3.023 | 3.0806 | 15.1173 | 0.8179 |
| 3C | 2.390 | 3.0827 | 7.5510 | 0.8165 |

Assuming the above described theoretical suppositions are correct, 3C polytype must be the less stable one. However, its occurrence on the initial stages of growth over large temperature range (1673-2273 K) may be due to its high symmetry and multiplicity of low-energy surfaces. These factors could result in easy nucleation and rapid growth along several directions yielding large crystals bounded by a low-energy form [48]. While this kinetic argument may explain the occurrence of 3C polytype over a wide temperature range, its high symmetry might also be expected to increase the vibrational entropy contribution to the free energy, thus also contributing to the equilibrium stability of 3C polytype at very high temperatures.

From the kinetic standpoint, it seems that 3C polytype may be the initial polytype to appear during growth at almost all temperatures, this polytype subsequently transforming into other polytypes depending on ambient conditions. Thus, many observed polytypic structures probably only occur as a result of β - SiC transformation. However, in the temperature range of 1673-1873K, β - SiC is observed to not undergo any further transformation. Thus it can be concluded that β - SiC polytype is somehow stabilized over this temperature range or that any subsequent transformation is too slow to occur. Still another interesting observation is the frequent occurrence of 3C polytype as an apparently unnecessary intermediary in the 2H to 6H transformation above 1673 K. Furthermore, this suggests either that 3C polytype is more stable than it was believed in this temperature range or that its occurrence is kinetically controlled.

It must be seriously considered that the whole situation might be complicated by the presence of trace impurities which may have a determining effect on controlling relative polytype stabilities either through structural or electronic influences. Thus some transformations are proven to be associated with the presence of specific impurities [21]:

- a) 6H to 3C "reverse" transformation is facilitated by nitrogen;
- b) 6H to 4H to 2H transformation is facilitated by either boron or aluminum;
- c) 4H to 6H transformation is facilitated by boron and nitrogen together.

All of these observations support the supposition that, in case of SiC, electronically p-type materials, such as B and Al, stabilize layers in hexagonal environments while electronically n-type materials, such as N and P, tend to stabilize layers in cubic environments.

Although the solubility of these impurities in silicon carbide is reported to be very low (<0.3%, [49, 50]), very limited information exists regarding the likely atomic positions of such solute atoms in SiC framework, that is whether the solutes are accommodated interstitially or substitutionally or whether, for example, local boron carbide or silicon nitride groups are formed. Thus, the actual mechanisms by which polytype stabilization may occur are not understood completely. However several possibilities may be considered in this regard:

- (i) band structure effects; as shown in [Table 1](#), the reported band gaps for different polytypes are significantly different and this could influence the energy levels available to *p*- or *n*-type solute atoms;
- (ii) if the solute species are substitutional, then the introduction of a range of bond-strength/length could influence the relative energy of different stacking sequences;
- (iii) if the solutes are predominantly interstitial, then it is conceivable that more favorable site types are available in some structures rather than in others;
- (iv) although elemental impurities are only soluble in small amounts in SiC [51, 52], there is extensive solubility of compounds such as boron carbide, boron nitride and aluminum nitride in SiC [50, 53, 54]; alloying with such compounds has been shown to affect the polytype formation, the structure of the resultant solid solution being influenced by the crystal structure of the alloying compound.

Finally, it must be taken into account that trace impurities, including deviations from stoichiometry, could be responsible for some aspects of all transformations. Few researchers worked with very high-purity materials and, in particular, there is some evidence that materials made from silicon-rich melts usually exhibit higher content of 3C polytype than the others [55]. This is obviously an area for future research that must be performed with the special emphasis on high-precision isolating and analyzing of trace levels of low atomic number impurities.

Transformation mechanisms and the sequence of polytype transformations in SiC

It has been established that a number of different transformation mechanisms can occur, often in parallel, which accounts for the wide range of transformation kinetics observed. In general, slow solid-state mechanisms are usually found in single crystals, while fast transport mechanisms, such as surface, vapor or liquid-phase diffusion, are predominant for polycrystalline, powder or compacted samples. Therefore, transformations in polycrystals are usually accompanied by other diffusion controlled phenomena such as grain growth and recrystallization. However, it seems that the fast transport mechanisms probably only control the growth of a region of a new polytype, the nucleus either pre-existing the transformation or being formed by the solid-state mechanisms. Further, these solid-state mechanisms can be divided into diffusion controlled processes and those accomplished by shear, i. e., dislocation mechanisms, but experimental distinction between them may present a problem [21].

While there exists a sufficient amount of information on the occurrence of polytypic transformations [56-59], considerably less data has been produced on transformation kinetics, and even fewer direct observations of transformations are available [60-62]. In regard of the transformations themselves, a considerable problem is why they occur in principle, i. e., do the transformations reflect genuine changes in stability from one polytype to another with changing conditions or are they a result of a tendency to move away from metastable structures, formed for kinetic reasons during growth, to more stable states.

As to the sequence of polytype transformations, a nomogram of such sequence was proposed by Page [21] and is presented in [Fig. 4](#). The outer clockwise circuit ...ABC... shows the layer sequence when stacked with a translational offset only to produce 3C. The inner anticlockwise circuit ...B'A'C'... shows the corresponding layer sequence if the whole stack is rotated by π to produce the structure twin-related to the 3C, the layers still being stacked by translation only, but now translated in the opposite direction because of the π rotation. Crossing a diameter, i. e., $A \leftrightarrow C'$, $B \leftrightarrow A'$, $C \leftrightarrow B'$ transformations, shows the h-operated layer allowed by either B (k-operation) or C' (h-operation); C' can only be followed by B' or A, etc. The 6H sequence then can easily be read as ...ABCB'A'C'ABCB'A'C'... etc., while 2H is ...AC'AC'... Further, since the only two layers which can be modeled in terms of the passage of an $\frac{a}{3} \langle 10\bar{1}0 \rangle$ dislocation between the original A and B (or A and C') layers. Thus, this simple nomogram may be useful in determining permissible stacking sequence in SiC polytypes together with the sequence changes which may occur during transformation.

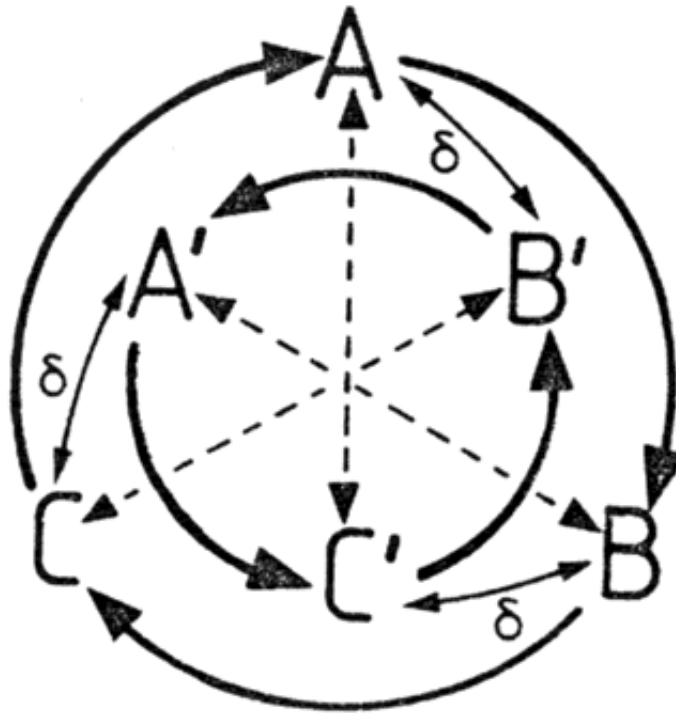
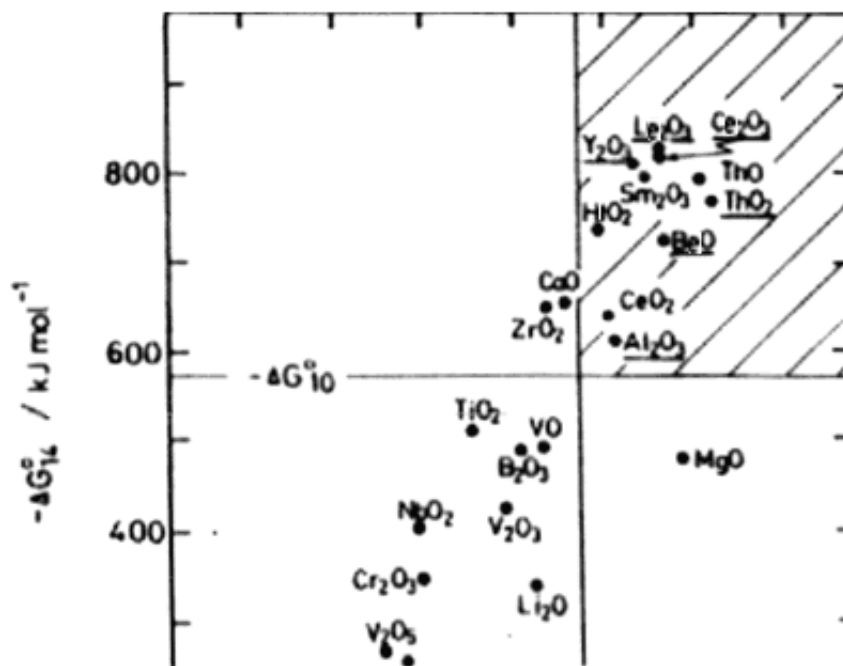


Figure 4: Nomogram of the sequence of polytype transformations in SiC [21].

Liquid phase sintering of silicon carbide

As it was mentioned in the Introduction part of the present paper, several techniques of producing dense SiC-based ceramics are known. In the present review the liquid-phase sintering of SiC will be discussed because its obvious advantages over all other processing techniques.

First successful attempts with pressure-less sintering of SiC with the help of oxide sintering aids were made by Omori *et al.* [8]. However, at the time the approach to the choice of the sintering aids was purely empirical. Later, Negita [63] suggested an approach to sintering aids choice based on the analysis of the reactivity of SiC with a variety of compounds, similarly to what was previously achieved by him for Si₃N₄ [64]. His results for metals and metal oxides are presented in [Fig. 5](#).



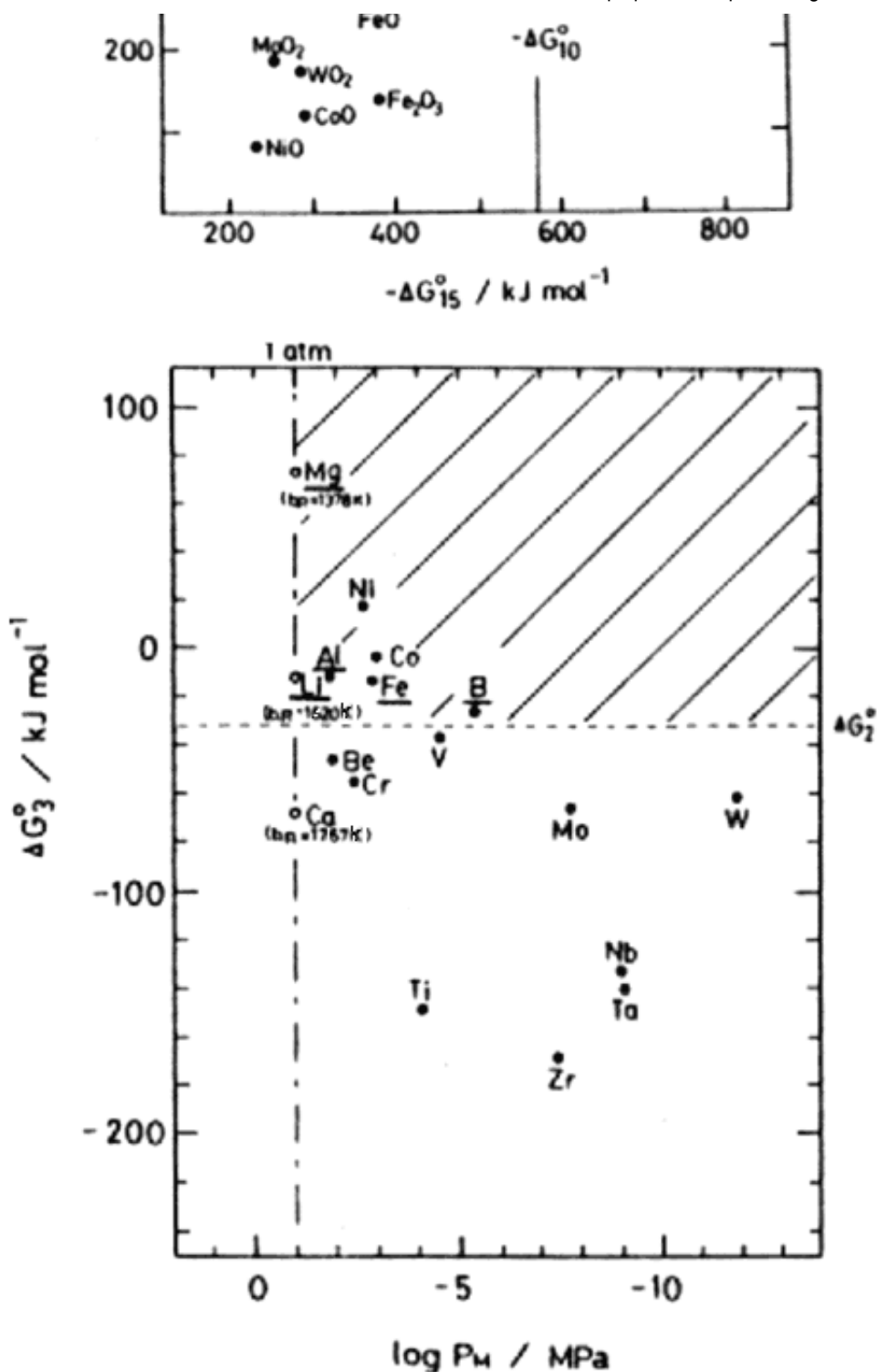
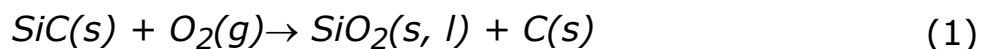
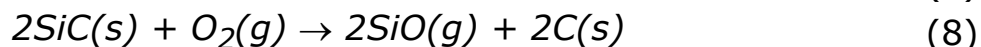
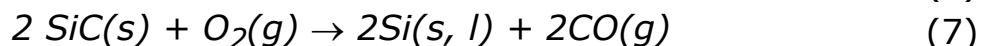


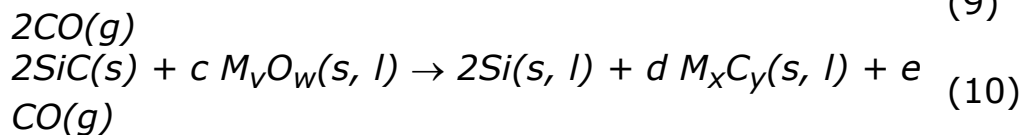
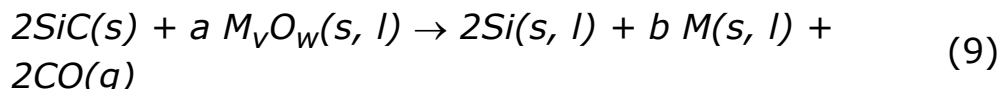
Figure 5: Effective sintering aids for SiC ceramics after Negita [63]: a) metals; b) oxides.

The main problem with using metal oxides as sintering aids for SiC is their active internal chemical interaction at the sintering temperatures. A variety of oxidation reactions between SiC and metal oxides resulting in gaseous species formation, and thus leading to severe weight loss and overall shift of the composition during heat treatment were suggested in [64]:



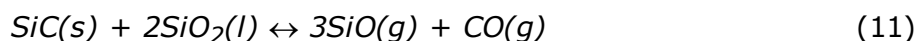


In terms of the reactions of SiC and metal oxides the reactions may be expressed as [64]:

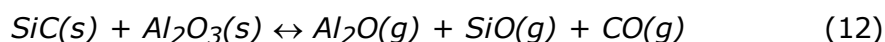


Based on the thermodynamic analysis of these latter reactions, it was shown that a limited number of oxides, such as Al_2O_3 , BeO , Y_2O_3 , HfO_2 , and rare earth oxides, do not decompose SiC during sintering (2300 to 2400K). However, the situation is further complicated by the presence of SiO_2 in a form of a surface oxide on the particles of any SiC powder. Until now, Al_2O_3 , Y_2O_3 , combination of the latter, and a limited number of rare-earth oxides, normally in combination with Al_2O_3 , have been reported to be effective sintering aids for SiC [11-15].

Development of liquid phase sintering of SiC gradually led to a conclusion that the process is very similar to the one of liquid phase sintering of Si_3N_4 . This triggered the attempts of structure tailoring by influencing by means of a variety of techniques the β to α transformation in SiC. The most well investigated and the most straightforward approach to structure tailoring is the implementation of post sintering heat treatment at temperatures of 1950-2000⁰C either in argon or in nitrogen. Such heat treatment results in a partial or complete β to α transformation which, in turn, leads to a heterogeneous grain structure consisting of equiaxed β grains and plate-like α grains. This technique is generally known as in-situ toughening or in-situ reinforcement. This method of structure tailoring has been well developed for Si_3N_4 -based materials [65, 66] and has several advantages over the conventional route, i. e., addition of whisker/platelets/particles to the standard initial powder mixtures followed by hot pressing or sintering. It presents no health hazards associated with whiskers, provides potential to fabricate complex shapes and large size components, to use atmospheric pressure sintering, to have high reinforcement phase volume fraction, to achieve considerable saving in cost of production. However, prolonged heat treatments at high temperatures necessary to trigger and achieve β to α transformation in SiC may result in relatively high weight loss and general degradation of the material [67]. The weight loss severely influences the final density and the microstructure of SiC ceramics. Particularly, the oxide sintering aids, which normally are homogeneously distributed in the green ceramics were observed to segregate and form particular patterns that were dependent on the temperature, sintering time, and the total weight loss. A sequence of heterogeneous reactions volatile products was discussed in [67]. According to the observations of the weight losses occurring during sintering of the SiC- Y_2O_3 - Al_2O_3 compositions in argon, initial weight loss occurs due to the interaction of SiO_2 present in the form of the oxide surface layers on the SiC powder particles with SiC according to the reaction:



According to thermodynamic data, this reaction starts already at 1300-1400 ⁰C. At temperatures higher than 1700 ⁰C the interaction of SiC with Al_2O_3 prevails according to the reaction:

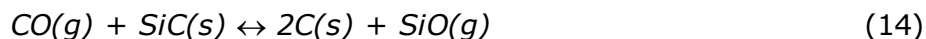


The interaction of SiC with Y_2O_3 is also considered plausible according to the reaction:

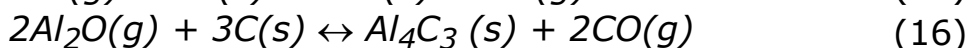
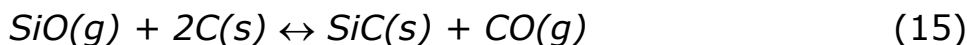


However, due to the lack of data thermodynamics of this reaction was not evaluated. In the opinion of the authors of the present review, the weight loss during heat treatment of SiC doped with Y_2O_3 and Al_2O_3 can be also explained if the parallel is drawn with the known effect of weight loss by yttrium garnet and other yttrium aluminates (such compounds are formed in the materials under discussion, and are present in the form of intergranular phase) via sublimation from the solid state or evaporation of the melt of Al-containing gaseous species at temperature in excess of $1850\text{ }^{\circ}C$ [68], which possibility was not considered for liquid phase sintered SiC previously.

Further, the oxidation of SiC by $CO(g)$ according to the reaction :



was considered as a prevailing one at high temperatures, the formation of $CO(g)$ and the increase of its partial pressure during heat treatment occurring due to the interaction of the previously formed volatile products with the graphite environment of the furnace according to the reactions:



In order to avoid, or at least diminish, the weight loss and microstructural degradation due to extended heat treatment, the so called seeding of the β – SiC based initial powder mixtures with either α – SiC or β – SiC large grains, which assists in controlling and facilitating the β to α transformation during heat treatment of the SiC- Y_2O_3 - Al_2O_3 compositions resulting in the in situ reinforcement with elongated grains [69-72]. Seeding of the β –SiC based compositions with large β – SiC grains yielded a bimodal structure of small matrix grains and large elongated grains. In contrast, the β – SiC based compositions seeded with α – SiC grains had a uniform microstructure consisting of elongated plate-like grains. However, according to [71] the fracture toughness of both seeded materials was very similar (about $5.5\text{ MPa}\cdot\text{m}^{1/2}$), which suggests that optimization of microstructure and hence of the structure-sensitive properties of SiC ceramics is possible by using both α – SiC and β – SiC "seeds". It should be noted that the size of the seeds should be as a minimum 2-3 times of that of the main SiC powder component used, and the amount of seeds normally is about 2-3% . The effect of the seeding techniques on the resulting microstructure of liquid-phase sintered SiC ceramics is shown in [Fig. 6](#).

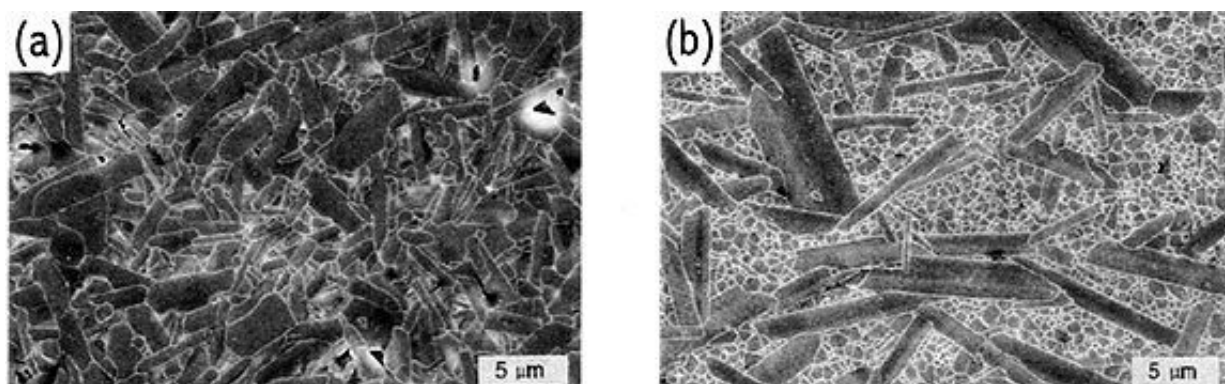


Figure 6: Microstructure of hot-pressed and annealed SiC- Al_2O_3 - Y_2O_3 ceramics seeded with large (a) α -SiC and (b) β -SiC grains.

The influence of the α – SiC/ β – SiC ratio in the starting mixtures of the powders with similar particle size on microstructure formation and properties of liquid-phase sintered SiC-based ceramics was investigated by I.-W. Kim et al. [72]. Their results suggest that there exists an optimal content of α – SiC in the initial mixture, which results both in high flexural strength and fracture toughness. In general, the increase of α – SiC content leads to the improvement of

strength but at the same time the fracture toughness decreases. The observations of properties modification are directly related to microstructural changes (see Fig. 7). The increase of α - SiC content resulted in a more fine and homogeneous microstructure consisting of equiaxed grains. However, with the amount of α - SiC additions not exceeding 10% both microstructure and the relevant mechanical properties were improved. With 10% α - SiC added, the quantitative microstructural analysis established the highest aspect ratio of the elongated grains, while the microstructure itself remained fine. Additions of α - SiC also improved the densification to some extent.

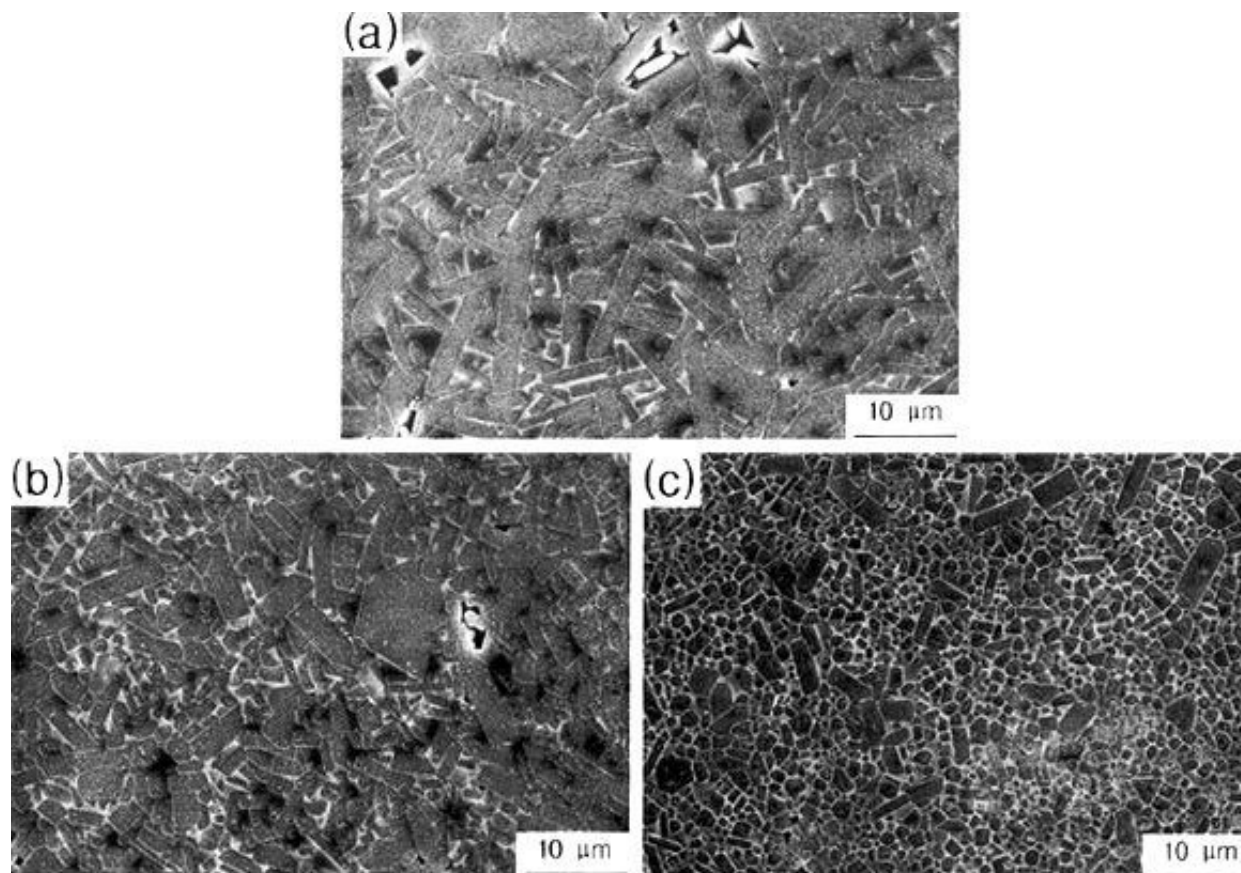


Figure 7: Microstructure of sintered and annealed SiC-Al₂O₃-Y₂O₃ ceramics with different α/β ratio in the starting mixtures: a) 100% β , b) 10% α - 90% β and c) 100% α .

The purpose of the heterogeneous microstructure formation consisting of a fine matrix with some fraction of high aspect ratio plate-like grains imbedded in the matrix is the same as the high aspect ratio prismatic grains formation in Si₃N₄-based ceramics: improvement of fracture toughness of the material. Large elongated grains have been shown to increase in SiC by crack bridging [73, 74] and/or crack deflection, and mechanical interlocking [75]. Recently, a fracture toughness of $>8 \text{ MPa} \cdot \text{m}^{1/2}$ has been reported for liquid-phase sintered SiC with tailored heterogeneous microstructure [76].

An even better sintering behavior of SiC leading to similar microstructure and properties formation was recently discovered for the Y₂O₃-AlN additive system [77, 78]. Initially, the interest in the system SiC-AlN was caused by the possibility of a composite materials development. Both SiC and AlN have many potential applications mainly in electronic and high-temperature fields. Furthermore, it has been found that a series of solid solutions is formed between SiC and AlN over a wide compositional range [79-82], which provides a lot of possibilities in tailoring the materials properties in this system by controlling the phase composition and microstructure. According to a tentative phase diagram of this system [81], SiC and AlN form a 2H solid solution at temperatures in excess of 1850 °C, which decomposes into

two isostructural 2H solid solutions at lower temperatures. During the past decade, the synthesis and properties of SiC-AlN solid solutions have received considerable attention [79, 81, 83-94]. Initially, hot pressing was commonly used to prepare the SiC – AlN solid solution samples from the mixture of SiC and AlN powders [81, 82, 86, 92] but high temperatures (over 2100⁰C) were required to obtain dense solid solution samples with homogeneous compositional distribution. The alternative method proposed approximately at the same time had been to synthesize the solid solution and/or composite powders by carbothermal reduction with subsequent densification by hot or hot isostatic pressing [78, 84, 85].

Later, pressureless sintering was successfully applied to this group of materials and mostly Y₂O₃ was used as a sintering aid, densification occurring via liquid phase sintering [95-98]. Materials with high densities (up to 98% TD) and good mechanical properties were developed. A mechanism of microstructure formation during sintering of these materials was proposed by Y. – B. Pan et al. in [98] as it is schematically presented in Fig. 8. Because the evaporation of AlN far exceeds that of SiC at temperatures higher than 1950 ⁰C, first AlN vaporizes from the large powder particles surface, which decrease in size, then AlN is deposited on the surface of SiC powder. Subsequently, AlN deposited on the SiC particles surface diffuses into the SiC grain body, and finally SiC and AlN form a SiC – AlN solid solution layer on the surface of SiC grains. This mechanism was proved by transmission electron microscopy (TEM) investigations. For complete overall homogeneity of the material to be achieved further extended heat treatments are necessary.

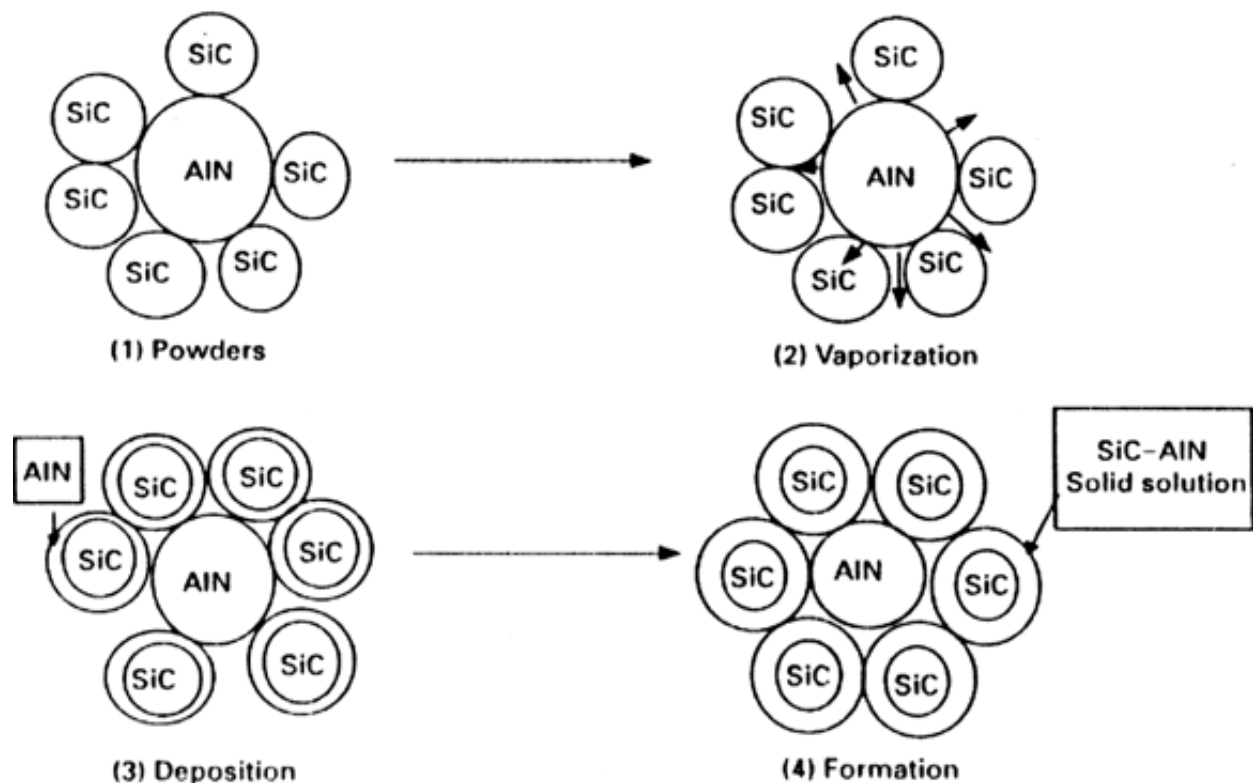


Figure 8: Schematic representation of microstructure formation during sintering of SiC-AlN composites after Pan *et al.* [98].

As it can be seen, the above described group of materials is characterized by relatively high AlN content, sometimes AlN being the main component, while Y₂O₃ was added in minor quantities as a sintering aid. It may also be noticed that AlN does not react with SiC the same way as Al₂O₃ and its presence in the mixtures with SiC does not lead to severe weight loss during sintering. On the other hand, the investigation of AlN – Y₂O₃ system [99] produced a tentative phase diagram (see Fig. 9), which shows the extensive liquid phase formation for certain compositions at about 1850 ⁰C. Exactly these considerations led to active investigations of the

possibility of liquid phase pressure-less or gas-pressure sintering of SiC with on the average, 10 vol.% of Y_2O_3 - AlN sintering aids content, Y_2O_3 being the major component of the sintering aids formulation, i. e., AlN being used as a substitute of Al_2O_3 in the sintering aids systems [75, 77, 78, 100].

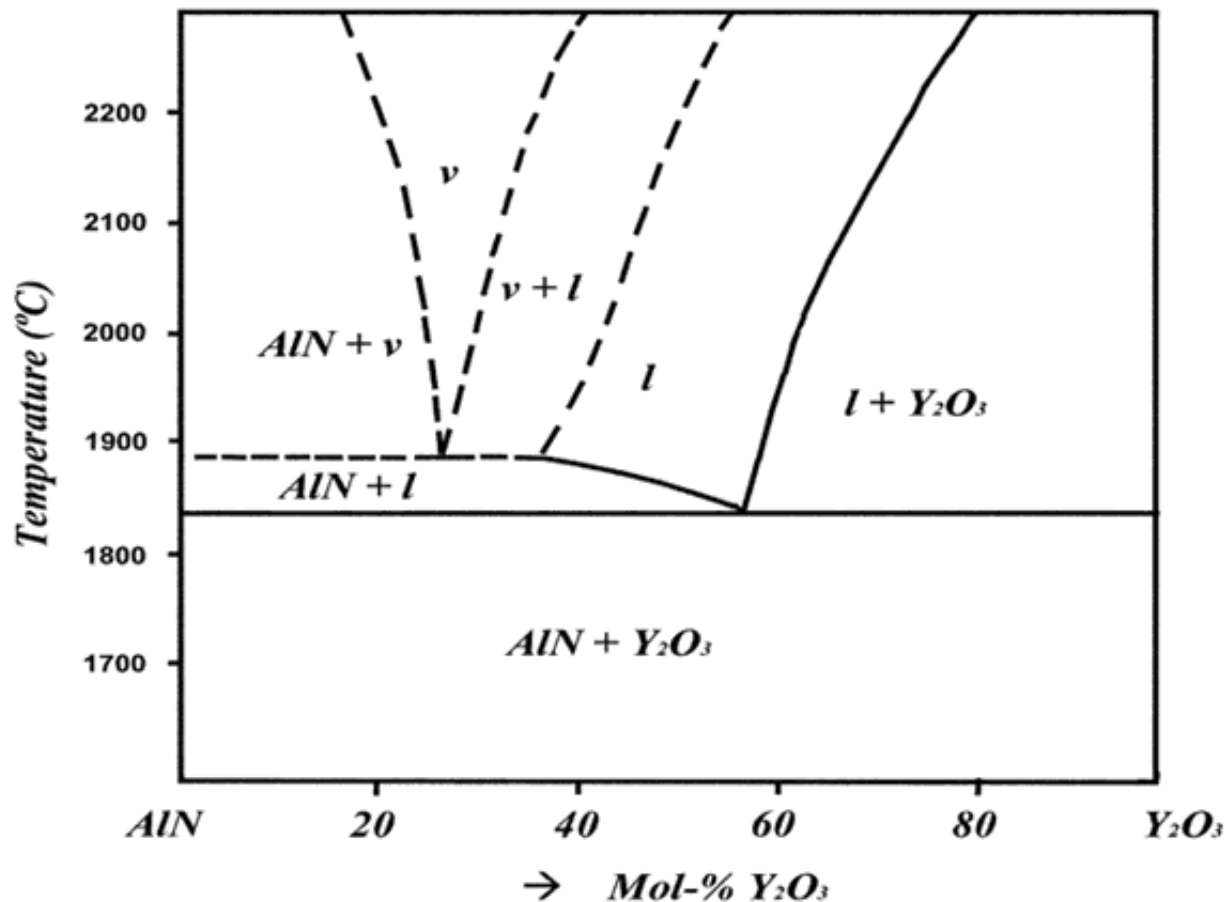


Figure 9: Tentative phase diagram of the AlN- Y_2O_3 system after Jeutter [99].

However, until present time there is a very limited amount of data on the liquid phase sintering of SiC with the AlN and Y_2O_3 sintering aids. Moreover, some of existing data are contradictory. For instance, successful sintering of various compositions SiC-AlN- Y_2O_3 both in argon and nitrogen atmosphere, with and without gas overpressure, was reported. However, some of the authors [75, 101] claim that sintering in nitrogen both under normal and high (up to 10 MPa) pressure results in a completely homogeneous microstructure and phase distribution in the material, while sintering in argon leads to secondary phase segregation and highly inhomogeneous microstructure in the whole bulk of the sintered body. Other investigations, including the one performed by the authors of the present review [78, 100], observed the opposite effect. Such contradiction may be partly explained by the use of different compositions, especially the different formulation of the sintering aids. This leads to a conclusion that further systematic experimental work is necessary for the full understanding of the regularities of the phase and structure formation under conditions of liquid phase sintering of this undoubtedly promising group of ceramic materials.

CONCLUSIONS

Silicon carbide based ceramics represent a family of covalent ceramics promising for a great number of technical applications. The recently discovered method of densification of these materials by means of liquid phase sintering, as well as the apparent similarity of the behavior of SiC under such conditions with the one of a much more well researched Si_3N_4 , provides

excellent possibility for structure and properties tailoring. The complicated nature of the crystal structure of SiC, namely its polytypism, although somewhat complicating the picture, if well understood may be an additional instrument in premeditated modification of materials properties.

The discovered transformation-controlled grain growth mechanism similar to the one operating in Si₃N₄ –based materials enables to transfer the vast knowledge accumulated with the latter group of materials during past decades to the research of SiC –based ceramics processing.

Overall, the recent findings indicate that a good basis for further systematic research of SiC –based materials has been made and this group of materials will be a next candidate for profound research.

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