(54) Title: DENSE CERAMIC PRODUCT

(57) Abstract

A process for the production of dense polycrystalline silicon carbide shaped articles, comprises (a) heating a powder compact containing silicon carbide and alumina or a precursor thereof to an intermediate temperature, and maintaining the said intermediate temperature for an extended dwell, and then (b) heating the product of step (a) to a higher temperature for sufficient time to produce a dense polycrystalline silicon carbide product.

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DENSE CERAMIC PRODUCT

This invention relates to a process for the
production of dense polycrystalline silicon carbide shaped
articles and the superior shaped articles produced by the
process. In one aspect the invention provides a new firing
cycle for the production of dense polycrystalline silicon
carbide shaped articles. In accordance with this firing
cycle, powder compacts containing silicon carbide and
alumina or a precursor thereof are first heated to an
intermediate temperature, as will be explained in more
detail below. After an extended dwell at the intermediate
temperature, the temperature is raised in a second stage to
a higher temperature to complete the densification process.

In the second stage, magnesia or a precursor
thereof may optionally be present as a sintering assist,
and the atmosphere is essentially carbon monoxide. It is
preferred that the original compact contains magnesia, or a
precursor thereof, but the magnesia may be introduced
during the firing cycle. Depending upon the particular
conditions, it may also be advantageous to have a
controlled amount of carbon present, as will be explained
in more detail below. In a preferred embodiment of the
invention, the first stage is carried out in an inert
atmosphere such as argon, and the atmosphere is changed
after the intermediate temperature dwell, for example by
purging the furnace chamber and introducing carbon monoxide
for the remainder of the firing cycle.

BACKGROUND OF THE INVENTION

Shaped articles comprising high density
polycrystalline silicon carbide are well known. They are
characterised by excellent physical properties such as high
resistance to thermal shock, abrasion and oxidation
together with high levels of strength and thermal

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conductivity. It is this combination of properties which
makes silicon carbide materials leading candidates for
engineering applications. However, the production of
satisfactory high density materials has been fraught with
5   difficulties.

          Early workers (eg Alliegro, Coffin and Tinkepaugh
J. Amer. Ceram. Soc., 39 [11] 386-89 [1956]) showed that
silicon carbide could be hot pressed to high density bodies
with the aid of sintering aids such as aluminium and iron,
10   and aluminium plus one of the metals zirconium, boron or
iron. It was further disclosed that for the hot pressing
of silicon carbide, magnesium additions and magnesium and
aluminium additions were ineffective, and impaired the
densification process as compared to a control sample of
15   silicon carbide, hot pressed under identical conditions
with no additives or additions. Lange (J. Mater.
Sci.(10[1975]314-320) disclosed the hot pressing of silicon
carbide using alumina as the densification aid. The
limitations of hot pressing for the attainment of dense
20   bodies are well known.

          The selection of suitable densification aids for
the sintering of silicon carbide has been considered by
Negita (J. Am. Ceram. Soc. 69[12]C308-10 [1986]). Using
thermodynamic arguments it was found that metal additives
25   such as boron, aluminium, iron, nickel and cobalt could be
effective densification aids. Using these principles,
alumina, beryllia, yttria, hafnia and rare earth oxides are
considered to be potential densification aids as they do
not decompose silicon carbide during sintering. Metal
30   oxides including zirconia, calcia, magnesia are not
considered suitable as they tend to decompose silicon
carbide to metallic silicon. In addition the use of carbon
with metal oxide additions was reported to be beneficial
for oxides such as alumina, beryllia, ytrria, rare earth

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oxides, calcia, zirconia, and hafnia. It is stated that
the carbon is added to react with the said oxides to form
the corresponding metal carbide and silicon metal. the
formation of the metal carbides was seen as desirable. In
5   the process according to the present invention, the
formation of such metal carbides was not observed.
Furthermore, in contrast to the work of Negita, in the
current work it has been found that the reaction of carbon
with the metal oxide densification aids is undesirable and
10 impairs the densification of the bodies. This indicates
that the role of carbon in the present work is different to
that proposed by Negita and others. In addition, given the
unstable nature of metal carbide phases, for some even in
air at room temperature, the formation of such phases is
15 seen as undesirable and are avoided in the present
invnetion. This aspect will be discussed in greater detail
for the calcia system.

        The work of Cutler and Miller (US Patent
4,141,740) describes a process for a refractory product
20 based on silicon carbide containing at least 1% by weight
of aluminium nitride and at least 1% by weight aluminium
oxycarbide. The presence of metal impurities (other than
aluminium and silicon) were seen to be detrimental to the
process and are limited to 0.1 percent by weight or less.
25 No indication was given as to the properties of such bodies
and the ease at which they can be made into dense bodies
with desirable physical properties and the commercial
utility of the process. Further work in this system was
described by Virkar et al in International Patent
30 application WO87/01693, where the pressureless sintering of
silicon carbide-aluminium nitride-aluminium oxycarbide
containing materials was described. A major drawback of
the process as disclosed is that the materials must be
heated at very rapid rates to minimise volatilisation of

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the active densification species. This could pose problems
for the production of large parts in which differential
sintering as a result of thermal gradients can lead to
distortion and ultimately to micro cracking due to thermal
5   stresses inevitably present as a result of the described
firing cycles. This would. make the maintenance of the
desired physical properties difficult. In addition, the
undesirable presence of aluminium oxycarbides in the final
body may prove difficult to avoid.

10   In Suzuki et al. (US Patent 4,354,991) the use of
aluminium oxide to densify silicon carbide is described.
In the process as described the use of non-oxidative
atmospheres is taught. These include nitrogen, carbon
monoxide, helium and argon. It is taught that argon or
15   helium are preferable and that the atmosphere should
preferably contain aluminium, silicon or carbon. In one
method, it is proposed that mixtures of these gases be fed
into the reaction chamber with a carrier gas such as
nitrogen, argon and helium. In another method, the use of
20   a powder bed or sintered product capable of generating the
gases around the silicon carbide article to be densified
was disclosed. It was a teaching of the document that it
is unnecessary to remove the silica present on the surface
of the silicon carbide. In fact it was stated that it is
25   feasible to add silica as a raw material. This is in
contrast to the present invnetion where the presence of
this phase has been found to exert a deleterious effect on
the densification behaviour at high temperatures and will
be explained later on. The fired bulk densities obtained
30   were inferior to those achieved by the present invention.
In addition, the sintering times were much longer. For a
continuous process for the densification of bodies, the
significantly longer reaction times for densification would
result in lower production rates.

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In the work of Fuentes US Patent 4,876,226 the
use of alumina and calcia as densification aids for silicon
carbide was disclosed. It was a requirement of the
invention to form liquid phases cdomprising aluminium

5   oxycarbides at the sintering temperatures to promote
densification. The addition of calcia was to increase the
amount. of the aluminium oxycarbide liquids and enhance
densification. It was further disclosed that the addition
of free carbon is preferred. It is believed that in the

10   system described by Fuentes, the addition of free carbon is
to react with aluminium containing phases to produce or
further enhance the formation of the oxycarbide phases
which are a requirement for the process. The level of free
carbon additions were prefereably greater than 0.4 % by

15   weight. No indication was given to an upper limit for the
carbon addition. This is in contrat to the teachings of
the present invention, where the reaction of carbon with
the aluminate phase is believed to be detrimental to the
densification process. It is claimed that the technique

20   excludes the use of rare earths but no reference was given
for their deletion. Indeed, in the work of Omori et al (US
Patent 4,569,921) the use of calcia and precursors for the
oxides of aluminium and rare earth elements for the
pressureless sintering of silicon carbide was disclosed

25   with excellent results. In addition, it has been reported
by Foster et al (J. Am. Ceram. Soc. 39[1]-11 [1956]) that
aluminium carbide and aluminium oxycarbide, the latter at
least required for the process as outlined, are very
unstable towards both moisture an xygen. They taught

30   . that these materials should not be used in applications
where these species are likely to be encountered. In the
process as disclosed, such aluminium oxycarbide species are
a key element of the process. The presence of such species
is expected to greatly degrade the performance and severely

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limit the suitability of the said materials. In the
present invention, aluminium oxycarbides, such as Al_4O_4C
and Al_2OC, have not been observed and their presence is not
a prerequisite for the process disclosed herein. Thus the
5   process and product as disclosed herein overcomes
significant disadvantages of the process as disclosed by
Fuentes.

          The use of rare earths and alumina as sintering
assists for silicon carbide has been disclosed (eg see
10   Mulla and Krstic Bull. Amer. Ceram. Soc. 70[3]439-443
[1991]). In order to obtain high density bodies, the
components had to be encapsulated in closed threaded
graphite crucibles sealed with graphite foil. It was
revealed that bodies could be produced with over 95% of
15   theoretical density and weight losses of less than 1
percent. When the same experiments were carried out
without encapsulation, the resulting bodies obtained less
than 80 percent of theoretical density and weight losses up
to 20 percent were recorded. Culter and Jackson (pp309-
20   318 in Ceramics Materials and Components for Engines,
Proceedings of the Third International Symposium, Las Vegas
NV 1988) also disclosed the use of yttria and alumina for
the sintering of silicon carbide. Although high density
bodies could be produced, the recorded weight losses were
25   high and increased with increasing temperature. The
decomposition reactions between the sintering assists and
the silicon carbide were cited as a major problem. As in
the case of Mulla and Krstic only very short times were
used, typically of 5 minutes duration at the maximum
30   temperature. The requirement to subject samples to minimum
times at high temperatures is considered difficult to carry
out on a commercial scale especially for the manufacture of
larger components or where large furnace loads are used.
This can lead to large thermal gradients giving rise to

problems such as differential sintering, leading to
distortion of the fired bodies. This would greatly reduce
the application utility of the process.

5   DESCRIPTION OF THE INVENTION

This invention provides a dense silicon carbide
product and a method of producing the same without the use
of pressure assisted processes such as hot pressing or hot
isostatic pressing, the use of boron or boron compounds and
10   carbon, the use of powder beds or the requirement for
sealed containers. It is an object of the present
invention to overcome the difficulties of existing
technologies and produce useful products based on silicon
carbide. This is achieved by the addition of sintering
15   assists, and by providing an environment in terms of
temperature and atmosphere that is conducive to
densification. It is believed that the densification of
the powder compacts is a result of a liquid phase sintering
mechanism (LPS).

20   In the sintering of silicon carbide by techniques
such as LPS, it is believed that it is crucial to maintain
the effective sintering aids within the body. In the
temperature range at which densification occurs, these
additives react to form a liquid phase into which silicon
25   carbide has some degree of solubility. In the initial
stages, the liquid which forms at high temperatures allows
densification by particle rearrangement. This is usually
followed by a solution precipitation step followed by a
stage characterised by grain growth.   If, as appears to be
30   the case, it is the liquid phase that is facilitating the
densification, the premature loss of sintering aids is to
be avoided. The use of excessive amounts of sintering aids
to compensate for the loss thereof is also to be avoided as
this results in increased cost, and can also result in the

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deposition of unwanted species in the cooler parts of the
furnace. In addition, the loss of sintering assists can
result in compositional gradients. These species can be
unstable with regard to the atmosphere and can result in
5   damage to the furnace and make the manufacture of
components hazardous. Thus, it is important in the
efficient manufacture of components to minimise the loss of
raw materials.

The use of powder beds in the manufacture of LPS
10   silicon carbide is known. The role of a powder bed is to
provide a suitable environment. However, there are major
drawbacks to the use of powder beds. These are:

Additional cost of the powder bed.

15   Additional costs associated with the increased
number of handling operations such as loading and
(after the firing) unloading the samples from the
powder bed.

20   Poor surface finish especially where the samples
are in prolonged contact with the powder bed.

The powder bed by providing active species for
the densification can result in warping or
25   distortion of the bodies as a result of gradients
of densification aids therein, and densification
gradients which can also lead to warping and
distortion of the bodies.

30   The use of sealed containers to encapsulate the
bodies to avoid the loss of volatile constituents also
imposes limitations for large scale production of bodies,
as a result of additional costs associated with increased
number of unit operations required to produce components,

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such as the requirement to load the samples into the sealed
containers.

DETAILED DESCRIPTION

5   Although it will be clearly understood that we do
not wish to be limited by any postulated or theoretical
mechanism for the observed beneficial results of the
process of the present invention, we do offer the following
discussion of what is believed to be the underlying
10   chemistry involved.

              According to the present invention a dense
product is produced which contains at least 65 weight
percent silicon carbide with the remainder substantially an
aluminate. Part or all of the aluminate may also
15   optionally contain magnesium in the form of spinel. The
spinel phase is not necessarily stoichiometric with respect
to the magnesium to aluminium ratio. The preferred
composition range, expressed as the equivalent amount of
oxide, for the product is alumina 3 to 35 weight percent;
20   and magnesia 0.01 to 5 weight percent. In addition, the
product may optionally contain silicon, aluminium or glassy
phases or a combination of the said phases. The presence
of alumina in the α-corundum form is typical when the
aluminium to magnesium ratio in the samples is high and or
25   the firing temperatures in the upper part of the specified
range are employed.

              Useful materials can be produced when the
sintering aids are added to finely divided silicon carbide
powder and the resultant mixture can be processed using
30   traditional ceramic processing techniques to form
consolidated powder compacts. The said materials are
heated using a two-stage firing cycle and densification of
the body results. The materials can be conveniently
densified in the temperature range of 1700°C to 2200°C,

with or without the application of pressure. It is
appreciated that the application of pressure can be useful
in reducing the temperature at which the densification is
carried out in order to produce a dense body, but is not a
5   prerequisite for the process.

It is thought that the additives interact to form
a liquid which promotes densification by a liquid phase
sintering process. The use of magnesium and aluminium
(both in the form as either oxides or their precursors; or
10   alternatively as a magnesium spinel or a mixture of the
aforementioned species, facilitates densification and the
ultimate formation of an aluminate grain boundary phase.
Depending on the starting compositions and the firing cycle
employed, the aluminate may be present in total or part as
15   a magnesium aluminate (or magnesium spinel). Furthermore,
magnesium spinel can exist as a solid solution
$(MgO)_x.(Al_2O_3)$, where x is less than or equal to 1. Thus
the grain boundary phase can accommodate shifts in chemical
composition without the formation of additional phases.
20   This is an important consideration for a high temperature
reaction such as the pressureless sintering process, where
the control and maintenance of volatile species (such as
magnesium and aluminium) could prove difficult and
expensive to carry out in practice.

25   At the higher temperatures used to promote
densification the said magnesium spinel which forms in the
body or is deliberately added, may undergo further change
leading to an increase in the aluminium to magnesium ratio.
This may continue to the point where the magnesium is
30   essentially lost from the body. It is also possible that
aluminium may be lost from the bodies during the firing
cycle. If the process continues still further, ultimately
aluminium metal or aluminium alloy may be detected in the
body.

The attainment of a suitable environment is a requirement for the successful densification of silicon carbide by the method of the present invention. It is an aim of the present invention to provide conditions
5   conducive for the densification of the bodies. It is considered that the formation of suitable liquids is a requirement of the process to produce high density bodies. In this regard it is important that the active species, responsible for the densification of the body, are retained
10   in the body until such times as the densification is completed or reaches such levels that other mechanism(s) can lead to the attainment of a high density bodies. This is common to liquid phase sintering techniques where it is a requirement that the liquid be stable. In addition, it
15   is a condition that unwanted components are removed by such techniques as volatilisation or decomposition and formation of phases that assist or do not interfere with the densification processes.

There are number of conditions that must be
20   satisfied in order to obtain useful products. These conditions relate to ensuring that the silicon carbide and the liquid phase responsible for densification, are stable at the densification temperature. At the high temperatures required for densification, the solid and liquid phases
25   require vapour pressure of elements, sub oxides and other vapour species to remain stable. The bodies generate their own stable atmosphere through partial decomposition of the said phases, but this decomposition should not be such that the generation of the stable atmosphere depletes the liquid
30   phase to such an extent that densification is so retarded or inhibited that it is not possible to make dense bodies.

It is advantageous to maintain a favourable effective sample volume to furnace volume, thus limiting the amount of decomposition of the solid and liquid phases

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to gaseous species and ensuring an adequate level of
additives remain in the body to obtain a dense body. This
coupled with a carbon monoxide atmosphere in the second
stage of the process, are successfully used to suppress the
5   amount of decomposition of these phases without the need to
resort to other means, such as powder beds or the
introduction of active species into the hot zone from
external sources. The importance of this aspect will be
illustrated with some of the findings of this
10   investigation.

For the production of bodies with thicker cross
sections, significant differences in fired bulk density can
occur on the inside with respect to the outside of the body
(coring). This can ultimately lead to cracking of the body
15   after fabrication. It is believed this behaviour is the
result of the presence of phase(s) that interfere with the
densification processes by either changing the nature of
the liquid phases or which decompose at the middle to
higher temperatures used. The densification of the bodies
20   is such that it is difficult to eliminate cores from the
interior of the thicker bodies. From the foregoing it can
be appreciated that the critical thickness above which the
formation of cores is a problem will depend on a number of
factors such as heating rate, stacking geometry of samples
25   in the furnace, effective gas flow rate, level of porosity
and pore size of the body.

The use of argon for the sintering of samples
results in the formation of dense bodies. However, an
unwanted competing reaction is the decomposition of the
30   silicon carbide. It is considered that this is a
consequence of the reaction of the sintering assists with
the silicon carbide. This leads to the formation of
silicon which condenses on the bodies with a deterioration
of the surface finish. It can also lead to the

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condensation of silicon on the contact points of the
samples with furnace furniture or other bodies making the
removal or separation of the bodies extremely difficult.
It is anticipated that the generation of silicon is the
result of the unwanted reaction of alumina with the silicon
carbide (for example see reaction 1):

$$2SiC + Al_2O_3 \rightarrow 2Si_{(1)} + Al_2O_{(g)} + 2CO_{(g)} \qquad .....(1)$$

The condensation of the silicon can be avoided by
the use of an atmosphere containing carbon monoxide. This
leads to a greatly improved surface finish. To suppress
reaction (1), at the upper end of the temperature range
used for the densification, a partial pressure of carbon
monoxide greater than one atmosphere is required. This
temperature is estimated to be of the order of 2100°C. It
has been found that at low temperatures there are
unfavourable reactions between the powder compacts and the
cabon monoxide furnace atmosphere. It is anticipated that
below roughly 1550°C the following reaction is
thermodynamically feasible and can proceed left to right.

$$SiC + 2CO \rightarrow SiO_2 + 3C \qquad .....(2)$$

Above roughly 1550°C in one atmosphere of carbon
monoxide reaction 2 goes from right to left (see reaction
3).

$$SiO_2 + 3C \rightarrow SiC + 2CO \qquad .....(3)$$

In addition, it is also possible that some of the
silica formed by reaction 2 can react according to reaction
4.

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$$SiC + SiO_2 \rightarrow 2SiO_{(g)} + C \qquad \qquad \ldots\ldots(4)$$

Further, the free carbon present can react with the aluminate phase leading to its decomposition and impairing the densification process (see reaction 5).

$$Al_2O_3 + 2C \rightarrow Al_2O_{(g)} + 2CO \qquad \qquad \ldots\ldots(5)$$

It must be appreciated, that as a raw material, the silicon carbide powder is inevitably covered by an oxide layer of silica. As silica is detrimental to the densification of bodies, it must be removed. This can be achieved by decomposition to gaseous species such as silicon monoxide (see reaction 6).

$$2SiO_2 \rightarrow 2SiO_{(g)} + O_{2(g)} \qquad \qquad \ldots\ldots(6)$$

For thinner bodies this reaction can proceed with the silica being removed by a decomposition reaction such as reaction 6. However, for thicker bodies the time required to remove this phase is appreciable. An alternative is the deliberate addition of carbon to react with the silica phase (reaction 3) to produce silicon carbide in the lower to mid temperature ranges of the firing cycle. Depending on the thickness of the components, stacking geometry and the furnace configuration the use of dwells can prove beneficial to ensure that this phase is removed. The carbon addition should be added such that it is sufficient to remove the silica phase only to prevent unwanted reactions such as reaction 5. The dwells or slow heating rates are also important to ensure that the amount of gas liberated, does not cause a pressure build up greater than the cohesive strength of the compact, leading

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to the formation of cracks. The use of slow heating rates
is in to contrast with much of the teachings of the prior
art.

5   Thus the presence of either or both the silica or
carbon at the higher temperatures at which densification
occurs, react to produce an unstable phase or phases. It
is believed that internal stresses are generated within the
body when the internal pores are closed off from the
outside atmosphere. At high temperatures these stresses
10   are sufficient to overcome the cohesive strength of the
compact, resulting in the rupture of the body. This
manifests itself in the bodies after firing exhibiting
macro cracks.

           The use of nitrogen for the densification of
15   bodies is not suitable as a result of unfavourable reaction
of the constituents of the bodies with the atmosphere to
form stable compounds. These compounds reduce the amount
of liquid present at high temperatures available for
densification. It is considered that this is the result of
20   the reaction of alumina with the silicon carbide in a
nitrogen atmosphere to produce aluminium nitride. The
formation of stable aluminium nitride is accompanied by a
corresponding decrease in the amount of liquid phases
necessary to allow densification to proceed by liquid phase
25   sintering. A possible reaction is as follows:

$3SiC + 2Al_2O_3 + 2N_{2(g)} \rightarrow 4AlN + 3SiO_{(g)} + 3CO_{(g)}$ .....(7)

           This demonstrates the importance of maintaining
30   the presence of the liquid phase at least until
densification is essentially completed.

           It has been found that the use of an inet
atmosphere below 1550°C and preferably at least 1600°C, but
below the termpatures at which the onset of the unwanted

reactions such as reaction 1 occur, is beneficial for the production of useful products. Thus at the temperatures at which there are unfavourable reactions between the silicon carbide based bodies and the carbon monoxide atmosphere,

5   the use of an inert atmosphere such as argon or possibly nitrogen can be used. Above this temperature the furnace chamber is purged and carbon monoxide is introduced into the hot zone for the remainder of the firing cycle. The temperature in the reaction zone is such that the unwanted

10 and detrimental reaction which leads to cracking of the body does not take place. In addition, the unwanted formation of silicon on the body is avoided.

An alternative is to use reduced pressure in the furnace chamber below 1550°C. Thus the unwanted reactions

15 of carbon monoxide with the compacts is avoided. Above this temperature, carbon monoxide is introduced into the reaction chamber to prevent the unwanted formation of silicon at high temperatures.

When it is the intention to produce bodies with

20 thicker cross sections, it has been found that it is advantageous to take steps to deliberately remove the silica from the system as this phase, or the oxide-based reaction product formed from the said phase with other phases present, interferes with the uniform densification

25 of the said bodies. For such bodies it can prove difficult to remove this phase by processes such as decomposition and diffusion. This phase as described can persist at higher temperatures. It has been found that carbon added according to equation (3) to react with the silica present

30 on starting materials is beneficial in eliminating the presence of low density cores in the fired samples. Care has to be taken to ensure that the evolution of gaseous species expected to be carbon monoxide does not lead to the cracking of the bodies. Further to this it has been found

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beneficial to hold the sample at a temperature at which the
reaction (3) is feasible and can proceed left to right at
an appreciable rate to ensure that the reaction is
essentially complete before heating to a higher temperature
5   but the rate of release does not lead to cracking of the
bodies. Note, it is thought that reaction 3 should be
essentially completed before heating above the equilibrium
temperature for the reaction in one atmosphere of carbon
monoxide. Under these conditions the generation of carbon
10   monoxide can exceed one atmosphere and produce conditions
which are condusive to cracking. Adding too much carbon
according to reaction (3) for the amount of silica present
leads to an observed decrease in the fired bulk density.
It is believed this is as a result of the unwanted reaction
15   of the residual carbon with oxides phases. This is in
contrast to the work reported by Fuentes where the reaction
of carbon with aluminium containing phases to produce
oxycarbides is beneficial.

It is hypothesised that when carbon monoxide
20   atmospheres are used exclusively, the use of extended
dwells above the 1600°C may overcome the problems
associated with the use of this atmosphere at low
temperatures that manifests itself in the macro cracking of
the samples. It is the intention that the use of an
25   interrupted firing cycle with a dwell above that
temperature at which the carbon monoxide adversely reacts
with the bodies but below the temperatures at which
densification occurs leading to sealing off of the internal
pores from the surface, thereby trapping volatile products
30   in the bodies could prove advantageous. It is speculated
that the use of temperature dwells above about 1550°C say
1600°C, but below the onset of extensive densification, in
particular before sealing of porosity of the bodies,
estimated to be around 1900°C could prove to be effective

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in preventing cracking. The firing cycle would be
continued after such times as the unwanted species have
been removed and the sample would then be heated to the
final sintering temperature to densify the powder compact
5   into a dense useful body.

The importance of the requirement to retain the
densification aids has been discussed. At the high
temperatures used for the densification of the bodies, the
vapour pressures of the various elements and other species
10   can be significant. A consequence of this is to limit the
unwanted reactions. In a static environment, the vapour
pressure of a species will be determined by thermodynamic
and kinetic considerations. At the temperatures used, the
rates of the reactions are typically rapid and thus the
15   main consideration are the thermodynamics of the reactions.
The amount of material in the hot zone is an important
variable. If insufficient material is fired, the amount of
decomposition (reflected in the weight loss after firing)
will be unacceptable and in extreme cases densification of
20   the body will not be achieved. The decomposition is the
result of the generation of the vapour species in the
atmosphere. The actual partial pressure of the species can
be predicted using thermodynamic calculations. The vapour
pressure is thus limited to either the equilibrium partial
25   pressure or until all the phase in question is consumed in
trying to establish the equilibrium partial pressure.
Depending on parameters such as the effective furnace
volume and its construction, as outlined previously, it is
possible to limit the amount of decomposition and
30   generation of a stable partial pressure of volatile species
without significantly changing the starting composition of
the samples and adversely affecting the densification of
the body. Furthermore, by incorporation of some of the
gaseous reaction products, specifically carbon monoxide,

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into the furnace atmosphere from external sources it is
possible to minimise decomposition of the samples using Le
Chatelier principle.

5   A method of forming a dense silicon carbide
product is disclosed without the use of boron, or boron
containing compounds and carbon associated problems of
uncontrolled grain growth degrading the physical properties
or alternatively the use of powder beds or the use need to
introduce active densification aids into the furnace
10   chamber via the furnace atmosphere.

The present invention will be further illustrated
by examples in a non limiting manner.

BRIEF DESCRIPTION OF THE DRAWINGS

15   In the accompanying drawings:
Figure 1 illustrates data relevant to Example 26
below.

EXAMPLES

20   In the following examples all quantities are
expressed in parts by weight, unless otherwise specified.

Example 1

The raw materials used were α silicon carbide
25   from Lonza known as grade UF10; alumina from Alcoa known as
grade A16SG; and magnesia from Ajax (Analytical Grade).
The powders were weighed and ball milled using silicon
carbide milling media. The conditions used for this
operation are shown in table 1.

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Table 1

Conditions used for ball milling operation

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Time	16 hours
Powder	300 g
Milling Media	1500 g
Fluid	600 ml iso-propanol
Binder	2 wt%

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After milling, the milling media was separated
from the slurry which was subsequently spray dried. The
powder was unaxially pressed using a steel die and punch
set and cold isostatically pressed at a pressure of 150 MPa
15 into a 70 mm square tile. The sample was then heated in
air to 400°C and held for 5 hours to remove the binder.
The sample was placed in a graphite work box with a loose
fitting lid. The work box was heated in a graphite
resistance furnace in an atmosphere of argon. At 1600°C
20 the furnace was evacuated and backfilled with carbon
monoxide (see table 2). The specimen after firing had a
smooth surface finish. The starting compositions and
results are given in table 3.

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Table 2
Firing Cycle

Heat at $1400°C.min^{-1}$ in Ar

Hold for 60 minutes

Heat to 1600°C at $5°C.min^{-1}$

Hold for 30 minutes

Evacuate and backfill with CO

Heat to 1900°C at $5°C.min^{-1}$

Heat to 2030°C at $2.5°C.min^{-1}$

Hold for 60 minutes

Cool at $10°C.min^{-1}$

Table 3
Sample Details

Example	1	2	3	4
SiC	87.8	87.8	87.8	87.8
Al_2O_3	10.7	10.7	10.7	10.7
MgO	1.4	1.4	1.4	1.4
Atmosphere	Ar/CO	Ar	CO	N_2
Mass(g)	164	174	179	147
GBD($g.cc^{-1}$)	1.70	1.69	1.72	1.75
FBD($g.cc^{-1}$)	3.16	3.08	3.16	2.07
Wt Change%	-5.9	-8.7	-8.2	-10.7
Comments	1	2,3	4	5

Where 1   Good surface finish   GBD   Green Bulk Density

2   Silicon on surface   FBD   Fired Bulk Density

3   Poor surface finish

4   Cracked

5   Sample porous

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Comparative Example 2

                The specimen preparation and the firing cycle
were the same as for Example 1 with the exception that
there was no evacuation step with backfill at 1600°C and an
argon atmosphere was used exclusively. After firing the
specimen had surface deposits of silicon (see table 3).
The surface finish of the specimen was rough in comparison
the specimen prepared according to example 1.

Comparative Example 3

                The specimen preparation and the firing cycle
were the same as for Example 2 with the exception that
carbon monoxide was used for the complete firing cycle.
After the firing operation, the surface finish of the
specimen was the same as example 1, however, the sample was
badly macro cracked and distorted (see table 3).

Comparative Example 4

                The specimen preparation was the same as Example
2 except that a disc 65 mm in diameter was used. The
firing cycle was the same as Example 2 except that nitrogen
was used. After the firing the sample had not densified to
any appreciable extent (see table 3).
                From the results in table 4 it can be seen the
advantage of the two stage firing cycle. This results in a
higher fired bulk density than the use of argon or nitrogen
atmospheres and eliminates the macro cracking observed with
the use of carbon monoxide only atmospheres. In addition,
it is possible to use relatively slow firing cycles and
still produce useful components. This is important for the
mass production of samples using large furnace loads or the
manufacture of large components where it is not often not
practical or feasible to use rapid heating rates.

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Comparative Examples 5 - 8

Samples were prepared according to Example 1 with the exception that discs 65 mm in diameter were used. The firing cycle used was identical to that used for Example 3

5   except for the dwell time at the maximum temperature. The results of the firings are given in table 4.

Table 4

10   Sample Details

Example	5	6	7	8
SiC	87.8	87.8	87.8	87.8
Al_2O_3	10.7	10.7	10.7	10.7
MgO	1.4	1.4	1.4	1.4
Atmosphere	CO	CO	CO	CO
Mass(g)	147	147	147	147
GBD($g.cc^{-1}$)	1.73	1.78	1.78	1.77
Time(min)	0	30	45	60
FBD($g.cc^{-1}$)	2.86	3.02	3.07	3.13
Wt Change%	-4.8	-6.2	-7.5	-8.7
Comments				Cracked

From the results listed in table 4, cracking only occurs at the later stages of the densification.

30 Furthermore, it is thought that this behaviour occurs after the sample has reached the closed porosity stage. It is well known that there is a general inverse relationship between the level of porosity and strength for such materials. The inability to produce crack free bodies with

35 low levels of porosity would greatly limit the application of such materials.

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<u>Comparative Examples 9-13</u>

       The samples were prepared according to the method
of Example 1, with the exception that 25 mm discs were
used. For samples heated to 1400°C and higher in the

5   atmospheres indicated, the samples were held at this
temperature for 60 minutes prior to heating the maximum
temperature. Samples 9, 11 and 12 were heated to the
maximum temperature and cooled. The results of the firing
are given in table 5.

10

Table 5
Sample Details

Example	9	10	11	12	13
SiC	87.8	87.8	87.8	87.8	87.8
Al_2O_3	10.7	10.7	10.7	10.7	10.7
MgO	1.4	1.4	1.4	1.4	1.4
Atmosphere	CO	CO	CO	CO	Ar
Max.Temp(°C)	1100	1400	1600	1900	1400
GBD(g.cc^{-1})	1.72	1.74	1.75	1.73	1.72
FBD (g.cc^{-1})	1.72	1.82	1.81	2.09	1.72
Wt Change%	-0.0	+6.2	+3.8	-2.8	-0.9
Colour	Grey	Black	Black	Grey	Grey

30   From the results of Examples 10 and 11 (see table
5), it can be seen that heating the samples in a carbon
monoxide atmosphere at 1400°C results in a weight gain. It
is thought that the colour change of the samples from grey
in the as pressed state to black, was the result of carbon

35 formation within the samples. Furthermore, the formation
of carbon occurs by oxidation of the silicon carbide
according to reaction 2. From the results of Example 9,

the weight change behaviour is not the result of the deposition or cracking of the carbon monoxide within the samples. Heating of the samples to higher temperatures results in a weight loss and colour change from black to the original grey colour (see Example 12). This behaviour is attributed to the carbothermal reduction involving the carbon and silica formed at lower temperatures according to reaction 3. It is thought that the presence of the silica has an adverse effect on the densification of silicon carbide. For a sample heated in an argon atmosphere (Example 13), there was no weight increase or colour change, indicating no reaction between the sample and the atmosphere.

Comparative Examples 14 - 17

The effect of additives on the oxidation of silicon carbide in a carbon monoxide atmosphere was studied. The results are given in table 6.

Table 6

Effect of composition on weight change behaviour in CO at 1400°C for 60 minutes

Example	14	15	16	17
SiC	100	90.0	98.6	87.8
Al_2O_3	0	10.0	0	10.8
MgO	0	0	1.4	1.4
Mass(g)	5	5	5	5
GBD(g.cc^{-1})	1.65	1.72	1.67	1.68
FBD(g.cc^{-1})	1.66	1.73	1.72	1.80
Wt Change%	+0.8	+0.9	+5.4	+9.2

26

Silicon carbide powder, with and without the addition of alumina is relatively stable under these conditions as evidenced by the negligible weight changes. By contrast, the addition of magnesia results in a
5   significant increase in weight being observed after firing. It is believed that this behaviour is the result of the reaction of the additives with the silica layer on the silicon carbide. This provides a rapid transport mechanism for the oxygen through the said layer to the silicon
10   carbide.

Examples 18 - 20

The effects of residual silica, with and without the presence of free carbon, on the densification behaviour
15   was studied. The samples were prepared as outlined for Example 5. The resulting powder slurries were spray dried and green discs (65 mm diameter) were unaxially pressed at 35 MPa and wet bag CIP at 150 MPa.

The samples were fired in an atmosphere of carbon
20   monoxide atmosphere at 1400°C to form silica and carbon (Example 18-a and 19-a). Example 18-a was subsequently heated to 600°C in air to remove the carbon, and the product is designated Example 18-b.

27

Table 7

Sample Details

Example	18-a	19-a	18-b
SiC	87.8	87.8	87.8
Al_2O_3	10.7	10.7	10.7
MgO	1.4	1.4	1.4
Atmosphere	CO	CO	Air
Max Temp (°C)	1400	1400	600
Mass(g)	177	178	187
Wt Change %	+5.4	+5.4	-2.8
Comments	1	1	2

Where   1   Colour Black

2   Light Grey

The results show that firing in a carbon monoxide atmosphere resulted in an increase in the weight of the sample. In addition the sample changed colour from a light grey to a black colour. This change in colour was attributed to the formation of carbon in the sample. After heating at 600°C in air (Example 18-b) there was a decrease in the weight of the sample and the colour changed back to its original colour. However, there was a net weight gain observed from the sample after the carbon monoxide and air firing. This was attributed to the formation of silica from the silicon carbide.

These samples (18-b and 19-a) were heated using the firing cycle given in table 8, and the products are designated 18-c and 19-b respectively.

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Table 8
Summary of Firing Cycles

Heat to 1400°C at 10°C.min^{-1} in Ar

Hold at 1400°C for 60 minutes

Heat 1400°C to 1600°C at 5°C.min^{-1}

Hold at 1600°C for 30 minutes

Evacuate to 1 mm Hg and fill with CO

Heat 1600°C to 1900°C at 5°C.min^{-1}

Heat 1900°C to 2030°C at 2.5°C.min^{-1}

Hold at 2030°C for 60 minutes

Cool to room temperature at 10°C.min^{-1}

until the natural cooling rate takes over.

The results are given in table 9.

Table 9
Sample Details

Example	18-c	19-b	20
SiC	87.8	87.8	87.8
Al_2O_3	10.7	10.7	10.7
MgO	1.4	1.4	1.4
Mass (g)	182	188	178
FBD (g.cc^{-1})	2.94	3.16	3.19
Wt Change %	-11.5	-10.0(-5.1)[2]	-5.2
Comments	1		

Comments

Where 1   Badly distorted

       2   Weight loss for sample before CO firing.

The results demonstrate the adverse effects of
silica on the densification of silicon carbide. Example
18-c (oxidised in a carbon monoxide atmosphere and
subsequently heated in air to remove the carbon), underwent
a large weight loss after densification at high
temperature. The final bulk density was relatively low and
the microstructure of the sample was characterised by
porous regions. Example 19-b (fired in carbon monoxide
atmosphere to 1400°C and refired using the two stage firing
cycle), also exhibited a large weight loss. By contrast,
the fired bulked density obtained after firing was
comparable to the two stage firing. For Example 19-b, it
is believed that the silica and carbon formed during the
first firing cycle to 1400°C, reacted to form SiC and
carbon monoxide in the argon atmosphere in the second
firing. It should also be noted that the overall weight
change (for both firings) for Example 19 was very similar
to that for Example 20 fired using the two stage firing
cycle. This demonstrates the adverse effect of silicon
carbide on densification and the its is possible to produce
high density samples in a carbon monoxide atmosphere if the
said phases which is inevitable formed at lower
temperatures is removed from the body prior to the high
temperature densification step.

Examples 21 - 25

        To confirm silica that has an adverse effect on
the densification of silicon carbide, free carbon was added
to react with the silica. The same source of silicon
carbide and magnesia as used for Example 1 were used to
produce the samples. The alumina used was obtained from
Alcoa was known as grade A1000 and the carbon source was a
phenolic resin. The powders were batched and ball milled
using silicon carbide milling media (see table 10).

Table 10

Milling Conditions

Time	16 hours
Powder	350 g
Balls	1500 g SiC
Fluid	700 ml iso propanol

The compositions of the batches are given in table 12. Note the ratio of Si:Al:Mg was kept constant for each mix. The weight loss after pyrolysis for the phenolic resin was 45.6%. Assuming a surface oxide layer of 3 weight percent for the silicon carbide, 1.8 g of carbon would be required for each 100 g of silicon carbide for conversion of the said silica layer to silicon carbide.

Table 11

Composition in Parts

Example	21	22	23	24	25
SiC	89.0	89.0	89.0	89.0	89.0
Al_2O_3	10.0	10.0	10.0	10.0	10.0
MgO	1.0	1.0	1.0	1.0	1.0
Resin	0.0	1.6	3.2	4.9	6.5
(C)	(0.0)	(0.9)	(1.8)	(2.6)	(3.5)

The resulting powder slurries were spray dried and green discs (65 mm diameter and mass 250 g) were

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unaxially pressed at 35 MPa and wet bag CIP at 150 MPa. The samples were heated in nitrogen to pyrolyse the resin and form free carbon (see table 12).

Table 12
Curing and Pyrolysis Conditions in Nitrogen

Heat to 100°C at $30°C.h^{-1}$

Hold for 1 h

Heat to 150°C at $30°C.h^{-1}$

Hold for 1 h

Heat to 600°C at $50°C.h^{-1}$

Hold for 1 h

Cool at $200°C.h^{-1}$

Details of the firing cycle are given in table 13.

Table 13
Summary of Firing Cycles

Heat to 600°C at $5°C.min^{-1}$ in Ar gas

Heat 600°C to 1400°C at $10°C.min^{-1}$

Heat 1400°C to 1550°C at $5°C.min^{-1}$

Hold at 1550°C for 30 minutes

Heat 1550°C to 1650°C at $5°C.min^{-1}$

Hold at 1650°C for 30 minutes

Evacuate to 1 mm Hg and fill CO gas

Heat 1650°C to 1900°C at $5°C.min^{-1}$

Hold at 1900°C for 60 minutes

Heat 1900°C to 2030°c at $2.5°C.min^{-1}$

Heat 2030°C to 2060°C at $1.5°C.min^{-1}$

Hold at 2060°C for 30 minutes

Cool to room temperature at $10°C.min^{-1}$

until the natural cooling rate takes over.

The results of the firing are listed in table 14.

Table 14

Effect of free carbon content on densification

using a two stage firing

Example	21	22	23	24	25
SiC	89.0	89.0	89.0	89.0	89.0
Al_2O_3	10.0	10.0	10.0	10.0	10.0
MgO	1.0	1.0	1.0	1.0	1.0
Resin	0.0	1.6	3.2	4.9	6.5
Mass (g)	245	248	247	247	246
GBD($g.cc^{-1}$)	1.69	1.70	1.70	1.71	1.72
Carbon Content	0	0.9	1.8	2.6	3.5
FBD($g.cc^{-1}$)	3.13	3.20	3.19	3.12	3.04
Wt Change %	-6.3	-5.8	-5.7	-6.3	-6.3
Comments	1	2	2	2	2

Comments

Where   1   Low density core

          2   Uniform

From the results in table 14, can be seen that
the addition of small amounts of carbon greatly enhances
the level of fired bulk density obtained (Examples 21 and
22). For higher levels of carbon addition, there is a
decrease in fired bulk density (Examples 24 and 25). It is
believed that this behaviour is the result of the
unfavourable reaction of the carbon at high temperatures.
Thus there exists an optimum range for the carbon content.
It is important to note that for thinner samples the
addition of carbon was not found to be necessary in order
to produce high fired bulk density products. It is

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believed that for these samples the silica layer is able to decompose and can be removed from the powder compact. This becomes more difficult with increasing thickness of the samples, as it requires considerable time to decompose and 5   remove the unwanted oxide from the powder compact.

Example 26

The reaction of the minor secondary phases was studied to determine the decomposition behaviour in regards 10   to the liberation of gaseous phases such as carbon monoxide. The raw materials used to produce the sample were silica from Pennyslvania Glass Sand Corporation known as Min-u-Sil grade 5 micron; alumina from Alcoa was known as grade A1000, magnesia from Ajax Chemicals (analytical 15   grade) and the carbon source was a phenolic resin. The oxide only powders were batched and ball milled. The resin was added as a separate step to the pre milled and spray dried oxide powders. A green discs (38 mm diameter and mass 60 g) was unaxially pressed to form a compact. The 20   starting composition used was formulated to correspond to the expected oxides and free carbon present in Example 22 and is given in table 15.

Table 15

Composition of Example 26

25

Component	Parts	Expected Oxide Composition (Example 22)
SiO_2	17.5	2.7
Al_2O_3	65.4	10.0
MgO	6.5	1.0
Resin	10.6	–
(Carbon)	(5.7)	(0.9)

30

35

The resin in the sample was pyrolysed to carbon according to the method outlined in Example 22. Details of the firing cycle are given in table 16. The sample was fired in an open crucible in a graphite tube furnace. The net gas flow rate and the CO content were continuously measured.

Table 16
Summary of Firing Cycle

Heat to 600°C at $10°C.min^{-1}$ in Ar gas
Heat 1400°C to 1650°C at $5°C.min^{-1}$
Hold at 1650°C for 30 minutes
Cool to room temperature at $10°C.min^{-1}$
until the natural cooling rate takes over.

The results obtained during the firing are shown in fig. 1. The results indicate a small amount of carbon monoxide was liberated at 700°C with a corresponding increase in the net gas flow rate. The main out gassing started at 1300°C and was rapid above 1500°C. The reaction was completed in a short time. The composition before and after firing is given in table 17.

Table 17
Atomic Ratios for Example 26

Element	Initial Ratio	Final Ratio
Al	1.00	1.00
Si	0.23	0.20
Mg	0.13	0.12
C^1	0.42	0.01

35

Notes (1) Free carbon

         The results indicate that the major change is the

5   loss of the free carbon as carbon monoxide. There was also

a small loss of silicon. This indicates that extreme care

should be taken with the use of carbon to ensure that the

samples are not damaged by excessive out gassing. The use

of a slow heating rate or a dwell in this critical

10   temperature range (of roughly 1300°C to 1600°C) can be used

to overcome any adverse affects of this phenomena. The use

of instruments such as gas flow meters or carbon monoxide

detectors can be used to monitor the outlet gas streams to

prevent rapid out gassing in the components being fired by

15   interrupting the firing cycle at the critical points.

Examples 27 - 29

         The effect of firing cycle was also examined for

thick specimens. The composition and the sample

20   preparation was the same as Example 22. The firing cycles

used are summarised in table 18 and the results of the

firing in table 19.

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Table 18

Summary of Firing Cycles	I	II
Heat room temperature to 600°C at 5°C.min^{-1} in Ar	Y	Y
Heat 600°C to 1400°C at 10°C.min^{-1}	Y	Y
Heat 1400°C to 1550°C at 5°C.min^{-1}	Y	Y
Hold at 1550°C for 30 minutes	Y	N
Heat 1550°C to 1650°C at 5°C.min^{-1}	Y	Y
Hold at 1650°C for 30 minutes	Y	Y
Evacuate to 1 mm Hg and fill	Y	Y
Introduce CO gas	Y	Y
Heat 1650°C to 1900°C at 5°C.min^{-1}	Y	Y
Hold at 1900°C for 60 minutes	Y	N
Heat 1900°C to 2030°C at 2.5°C.min^{-1}	Y	Y
Heat 2030°C to 2060°C at 1.5°C.min^{-1}	Y	Y
Hold at 2060°C for 30 minutes	Y	Y
Cool to RT at 10°C.min^{-1} until the natural cooling rate takes over.	Y	Y

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Table 19

Effect of firing cycle

Example	27	28	29
SiC	89.0	89.0	89.0
Al_2O_3	10.0	10.0	10.0
MgO	1.0	1.0	1.0
Carbon	0.9	0.9	0.9
Mass (g)	248	248	70
GBD (g.cc^{-1})	1.70	1.68	1.71
Firing Cycle	I	II	II
FBD (g.cc^{-1})	3.20	3.18	3.20
Wt Change%	-5.8	-5.9	-8.0
Comments	2	1	2

Comments

Where 1   Low density core

        2   Uniform

        From the results it can be seen that the use of
dwells in the middle temperature range is beneficial in
increasing the fired bulk density of thick samples. In
addition, it has been shown that a dwell or slowing down of
the heating rate is beneficial as a result of the reaction
of carbon with the silica inevitably present on the silicon
carbide. The elimination of this silica is crucial to the
successful densification of bodies. It will be appreciated
that for thin bodies the deliberate elimination of the
silica is not required as it is evolved during the heating
cycle (Example 29). For thicker bodies, the reliance on
the diffusion and elimination of the silica from the body
is not practical. In addition, the firing of multiple
samples can also increase the amount of time required for

the elimination of silica or silicate phases from the
samples as a result of a build up of silicon containing
vapour species in the furnace atmosphere, stabilising the
said silicon containing phases. The effect of furnace
5   design could also be a factor in this process.

Examples 30-39

        The effect of alumina and magnesia additions on
densification were examined for a fixed firing cycle for
10   thick specimens. The carbon addition was based on the
amount of silicon carbide in the starting mix. The mass
ratio of carbon to silicon carbide was 0.015. The sample
preparation and the firing cycle used was the same as
Example 22. The results of the firings are summarised in
15   table 20.

Table 20
Effect of composition on densification

Example	30	31	32	33	34
SiC	95.0	93.4	91.9	89.9	87.0
Al_2O_3	4.0	6.3	6.3	10.0	12.0
MgO	1.0	0.3	1.7	0.1	1.0
Carbon	1.4	1.4	1.4	1.3	1.3
Mass (g)	249	248	249	248	248
GBD ($g.cc^{-1}$)	1.68	1.70	1.71	1.70	1.71
FBD ($g.cc^{-1}$)	3.00	3.11	3.08	3.20	3.23
%TD (calc)	92.7	92.7	95.5	97.6	98.4
Wt Change %	-3.9	-4.0	-5.4	-4.5	-5.8

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Table 20 (continued)
Effect of composition on densification

Example	35	36	37	38	39
SiC	87.0	86.0	82.0	80.6	79.0
Al_2O_3	12.0	12.0	17.7	17.7	20.0
MgO	1.0	2.0	0.3	1.7	1.0
Carbon	1.3	1.3	1.2	1.2	1.2
Mass (g)	248	248	248	248	248
GBD ($g.cc^{-1}$)	1.72	1.73	1.74	1.74	1.77
FBD ($g.cc^{-1}$)	3.22	3.23	3.29	3.27	3.30
%TD (calc)	98.3	98.4	99.0	98.7	99.1
Wt Change %	-5.9	-5.8	-5.2	-5.6	-6.1

From the results it can be seen that in the range
examined, increasing the alumina content had a greater
effect on fired bulk density than the magnesia content.
Low levels of addition of magnesia were effective in
promoting densification. By contrast, to achieve greater
than 95% of the theoretical density, alumina had to be
added in excess of 6 weight percent. It can also be seen
that there is good repeatabiity between firings (compare
examples 34 and 35).

Example 40

        The effect of alumina addition, in the upper
range was examined for thick specimens. The carbon
addition was based on the amount of silicon carbide in the
starting mix. The mass ratio of carbon to silicon carbide
was 0.015. The sample preparation used was the same as
Example 22. The firing cycle is shown in table 21. The
results of the firings are summarised in table 22.

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Table 21
Summary of Firing Cycle

Heat to 600°C at $5°C.min^{-1}$ in Ar gas

Heat 600°C to 1400°C at $10°C.min^{-1}$

Heat 1400°C to 1550°C at $5°C.min^{-1}$

Hold at 1550°C for 30 minutes

Heat 1550°C to 1650°C at $5°C.min^{-1}$

Hold at 1650°C for 30 minutes

Evacuate to 1 mm Hg and fill CO gas

Heat 1650°C to 1900°C at $5°C.min^{-1}$

Hold at 1900°C for 60 minutes

Heat 1900°C to 2000°C at $2.5°C.min^{-1}$

Hold at temp for 60 minutes

Cool to room temperature at $10°C.min^{-1}$

until the natural cooling rate takes over.

Table 22
Effect of composition on densification

Example	40
SiC	64.8
Al_2O_3	35.0
MgO	1.8
Carbon	1.0
Mass (g)	248
GBD $(g.cc^{-1})$	1.82
FBD $(g.cc^{-1})$	3.27
%TD (calc)	97.1
Wt Change %	-4.3

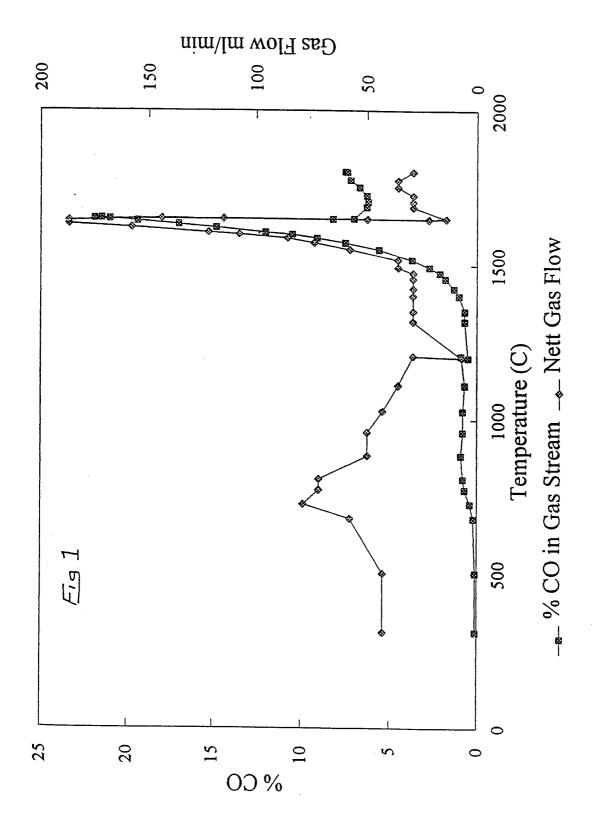It can be seen that even in the upper limits of
alumina addition, dense bodies can be produced. It is
thought that high levels of alumina result in considerable
levels of residual stresses as a consequence of the thermal
5   expansion mismatch between alumina and silicon carbide.

It will be clearly understood that the invention
in its general aspects is not limited to the specific
details given hereinbefore.

CLAIMS:

1.   A process for the production of dense polycrystalline silicon carbide shaped articles, characterized in that the process includes the following steps:

    (a)   heating a powder compact containing silicon carbide and alumina or a precursor thereof to an intermediate temperature, and maintaining the said intermediate temperature for an extended dwell, and then

    (b)   heating the product of step (a) to a higher temperature for sufficient time to produce a dense polycrystalline silicon carbide product.

2.   Process accordign to claim 1 in which in step (b) there is an upper temperature dwell at a temperature above the intermediate temperature and before the onset of appreciable densification.

3.   Process according to claim 2 in which the upper temperature dwell is carried out at less than 1900°C.

4.   Process according to claim 1 in which in step (b), magnesia is present as a sintering assist, and the atmosphere is essentially carbon monoxide.

5.   Process according to claim 4 in which the powder compact heated in step (a) contains magnesia or a precursor thereof.

6.   Process according to claim 4 in which magnesia is added during step (a) and/or step (b).

7.   Process according to claim 4 in which step (a) is carried out in an inert atmosphere which is replaced by carbon monoxide prior to commencement of step (b).

8.   Process according to claim 7 in which the inert atmosphere comprises argon.

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9.   Process according to claim 1 in which the intermediate temperature in step (a) is below the temperature at which extensive densification of the compact occurs.

10.   Process according to claim 9 in which the intermediate temperature is less than 1650°C.

11.   Process according to claim 1 in which any silica or silicate present is eliminated before the onset of appreciable densification in step (b).

12.   Process according to claim 10 in which the silica or silicate is eliminated by reaction with carbon.

13.   Process according to claim 1 in which the higher temperature in step (b) is above 1900°C and below 2200°C.

14.   Process according to claim 1 carried out at ambient pressure.

15.   A dense polycrystalline silicon carbide produced by the process of any one of claims 1 to 14.

16.   A dense polycrystalline silicon carbide according to claim 15 containing at least 65 weight per cent silicon carbide with the remainder substantially an aluminate.

17.   A dense polycrystalline silicon carbide according to claim 16 in which the aluminate contains magnesium.

Fig 1

A.	CLASSIFICATION OF SUBJECT MATTER

Int. Cl.^{5} C04B 35/56, C04B 35/60, C04B 35/64

According to International Patent Classification (IPC) or to both national classification and IPC

B.	FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC C04B 35/56, 35/60, 35/64 (FULL)
IPC C04B 35/10 (KEYWORD)

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
AU : IPC C04B 35/56, 35/60, 35/64

Electronic data base consulted during the international search (name of data base, and where practicable, search terms used)
DERWENT : SILICON ( ) CARBIDE OR SIC AND ALUMIN :
CHEM ABS : SILICON ( ) CARBIDE OR SIC AND ALUMIN : AND POLYCRYSTALLINE

C.	DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
X	AU,A, 66206/90 (WESTERN MINING CORPORATION LIMITED and FOSECO PTY LIMITED) 16 May 1991 (16.05.91) Whole document	1-17
X	US,A, 4569921 (OMORI et al) 11 February 1986 (11.02.86) Columns 2-9	1-15
X	US,A, 4564490 (OMORI et al) 14 January 1986 (14.01.86) Columns 2,3 and 6 and Examples 1-3	1-3,9-15

☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

*	Special categories of cited documents :	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A"	document defining the general state of the art which is not considered to be of particular relevance		
"E"	earlier document but published on or after the international filing date	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O"	document referring to an oral disclosure, use, exhibition or other means		
"P"	document published prior to the international filing date but later than the priority date claimed	"&"	document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
17 March 1993 (17.03.93)	2 5 MAR 1993 (25·03·93)

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C(Continuation).	DOCUMENTS CONSIDERED TO BE RELEVANT	
Category*	Citation of document, with indication, where appropriate of the relevant passages	Relevant to Claim No.
X	AU,A, 63095/90 (THE CARBORUNDUM COMPANY) 28 March 1991 (28.03.91) Pages 11,18,29 and 30 and Claim 45	1-3
X	GB,A, 2170516 (ASAHI GLASS COMPANY LTD (JAPAN)) 6 August 1986 (06.08.86) Page 2, lines 11-19 and Page 4, lines 17-32	1-3
X	Derwent Abstract Accession No. 86-185381/29, Class L02, JP,A, 61-117159 (HITACHI KK) 4 June 1986 (04.06.86) Abstract	1-3
X	Patents Abstracts of Japan, C-612, Page 63, JP,A, 1-76967 (MAMORU OMORI) 23 March 1989 (23.03.89) Abstract	1-3
X	Derwent Abstract Accession No. 89-003885/01, Class L02, JP,A, 63-282161 (JGC CORP) 18 November 1988 (18.11.88) Abstract	1
A	US,A, 4829027 (CUTLER et al) 9 May 1989 (09.05.89) Whole document	
A	CA,A, 1256459 (ELEKTROSCHMELZWERK KEMPTEN G.m.b.H.) 27 June 1989 (27.06.89) Whole document	
A	JOURNAL OF THE AMERICAN CERAMIC SOCIETY, Volume 71, No. 1, Issued January 1988, TOSIKAZU SAKAI, "PHASE TRANSFORMATION AND THERMAL CONDUCTIVITY OF HOT-PRESSED SILICON CARBIDE CONTAINING ALUMINA AND CARBON", Pages C-7 to C-9 Whole document	

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report		Patent Family Member					
AU	66206/90	BR	9007779	EP	497822	NO	921608
		NZ	235844	WO	9106515	ZA	9008602
US	4569921	DE	3326176	FR	2531068	GB	2125066
		JP	59-021579				
US	4564490	DE	3210987	FR	2502612	GB	2109810
		JP	57-160970	JP	1-039989		
AU	63095/90	BR	9004750	CA	2025862	EP	419271
		JP	3-242375	NO	904118		
GB	2170516	DE	3603331	JP	62-003072		
US	4829027						
CA	1256459	DE	3621450	EP	251218	JP	63-008261

END OF ANNEX