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(54) **MATRICE POUR COMPOSITE A MATRICE CERAMIQUE HAUTE PERFORMANCE**

(54) **MATRIX FOR HIGH-PERFORMANCE CERAMIC MATRIX COMPOSITE**

(57) The present invention provides a matrix for high performance ceramic composites containing inorganic fibres for reinforcement. The matrix comprises silicon carbide and an oxide phase which is dispersed in the silicon carbide phase.

ABSTRACT

The present invention provides a matrix for high performance ceramic composites containing inorganic fibres for reinforcement. The matrix comprises silicon carbide and an oxide phase which is dispersed in the silicon carbide phase.

(a) TITLE OF THE INVENTION

MATRIX FOR HIGH-PERFORMANCE CERAMIC MATRIX COMPOSITE

(b) TECHNICAL FIELD TO WHICH THE INVENTION BELONGS

The present invention relates to a matrix for ceramic matrix composite which contains inorganic fibre for reinforcement.

(c) BACKGROUND ART

A ceramic matrix composite is typical of various materials having excellent heat resistance and mechanical characteristics that have been proposed for use in the aerospace industry.

Conventional ceramic matrix composites include one composed of silicon carbide ceramic as a matrix and silicon carbide fibre as reinforcing inorganic fibre for its high heat resistance and high-temperature oxidation resistance. Composites for large-sized parts are generally produced by forming a silicon carbide matrix on fabric of silicon carbide fibre by chemical vapour infiltration (CVI), polymer impregnation and pylorysis (PIP), or a like technique.

However, where the conventional techniques are followed, pores or microcracks often remain in the silicon carbide matrix. Stress is concentrated around the pores and microcracks, and the stress cannot be transmitted sufficiently to the reinforcing fibre resulting in reduction of the strength of the composite. Further, oxygen tends to enter through the pores or microcracks to oxidize the fibre in an elevated temperature oxidizing atmosphere, also resulting in reduction of the strength.

(d) DESCRIPTION OF THE INVENTION

Accordingly, an object of the present invention is to provide a matrix for high-strength composites excellent in heat resistance, oxidation resistance and mechanical characteristics.

As a result of extensive studies, the inventors of the present invention have found that the above object can be accomplished by using a matrix comprising silicon carbide ceramic having dispersed therein an oxide phase.

Having been completed based on the above finding, the present invention provides a matrix for high-performance ceramic matrix composite containing inorganic fibre for reinforcement, which comprises silicon carbide ceramic and an oxide phase having dispersed in the silicon carbide ceramic.

According to the present invention, there is provided a matrix for a high-performance composite having excellent heat resistance, oxidation resistance and mechanical characteristics in high temperature. Ceramic matrix composites produced by using the matrix of the present invention are particularly useful for various formed parts in the aerospace industry.

(e) GENERALIZED DESCRIPTION OF THE INVENTION

The matrix for high-performance ceramic matrix composite according to the present invention will hereinafter be described in detail. The matrix comprises silicon carbide ceramic and an oxide phase that is dispersed in the silicon carbide ceramic. In other words, the matrix is a complex matrix comprising the silicon carbide ceramic and the oxide phase.

The oxide phase includes a crystalline oxide, glass e.g., amorphous silicate glass, phosphate glass and borate glass, and glass-ceramics (crystallized glass).

Specific examples of the crystalline oxide are oxides and complex oxides of aluminum, magnesium, silicon, yttrium, calcium, titanium, zirconium, niobium, iron, barium, strontium, beryllium, indium, uranium, tantalum, neodymium, scandium, ruthenium, rhodium, nickel, cobalt, molybdenum, manganese, germanium, hafnium, vanadium, gallium, iridium, rare earth elements, etc. Among of them, those having a coefficient of thermal expansion of 8×10^6 or smaller at 1000°C, e.g., SiO_2, Al_2O_3, Y_2O_3, HfO_2, $MgO{\cdot}Al_2O_3$, $BaO{\cdot}ZrO_2$, $MgO{\cdot}Cr_2O_3$, $ZrSiO_4$, $3Al_2O_3{\cdot}2SiO_2$, $2MgO{\cdot}2Al_2O_3{\cdot}5SiO_2$, and α-$Al_2O_3{\cdot}TiO_2$, are preferred, and $ZrSiO_4$ is particularly preferred.

Specific examples of the glass-ceramics include LiO_2-Al_2O_3-MgO-SiO_2 glass-ceramics and LiO_2-Al_2O_3-MgO-SiO_2-Nb_2O_5 glass-ceramics whose main crystalline phase is β-spodumene; MgO-Al_2O_3-SiO_2 glass-ceramics whose main crystalline phase is cordierite; BaO-Al_2O_3-SiO_2 glass-ceramics and SrO-Al_2O_3-SiO_2 glass-ceramics whose main crystalline phase is mullite or celsian; CaO-Al_2O_3-SiO_2 glass-ceramics whose main crystalline phase is anorthite; and BaO-MgO-Al_2O_3-SiO_2 glass-ceramics whose main crystalline phase is barium osumilite. Preference is given to SrO-Al_2O_3-SiO_2 glass-ceramics and BaO-MgO-Al_2O_3-SiO_2 glass-ceramics.

The oxide phase may be dispersed in the form of particles or may form a continuous phase (a network structure) in the matrix. The oxide phase can be made up of a single substance or a combination of two or more substances.

While the process for forming the oxide phase is not particularly limited, the following processes A to C are preferred for ease of formation.

Process A:

A process using powdered substance or substances forming the oxide phase.

Process B:

A process comprising impregnating silicon carbide ceramic with a solution of an oxide precursor capable of forming the oxide phase after being rendered inorganic, for example, a solution of an alkoxide (precursor) in a solvent, e.g., an alcohol (called a sol-gel solution), or a solution of a salt (precursor) in a solvent, e.g., water, and heat treating the impregnated ceramic in an atmosphere containing NO_2 gas and/or O_2 gas and/or H_2O gas.

Process C:

Vapor phase techniques, e.g., chemical vapor deposition (CVD), CVI or physical vapor deposition (PVD). CVD or CVI can be carried out in a known manner by using a mixture of gas or steam of at least one of a halide, a hydride and an organometallic compound of the metal(s) constituting the oxide phase and NO_2 gas and/or O_2 gas and/or H_2O gas as a raw material gas. In carrying out PVD, a compound or a mixture having the same or nearly the same composition as the desired oxide phase is used as a target, or a plurality of such compounds or mixtures are used alternately to give the same composition as the desired oxide phase. If desired, PVD treatment is followed by heat treatment to form the oxide phase.

It is preferable in view of the characteristics of the ceramic matrix composite that the oxide phase be present in the matrix in an amount of 1 to 80% by weight, particularly 5 to 60% by weight, based on the whole weight of the matrix.

The silicon carbide ceramics preferably include those having the following structure (1) or (2) from the standpoint of elastic modulus, heat resistance, oxidation resistance, creep resistance and the like.

Structure (1):

(a) an amorphous substance substantially comprising Si, Ti and/or Zr, C, and O;

(b) (b-1) the amorphous substance (a) and (b-2) an aggregate of a crystalline substance having a grain size of 1000 nm or smaller, particularly 10 to 500 nm, comprising β-SiC and TiC and/or ZrC; or

(c) a mixed system of (c-1) the crystalline substance (b-2) and (c-2) an amorphous structure which is present in the vicinity of the crystalline substance and comprises SiO_x and TiO_x and/or ZrO_x ($0<x\leq2$); and

the average elemental composition of (a), (b) and (c) comprising 30 to 80 wt% of Si, 15 to 69 wt% of C, and 0.005 to 20 wt% of O.

Structure (2):

(d) an amorphous substance substantially comprising Si, C, and O;

(e) an aggregate of (e-1) an aggregate of a crystalline substance comprising β-SiC having a grain size of 1000 nm or smaller, particularly 10 to 500 nm, and (e-2) amorphous SiO_2 and/or the amorphous substance (d); or

(f) a mixture of (f-1) the crystalline substance (e-1) and/or the aggregate (e) and (f-2) a carbon flocculate; and

the average elemental composition of structure (d), (e) and (f) comprising 30 to 80 wt% of Si, 10 to 65 wt% of C, and 0.005 to 25 wt% of O.

The term "an aggregate of a crystalline substance" as used for the structure (b) denotes an aggregate comprising a plurality of crystals having a grain size of 0.1 to 1000 nm. The term "in the vicinity of" as used for the structure (c) preferably means the region within a distance of 100 nm from the crystalline particle. The above-specified average elemental composition of Si, C and O of the structure (a), (b) and (c) is preferred for strength, elastic modulus, heat resistance, oxidation resistance, creep resistance, and the like. A still preferred elemental composition comprises 40 to 70 wt% of Si, 20 to 40 wt% of C, and 0.005 to 18 wt% of O.

The term "an aggregate of a crystalline substance" as used for the structure (e) has the same meaning as that used for the structure (b). The language "an aggregate of (e-1) an aggregate of crystalline substance and (e-2) amorphous SiO_2 and/or the amorphous substance (d)" as used for the structure (e) is intended to mean a plurality of aggregates each comprising (e-1) an aggregate of crystals having a grain size of 0.1 to 1000 nm and (e-2) a plurality of amorphous SiO_2 particles and/or a plurality of the amorphous particles (d), the particles (e-2) gathering in the vicinity (in the above-defined meaning) of the aggregate (e-1). The term "carbon flocculate" as used for the structure (f) denotes a plurality of crystalline and/or amorphous carbon particles having a particle size of 100 nm or smaller. The above-specified average elemental composition of Si, C and O of the structure (d), (e) and (f) is preferred for strength, elastic modulus, heat resistance, oxidation resistance, creep resistance, and the like. A still preferred elemental composition comprises 40 to 70 wt% of Si, 20 to 40 wt% of C, and 0.005 to 20 wt% of O.

While the process for forming the silicon carbide ceramic is not particularly limited, the following processes D to F are preferred for ease of formation.

Process D:

A process comprising mixing powdered raw materials for silicon carbide ceramic, and subjecting the mixed powder to heat treatment or pressing at high-temperature.

Process E:

A process comprising impregnating a preform of inorganic fiber with a solution of a precursor polymer capable of becoming silicon carbide ceramic after being rendered inorganic, e.g., polycarbosilane, polyzirconocarbosilane, polytitanocarbonosilane, perhydropolysilazane, polysilastyrene, polycarbosilazane, and polysilazane, in an organic solvent capable of easily dissolving the precursor, e.g., toluene, xylene and tetrahydrofuran, removing the solvent from the impregnated preform, and heat treating the impregnated preform to form silicon carbide ceramics. A series of the steps of impregnation, solvent removal, and heat treatment are preferably repeated several times for obtaining void-free silicon carbide ceramic. In this process rendering the polymeric precursor inorganic and consolidation or sintering proceed simultaneously.

Process F:

A vapor phase techniques, e.g.,, CVD, CVI and PVD. CVD or CVI can be carried out in a known manner by using a mixture of gas or steam of at least one of a halide, a hydride and an organometallic compound of the metal(s) constituting silicon carbide ceramic and C_nH_{2n+2} (n is equal to or greater than 1) gas and/or H_2 gas as a raw material gas. In carrying out PVD, a compound or a mixture having the same or nearly the same composition as the desired silicon carbide ceramic is used as a target, or a plurality of such compounds or mixtures are used alternately to give the same composition as the desired silicon carbide ceramic. If desired, PVD treatment is followed by heat treatment to form the silicon carbide ceramic.

The heat treating temperature in processes D to F usually ranges from 800 to 2000°C. The heat treatment is carried out in an inert atmosphere e.g., N_2 gas and Ar gas, in vacuum, or in a reducing atmosphere e.g., H_2 gas and CO gas.

It is preferable for the characteristics of the ceramic matrix composite that the silicon carbide ceramic be present in an amount of 20 to 99% by weight, particularly 40 to 95% by weight, based on the whole weight of the matrix.

The ceramic matrix composite obtained by using the matrix of the present invention exhibits excellent mechanical characteristics and fatigue characteristics in high temperature for unknown reasons, probably because (i) the oxide phase reduces stress concentration in the matrix thereby transmitting the stress to reinforcing fibers effectively, which brings about improvement in strength of the composite and (ii) the oxide phase hinders crack extension and seals the microcracks in the matrix thereby to improve the durability of the composite.

The inorganic fibre which can be used as a reinforcing material of the ceramic matrix composite is not particularly limited. For example, silicon carbide fibre, silicon nitride fibre, alumina fibre and carbon fibre are suitable, with silicon carbide fibre being preferred.

Useful silicon carbide fibres include inorganic fibre comprising Si-Ti or Zr-C-O, polycrystalline inorganic fibre comprising Si-Al-C-O available from Ube Industries, Ltd. under the trade-mark TYRANO FIBER$_{TM}$ and inorganic fibre comprising Si-C-O available from Nippon Carbon Co., Ltd. under the trade-marks NICALON$_{TM}$, HI-

NICALON$_{TM}$ and HI-NICALON TYPE S$_{TM}$

The inorganic fibre is preferably used in an amount of 5 to 85% by volume based on the total ceramic matrix composite.

The ceramic composite material can be produced easily by using the matrix obtained by a combination of process D, E or F (process for forming the silicon carbide ceramic) and process A, B or C (process for forming the oxide phase) and the inorganic fibre in accordance with the following processes G or H.

Process G:

A process comprising mixing or combining the inorganic fibre with the matrix comprising the powdered material forming an oxide phase (used in process A) and the powdered material forming silicon carbide ceramic (used in process D), and subjecting the resulting mixture or combination to heat treatment or pressing at high-temperature. When in using inorganic short fibres, the fibres are mixed with the mixed powder providing the matrix. When in using long fibres or woven fabric, nonwoven fabric or sheeting of inorganic fibres, such a fibrous layer and the mixed powder are built up alternately, or bundles of the long fibres having adhered thereto the mixed powder of the matrix are fabricated into woven fabric, nonwoven fabric or sheeting, and the resulting structures are laid up. The resulting powder mixture or overlaid structure is shaped as desired. After or simultaneously with the shaping, heat treatment is conducted to consolidate or sinter the mixed powder for the matrix to obtain a ceramic matrix composite.

Process H:

A process comprising forming an oxide phase by process A, B or C and silicon carbide ceramic by process E or F in the inside of the above-mentioned woven fabric, nonwoven fabric or sheeting of the inorganic fibre or an aggregate of small cut pieces thereof. In order to change the degree of dispersion of the oxide phase or the proportion of the oxide phase, formation of the oxide phase and formation of the silicon carbide ceramic can alternate. Alternatively, formation of the oxide phase and formation of the silicon carbide ceramic can proceed simultaneously. For example, the powdered material providing an oxide phase (used in process A) is dispersed in the solution of a silicon carbide ceramic precursor polymer used in process E, the resulting dispersion is infiltrated into the inorganic fibre aggregate, and the impregnated fibre aggregate is rendered inorganic.

The ceramic matrix composite obtained by using the matrix according to the present invention exhibits excellent mechanical characteristics and fatigue characteristics at high temperature. It is therefore useful as a forming material for various parts particularly in the aerospace industry which are used under extremely severe conditions.

(f) AT LEAST ONE MODE FOR CARRYING OUT THE INVENTION

EXAMPLES

The present invention will now be illustrated in greater detail with reference to Examples. Unless otherwise noted, all the parts and percents are by weight.

PREPARATION EXAMPLE 1

Preparation of Raw material for Silicon Carbide Ceramic

In a 5 liter three-necked flask were charged 2.5 liters of anhydrous xylene and 400 g of sodium. After the mixture was heated to the boiling point of xylene in an N_2 gas stream, 1 liter of dimethyldichlorosilane was added thereto dropwise over 1 hour, followed by heating under reflux for 10 hours. The precipitate thus formed was collected by filtration, washed successively with methanol and water to obtain 410 g of polydimethylsilane as white powder.

Separately, 750 g of diphenyldichlorosilane and 124 g of boric acid were heated in n-butyl ether under an N_2 gas stream at 100 to 120°C. The white resinous substance thus formed was heat treated in vacuo at 400°C for 1 hour to obtain 515 g of polyborodiphenylsiloxane. A 8.2 g portion of the resulting polyborodiphenylsiloxane and 250 g of the above-obtained polydimethylsilane were mixed and heated to 350°C in a quartz tube equipped with a refluxing tube in an N_2 gas stream and maintained at that temperature for 6 hours while stirring to obtain 138 g of polycarbosilane having a siloxane bond in parts. In 0.3 liters of xylene were dissolved 40 g of the polycarbosilane and 7.3 g of titanium tetrabutoxide, and the solution was refluxed at 120°C for 30 minutes in an N_2 gas stream while stirring. Thereafter, xylene was evaporated, and the residue was further heated at 300°C for 1 hour in an N_2 gas stream and allowed to cool to give solid polytitanocarbosilane which was solid at room temperature.

PREPARATION EXAMPLE 2

Preparation of Raw Material for Oxide Phase

BaO powder, MgO powder, Al_2O_3 powder and SiO_2 powder were weighed out and mixed to prepare mixed powder for glass having a total weight of 1000 g at a $BaO:MgO:Al_2O_3:SiO_2$ ratio of 14:8:28:50. The mixed powder was packed into a platinum crucible, fused by heating to 1600°C or higher, and quenched. The resulting glass was ground to glass-ceramic powder having an average particle size of 10 μm or smaller (hereinafter designated BMAS glass-ceramic powder).

PREPARATION EXAMPLE 3

Preparation of Raw Material for Oxide Phase

A hundred parts of a mixture consisting of 17.7% of strontium diethoxide ($Sr(OC_2H_5)_2$), 40.7% of aluminum isopropoxide ($Al(OCH(CH_3)_2)_3$), and 41.6% of tetraethoxysilane ($Si(OC_2H_5)_4$) were heat-refluxed in 100 parts of isopropyl alcohol to prepare a solution (hereinafter designated SAS sol-gel solution).

EXAMPLE 1

In a mixed solution of 100 parts of the polytitanocarbosilane obtained in Preparation Example 1 and 100 parts of xylene was added 10% of the BMAS glass-ceramic powder obtained in Preparation Example 2 to prepare a slurry in such a manner that the weight ratio of the BMAS glass-ceramic powder becomes 10 % based on the whole weight of the resulting matrix. Commercially available silicon carbide fibre TYRANO FIBER TM-S6$_{TM}$ produced by Ube Industries, Ltd. was disentangled and soaked in the resulting slurry. After deairing under reduced pressure of 500 Torr, the fibre bundle was impregnated with the slurry in an argon atmosphere at 4 atm. The impregnated fibre bundle was heated at 100°C in an argon gas stream to remove xylene by evaporation. The fibre bundle was then fired in an electric furnace by heating up to 1300°C at a rate of temperature rise of 50°C/hr in a nitrogen gas stream, maintaining at that temperature for 1 hour, cooling to 1000°C at a rate of temperature drop of 100°C/hr, and allowing to cool further to room temperature. The impregnation and firing were repeated 5 times to obtain a composite using the matrix of the present invention. The tensile strength of the resulting composite was measured in accordance with "Test method for stress-strain behavior of continuous fiber reinforced ceramic matrix composite at room and elevated temperatures (PEC-TS CMC 01-1997)" specified in the standards of Petroleum Energy Center, Japan. The results of the measurement are shown in Table 1 below.

EXAMPLES 2 TO 5 AND COMPARATIVE EXAMPLE 1

Ceramic matrix composites were prepared in the same manner as in Example 1, except for varying the weight ratio of the BMAS glass-ceramic powder as shown in Table 1. The tensile strength of the resulting composites is shown in Table 1.

EXAMPLE 6

A ceramic matrix composite was prepared in the same manner as in Example 1, except for replacing TYRANO FIBER TM-S6$_{TM}$ with TYRANNO FIBER ZMI-S5$_{TM}$ produced by Ube Industries, Ltd. and replacing BMAS glass-ceramic powder with commercially available $ZrSiO_4$ powder produced by Wako Pure Chemical Industries, Ltd. The tensile strength of the resulting composite is shown in Table 2 below.

EXAMPLES 7 TO 10 AND COMPARATIVE EXAMPLE 2

Ceramic matrix composites were prepared in the same manner as in Example 6, except for varying the weight ratio of $ZrSiO_4$ powder as shown in Table 2. The tensile strength of the resulting composite materials is shown in Table 2.

EXAMPLE 11

The impregnated fibre bundle prepared in Example 6 was fired once to partially form a silicon carbide matrix. The fibre bundle in which a silicon carbide matrix had been partially formed was soaked in the SAS sol-gel solution prepared in Preparation Example 3. After deairing under reduced pressure of 500 Torr, the fibre bundle was impregnated with the sol-gel solution in an argon atmosphere at 4 atm. The impregnated fibre bundle was heated at 80°C in an air stream to remove isopropyl alcohol by evaporation and then fired in an electric furnace by heating up to 800°C at a rate of 50°C/hr and maintaining at that temperature for 1 hour, followed by allowing to cool to room temperature thereby to render the impregnated fibre bundle inorganic. The impregnation and rendering inorganic, which formed an oxide phase comprising $SrO\text{-}Al_2O_3\text{-}SiO_2$ glass-ceramics, were repeated three times to obtain a ceramic matrix composite using the matrix of the present invention. The weight ratio of the oxide phase was 35% based on the whole weight of the resulting matrix. The tensile strength of the resulting composite material is shown in Table 3 below.

TABLE 1

	BMAS Glass-ceramic Powder (%)	Tensile Strength (MPa)				
		room temp.	1000°C	1200°C	1300°C	1400°C
Example 1	10	500	320	290	260	200
Example 2	20	520	330	300	270	220
Example 3	30	440	390	380	340	280
Example 4	50	380	300	270	220	170
Example 5	80	320	260	230	180	150
Comparative Example 1	0	250	200	180	160	140

It was found that the silicon carbide ceramic in the matrix of the composites obtained in Examples 1 to 5 had an amorphous structure substantially comprising Si, Ti, C, and O and that the oxide phase of the matrix was formed of glass-ceramic and uniformly dispersed throughout the matrix, forming a network structure. In Comparative Example 1, no oxide phase was found dispersed in the matrix.

TABLE 2

	$ZrSiO_4$ powder (%)	Tensile Strength (MPa)				
		room temp.	1000°C	1200°C	1300°C	1400°C
Example 6	10	450	400	390	380	360
Example 7	20	480	410	400	390	380
Example 8	30	500	430	420	410	400
Example 9	50	420	400	380	340	300
Example 10	80	380	360	330	300	250
Comparative Example 2	0	310	250	220	190	180

It was found that the silicon carbide ceramic in the matrix of the composites obtained in Examples 6 to 10 had an amorphous structure substantially comprising Si, Ti, C, and O and that the oxide phase of the matrix was formed of $ZrSiO_4$ and uniformly dispersed throughout the matrix, forming a network structure. In Comparative Example 2, no oxide phase was found dispersed in the matrix.

TABLE 3

	Tensile Strength (MPa)				
	room temp.	1000°C	1200°C	1300°C	1400°C
Example 11	490	420	400	380	370

It was found that the silicon carbide ceramic in the matrix of the composite obtained in Example 11 had an amorphous structure substantially comprising Si, Ti, C, and O and that the oxide phase of the matrix was formed of glass-ceramic and uniformly dispersed throughout the matrix, forming a network structure.

CLAIMS

1. A matrix for high-performance ceramic matrix composite containing inorganic fibre for reinforcement, which comprises silicon carbide ceramic and an oxide phase which is dispersed in the silicon carbide phase.

2. The matrix according to claim 1, wherein said oxide phase comprises an oxide, glass or glass-ceramic.

3. The matrix according to claim 1, wherein said silicon carbide ceramic comprises:

(a) an amorphous substance substantially comprising Si, Ti and/or Zr, C, and O;

(b) (b-1) the amorphous substance (a) and (b-2) an aggregate of a crystalline substance having a grain size of 1000 nm or smaller comprising β-SiC and TiC and/or ZrC; or

(c) a mixed system of (c-1) the crystalline substance (b-2) and (c-2) an amorphous structure which is present in the vicinity of the crystalline substance and comprises SiO_x and TiO_x and/or ZrO_x $(0<x\leq2)$; and

the average elemental composition of (a), (b) and (c) comprising 30 to 80 wt% of Si, 15 to 69 wt% of C, and 0.005 to 20 wt% of O.

4. The matrix according to claim 1, wherein said silicon carbide ceramic comprises:

(d) an amorphous substance substantially comprising Si, C, and O;

(e) an aggregate of (e-1) an aggregate of a crystalline substance comprising β-SiC having a grain size of 1000 nm or smaller and (e-2) amorphous SiO_2 and/or the amorphous substance (d); or

(f) a mixture of (f-1) the crystalline substance (e-1) and/or the aggregate (e) and (f-2) a carbon flocculate; and

the average elemental composition of structure (d), (e) and (f) comprising 30 to 80 wt% of Si, 10 to 65 wt% of C, and 0.005 to 25 wt% of O.

5. The matrix according to claims 1 to 4, wherein said oxide phase is present in an amount of 1 to 80% by weight, based on the whole weight of the matrix.

6. The matrix according to claims 1 to 5, wherein said oxide phase is present in the form of particles.

7. The matrix according to claims 1 to 5, wherein said oxide phase forms a continuous network structure.