THERMAL RESISTANT COMPOSITE MATERIALS IN USE TODAY – A REVIEW

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Abstract. This paper presents a brief bibliographic summary of the thermal resistant composite materials. The attention focuses on the structure and properties of the thermal resistant composite materials.

In the composite materials structure are described characteristics of ceramic matrix and reinforcing elements. As reinforcing elements were studied the continuous fibers (fibers of silicon carbide, alumina, fiber glass and quartz) the discontinuous fibers and the particles.

As the thermal resistant composite materials properties were studied mechanical properties: mechanical strength, fatigue strength, abrasion strength, modules of elasticity, thermal properties: thermal conductivity and thermal contraction, chemical properties: oxidation resistance.

Keywords: thermal resistant composites, ceramic matrix, fiber, mechanical properties

1. Introduction

The composite material is composed of a basic material, the matrix, in which the additional material is dispersed in the form of particles or fibers [7, 8, 9, 17, 22]. Matrix of material composites must be composed of a material capable of blending disperse component, which does not destroy by dissolution, melting, chemical reaction or mechanical action.

Primarily, composite resistance to temperature and corrosion or oxidation is determined by the nature of the matrix. The matrix is the plastic part, deformable of the composite material, having a lower mechanical strength than the complementary material that is included. Complementary materials used in order to reinforce the matrix or to induce the self-lubricating properties of composite material, differ between each other by chemical nature and configuration.

2. Composite thermal resistances structure

The matrix

As the ceramic matrix may be used: alumina (Al_2O_3), zirconium oxide (ZrO_2), silicon carbide (SiC), silicon nitride (Si_3N_4), titanium carbide (TiC), boron carbide (B_4C), boron nitride (BN) or mixtures of these components and complex compounds (Al_2O_3•Y_2O_3, $3Al_2O_3$•SiO_2, Al_2O_3•MgO) [1, 2, 3, 8, 9].

Silicon carbide (SiC) has a crystalline structure like diamond, which gives it great rigidity, tensile strength and hardness of high values as given in table 1, which make it difficult machinable.

The characteristics of the Si_3N_4 and SiC ceramics are superior to most conventional alloys. A further advantage of the ceramics is represented by the chemical inertia at high temperatures. For example SiC withstand at over 1400 °C, Si_3N_4 at over 1600 °C and Al_2O_3 at over 1800 °C [2].

Table 1. Ceramic matrix properties [1, 2, 3, 13, 15]

Material	Tensile strength [N/mm^2]	Thermal expansion [10^{-6}/°C]	Elastic modulus [10^3 N/mm^2]	Strength to thermal shock [°C]
Al_2O_3	350	7.4	385	96
SiC	420	3.8÷4.6	~ 406	230
Si_3N_4	315	2.4	175	570

Reinforcing elements

Continuous fiber

<u>Silicon carbide fiber.</u> Silicon carbide (SiC) is an excellent candidate for reinforcing ceramics. It has many physical and chemical characteristics: high strength and stable to high temperatures, hardness between 3000 ... 3500 HV, low thermal expansion, high strength to oxidation and high modulus as given in Table 2. Bending strength of SiC filed exceeds 950 N/mm^2 in the temperature range of 20 ... 1400 °C. SiC fibers maintain their initial strength up to temperatures of 800 ... 900 °C, but have great fragility. Regarding the behavior of creep, SiC fibers shows a rapid primary creep followed by a slowly secondary creep, with average values of 0.01% elongation at 1000 h, which means very small deformations [11].

Table 2. Properties of the silicon carbide fiber [1, 2, 3, 11]

Name / manufacturer	Chemical composition	Diameter [μm]	Density [g/cm^3]	Tensile strength [10^3 N/mm^2]	Young modulus [10^3 N/mm^2]	Specific elongation [%]
SCS-6 / Textron	β-SiC	140 ÷ 143	3 ÷ 3.29	3.79 ÷ 4	400 ÷ 420	-
SCS-9 / Textron	β-SiC	78	2.8	2.9	330	-
Nicalon (CG) / Nippon Carbon	Si-C-O	12 ÷ 15	2.55 ÷ 2.6	2.7 ÷ 2.97	185 ÷ 193	1.5
Carburandum / Carburan-dum	α-SiC	30 ÷ 50	3.1	1.38	415	-
Dow-Corning / Dow-Corning	β-SiC	8 ÷ 10	2.9	2.28	393	-
X9-6371 HPZ / Dow-Corning	57%Si-28%N -10%C-4%O	11	2.4	2.24	206	-
Tyranno / UBE Ind.	Si-Ti-C-O	8.1	2.35	3.38	193	-
Borsic	SiC/B	107	2.66	2.41	400	-

Alumina fiber. The best property of the alumina fibers consist of their high stability in air. Most of them can be treated in air at temperatures up to 1300 °C without decreasing strength [6]. The alumina fibers have a high elastic modulus, good electrical isolating properties but moderate strength. The main characteristics of several types of fibers, made from silica-alumina and alumina, are given in Table 3.

Table 3. Properties of the alumina and silica-alumina fiber [1, 2, 3]

Name, manufacturer	Chemical composition	Diameter [μm]	Density [g/cm^3]	Tensile strength [10^3 N/mm^2]	Young modulus [10^3 N/mm^2]	Specific elongation [%]
Fibra FP / Du Pont	> 99% α-Al_2O_3	20	3.9 ÷ 3.95	1.38 ÷ 1.4	379 ÷ 400	0.35
PRD/ Du Pont	80% α-Al_2O_3; 20% ZrO_2	20	4.2	2.07	379	-
Sumitomo, Textron / Sumitomo	85% Al_2O_3; 15% SiO_2	17	3.25	1.5	200	-
Almax / Mitsui Mining	99% α-Al_2O_3	10	3.6	1.8	280	-
Nextel 312 / 3M	62% Al_2O_3; 14% B_2O_3; 24% SiO_2	11	2.7	1.72	152	1.2
Nextel 440 / 3M	70% Al_2O_3; 2% B_2O_3; 28% SiO_2	11	3.1	1.4 ÷ 2.1	193 ÷241	1.2
Nextel 480 / 3M	70% Al_2O_3; 2% B_2O_3; 24% SiO_2	11	3.05	1.9	220	-
Saphicon / Saphicon	α-Al_2O_3	150	3.96	2	480	-
Saffil / Ici	95% Al_2O_3; 5% SiO_2	3	2.8	1.0	100	-
Saffil / Ici	97% Al_2O_3; 3% SiO_2	3	3.3	2.0	300	-

Glass and quart fiber. Glass fibers can be used at temperatures up to 700 °C and they have the following technological characteristics: high mechanical strength and elastic modulus, low thermal conductivity (λ = 0.035 ... 0.058 W/m·K), high corrosion strength (for a total alkali oxides content of less than 1%) and virtually zero hygroscopicity. It can be used various types of glass to produce the fibers such as the glass type A (less water resistant), type C (with remarkable strength to corrosion caused by acids), type D (low density, 2.16 g/cm^3 and a low dielectric constant), type E (with corrosion strength and good electrical resistivity), type M (high hardness, caused by beryllium oxide, BeO, inserted in the proportion of 8%), type S (with a high mechanical strength which is maintained at high temperatures) as given in Table 4 [1].

Table 4. The main characteristics of the glass [1, 2]

Type of glass	Density [g/cm^3]	Expansion coefficient [10^{-6}/°C]	Melting temperature [°C]	Tensile strength [10^3 N/mm^2]	Young modulus [10^3 N/mm^2]	Filament diameter [μm]	Breaking deformation [%]	Poisson coefficient
E	2.52÷2.54	5	846	3500 ÷ 3600	72.4 ÷ 79	10 ÷ 11.25	2	0.21
C	2.48÷2.50	-	749	2820 ÷ 3150	70 ÷ 70.5	-	-	-
S	2.48÷2.50	2.9 ÷5	970	4570 ÷ 4900	87 ÷ 90	10	-	-
M	2.890	5.7	-	3500	110	12	-	-

The most used glass to produce the fiber is the glass type E. This is a calcium-alumina-borosilicate glass with a total alkaline content (Na_2O-K_2O-Li_2O) under 2%. The low alkaline substance content ensures corrosion strength and good electrical resistivity. The fiber properties depend of the manufacturing process and the size of the fibers. Young's modulus and elastic transversal modulus increases slightly with diameter increasing [2].

The quartz fibers have good strength to high temperatures up to 1050 °C and shows good properties in the range temperature 1050 ... 1250 °C for a shorter period (about 100 h at 1100 °C). The softening point is located at 1650 °C, and the sublimation point at 1800 °C. The thermal expansion coefficient values are low and identical in radial and axial direction. The following quartz fibers has a remarkable strength to thermal shock.

Tensile strength is close to that of aramid fibers, but the elongation is slightly higher (4.6%).

In Table 5 are presented the main properties of quartz fibers (the values for tensile strength and elastic modulus is determined on unidirectional composites with epoxy resins).

Besides the properties described quartz fibers presents a number of useful features such as high strength to chemical agents (especially acids), high strength to radiation, high hardness (7 on the Mohs scale) and remarkable dimensional stability.

Discontinuous fiber

The discontinuous fibers may be obtained from various materials, such as aluminium oxide (Al_2O_3), aluminium nitride (AlN), silicon carbide (α or β), silicon nitride (Si_3N_4), magnesium oxide (MgO), and so on [1, 3, 4, 5]. Because of the small size and almost perfect structure, the discontinuous fibers have properties that can differ in terms of value, in small measure, from the calculated material properties without defects (Table 6).

Table 5. Properties of the quartz fiber [1, 3]

Density [g/cm^3]	Tensile strength [10^3 N/mm^2]	Elastic modulus [10^3 N/mm^2]	Breaking elongation [%]	Expansion coefficient [10^{-6}/°C]
2.2	3.6	78	4.6	0.5

Table 6. Properties of the discontinuous fiber [1, 3]

Material	Density [g/cm^3]	Tensile strength [10^3 N/mm^2]	Elastic modulus [10^3 N/mm^2]	Melting temperature [°C]
Al_2O_3	4.0	22.3	420	2561
SiC	3.2	21.0	700	3273
Si_3N_4	3.1	14.0	385	2473
AlN	3.3	7.0	350	2573
BeO	3.0	24.8	133	3076

Whiskers fibers

The most used whiskers fiber are SiC fiber. SiC whiskers fibers found in two crystallographic variations: α and β as given in Table 7. Cubic crystal structure of SiC is known to be β and the hexagonal and rhombohedral structures are known α. Mechanical properties of the variant β are that found in commerce are generally superior to variant α because of structural differences of two. Physical characteristics depend on the methods of manufacture resulting in different diameters, lengths and crystalline structures. Also the properties will be affected by chemical reactions that may occur on the whiskers surface [2].

Particles

There are a variety of particles produced from SiC, graphite, Al_2O_3, mica, SiO_2, zirconia, boron nitride, glass, MgO, TiC, AlN, Si_3N_6, steel or iron alice, ZrO_2, TiO_2, Pb, Zn, with size variations within wide limits, from less than one micron (micro-crystals) up to 500 microns or even higher.

Table 7. Properties of the whiskers fiber [2]

Material, name, phase	Diameter [nm]	Density [g/cm^3]	Tensile strength [10^3 N/mm^2]	Young modulus [10^3 N/mm^2]	Length [nm]
SiC, Silar SC-9, α	0.6	3.2	6.89	689	10÷80
SiC, SCW, 95% β-5% α	0.05÷0.2	3.21	20.68	483	10÷40
SiC, Tokama, β	0.1÷0.5	3.19	3÷14	400÷700	50÷200

Particles, large or small (microparticles), spherical, flat or other configuration, are used in particular, to produce composites with high strength to wear, ensuring product light weight, outstanding dimensional stability and high vibration damping capacity as given in table 8. This particle leads to reducing the elongation and thus the material toughness (compared with matrix elongation and toughness) that cause limited use only in producing composites that are not requested to mechanical and thermal shock [1].

Table 8. Materials in the form of particles used in the composite manufacture [1, 3]

Material	Density [g/cm^3]	Expansion coefficient [10^{-6}/°C]	Tensile strength [N/mm^2] (temperature [°C])	Young modulus [10^3 N/mm^2] (temperature [°C])
SiC	3.21	5.40	-	324 (1090)
Al_2O_3	3.98	7.92	0.221 (1090)	379 (1090)
BeO	3.01	7.38	0.024 (1090)	190 (1090)
B_4C	2.52	6.08	2.759 (24)	448 (24)
CeO_2	7.13	12.42	0.589 (24)	185 (24)
MgO	3.58	11.61	0.041 (1090)	317 (1090)
$MoSi_2$	6.31	8.91	0.276 (1090)	276 (1260)
Si_3N_4	3.18	1.44	-	207
SiO_2	2.66	<1.08	-	73
TiC	4.93	7.60	0.055 (1090)	269 (24)
ZrC	6.73	6.66	0.090 (1090)	359 (24)
ZrO_2	5.89	12.01	0.083 (1090)	132 (1090)

3. Properties of thermal resistances composite

Mechanical properties

SiC matrix composite reinforced with SiC fibers (Nicalon) shows a tensile strength of 30-50 N/mm^2 [18], a shear strength of 10 to 20 N/mm^2 [18], a good resilience [11, 14] and an elastic modulus of 240 N/mm^2 [19]. This composite material was studied at a temperature of 1200 °C, at a frequency of 1.0 Hz for a range of fatigue stress between 80-200 N/mm^2 [10, 19].

Al_2O_3 matrix composite reinforced with Al_2O_3 fibers shows the different values of the tensile strength of 55 N/mm^2 [21] to 153 N/mm^2 [20] due to the orientation of fibers in the composite at 45° [21] and an elastic modulus in the range of 46 to 74.5 [20, 21].

Boron carbide (B_4C) matrix composite reinforced with titanium diboride (TiB_2) fiber shows an improvement of tensile and flexural strength and other properties (hardness and toughness) for different amounts (5 to 30% of TiB_2) [12].

Li_2O-ZrO_2-SiO_2-Al_2O_3 (LZSA) matrix composite reinforced with $ZrSiO_4$ particles and bentonite binder shows a flexural strength in the range of 190-220 N/mm^2 and an abrasion strength of 51 mm^3 [16].

Siloxane matrix composites (Lukosil 901 and Lukosil M130) reinforced with SiC (Nicalon) fiber shows a lower elastic modulus than the siloxane matrix composites (Lukosil 901 and Lukosil M130) reinforced with alumina fibers (Nextel) [6].

Thermal properties

SiC composite matrix shows the thermal conductivity of 25-30 W/m·K at 25 °C [11].

Li_2O-ZrO_2-SiO_2-Al_2O_3 (LZSA) matrix composite reinforced with $ZrSiO_4$ particles and bentonite binder shows a linear thermal contraction of 14% [16].

Chemical properties

An example of a ceramic matrix composite material with high oxidation strength consists in B_4C matrix composite reinforced with TiB_2 fiber and SiC matrix composite reinforced with SiC fibers [15, 17]. The final one is resistant to oxidation at high temperatures ~ 1500 C due to the formation of a protective layer of SiO_2 on the surface of the composite [11, 22].

Acknowledgement. This paper is supported by the Sectoral Operation Programme Human Resources Development (SOP HRD), ID137070 financed from the European Social Fund and by the Romanian Government.

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Received in September 2014