

Protection of Carbon/Carbon Composites against Oxidation

Zaščita kompozitov tipa ogljik/ogljik pred oksidacijo

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A mayor problem of carbon/carbon composites is use in oxidative environments. Protective coating in this study consists of SiC outer and B4C inner coating and offer efficient protective of composites against oxidation. Because of cracks and erosion of microstructure as a result of oxidation oxidized samples have lower mechanical properties.

Key words: carbon/carbon composites, oxidation, protective coatings, mechanical properties of oxidized composites.

Največji problem kompozitov tipa ogljik/ogljik je njihova uporaba v oksidativnih atmosferah. Ugotavljali smo učinkovitost večplastne zaščite grafita pred oksidacijo, sestavljene iz zunanje SiC in notranje B4C plasti. Rezultati kažejo, da je takšna zaščita učinkovita v temperaturnem intervalu 600–1000°C. Zaradi razpok in erozije strukture grafita, ki so posledica oksidacije, so mehanske lastnosti oksidiranih kompozitov slabše. Ključne besede: kompoziti tipa ogljik/ogljik, oksidacija, zaščitne plasti, mehanske lastnosti oksidiranih kompozitov.

1. Introduction

Carbon fibers and carbon/carbon (C/C) composites are attractive materials because of strength-to-weight properties superior to those of any other materials.

Potential uses range from those in aircraft, autoindustry to medical and sport applications (boat making, fishing rod...).

C/C composites consist of carbon fibers set in a graphite matrix. Mechanical properties of C/C composites depend on fibers, which exhibit high Young's modulus E ($E = 250\text{--}500$ GPa) compared to the graphite matrix ($E_y = 30$ GPa).¹

Strong bonding between the matrix and the fibers results in high shear strength while weak bonding increases the toughness, so that crack propagation in the matrix can be arrested at the fiber surface.

High tensile strength is a consequence of very strong covalent bonds between carbon atoms and high anisotropic crystalline fibers.²

2. Protection of C/C Composites against Oxidation

The most obvious advantage of using C/C composites in aerospace application is their high relative strength compared with low weight.

A mayor problem is using such materials in oxidizing environments (hot flowing gases). Carbon rapidly reacts with oxygen at temperatures as low as 500°C, forming gaseous products (CO,

CO₂). Gasification leads to a rapid degradation of the composite. This oxidation process results in the erosion of the structure and in the degradation of the mechanical properties which the material originally possessed.

Many protective coatings are being considered to prevent contact between oxygen and carbon. Most of these coatings rely on oxide films formed during oxidation as oxygen diffusion barriers.

2.1. Protective Coatings

The most important 1934 U.S. patent¹ in work on protection against oxidation for C/C composites describes a coating system for graphite materials composed of a SiC and vitreous overlay coatings.

Work on oxidation protection for C/C composites started in 1970's. The coating system was very similar to that in the 1934 patent and was composed of a SiC conversion layer and silicate glaze overlay.

Any coating material used to protect the composite from oxidation must prevent the inward diffusion of oxygen, and has low volatility to prevent erosion. Coating issues associated with oxidation protection are coating erosion, spallation and oxygen permeation of the intact coating system.

Erosion resistance requires the use of outer coatings that have low vapor pressures. The high thermal expansion coefficient is a strong negative factor because the large differences in thermal expansion behavior often results in tension-induced coating cracks.

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In the presence of an oxide film on the surface, the oxygen has to diffuse through it to reach the substrate/oxide surface. Oxide film acts as a diffusion barrier. The oxidation of a substrate involves five steps, shown schematically in Figure 1:⁴

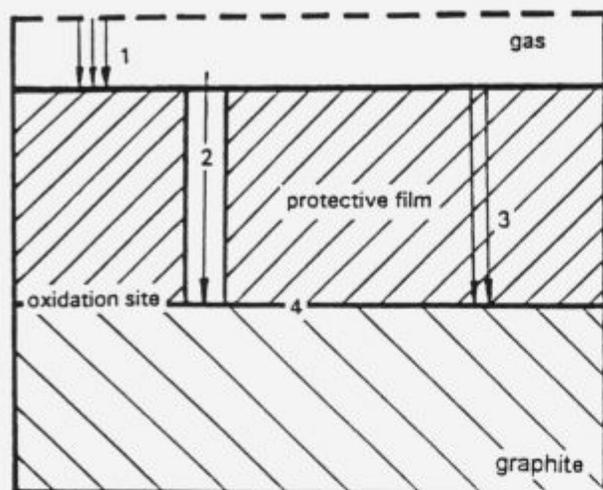


Figure 1: The oxidation of a protected graphite

Slika 1: Oksidacija zaščenega grafita

1. gas phase diffusion across the boundary layer;
2. oxygen diffusion through cracks: if the oxide film is cracked, (oxygen diffuse through it to the substrate/oxide film interface);
3. condensed phase diffusion (if the oxide film is nonporous);
4. reaction at the interface substrate/oxide;
5. counter diffusion of gas products back to atmosphere.

Oxides have usually higher thermal expansion coefficients than corresponding carbides. For this reason it is advantageous to start with a nonoxide outer coating that converts to an appropriate oxide upon exposure. Such deposition reduce differences between thermal expansion behaviour of coating and substrate.

Studies have shown the utility of borate glasses for protecting C/C composites from oxidation. Current coating system for protecting C/C composites are composed of an outer coating of SiC and an inner B₄C coating. Due to oxidation SiC is converted to SiO₂ which acts as primary oxygen barrier.⁵

Oxidation of the inner B₄C coating through cracks in the SiC outer coating produces a borate glass B₂O₃. Above the melting point of B₂O₃ it flows to fill cracks present in the inner and outer coatings.

3. Mechanical Properties of Oxidized C/C Composites

Oxidation of the graphite leads to pitting, degradation and porosity of C/C composites. Gasification appeared to lead progressively to the formation of pores in the matrix, followed by propagation of longitudinal channels along the fiber axes.

Cracks, which appears under loading, leads to a loss in strength of the composite. One of the most oxidized and loaded fibers rupture and this leads to crack initiation and propagation of transversional cracks because of shear stresses.⁷ Strength of oxidized composites is reduced because of cracks and microstructure erosion.

Bending strains for oxidized C/C composites are much lower than that for unoxidized ones.

4. Experimental Procedure

Graphite EK 986 used in this study were supplied by Ringsdorf, Germany. The average density was 1.85 g/cm³ and open porosity 8%. Graphite samples were cut in approximately cube form, side 0.7 ± 0.01 mm.

Multilayer coating was composed of an outer coating of SiC and of an inner B₄C coating.

SiC and B₄C coatings various thicknesses were deposited by Physical Vapor Deposition (PVD) process with High Frequency (HF) Sputtering.

Samples were sputtered in vacuum at 2-3 × 10⁻⁵ mbar, frequency 10 MHz and voltage 1kV. 80 min of sputtering was sufficient to deposit a B₄C film of 0.30 μm and 75 min to deposit a SiC film of 0.70 μm on the surface of the samples. Some graphite samples were only B₄C coated.

Measurements of the oxidation kinetics of all graphite samples were carried out in a vertically open-ended furnace in stagnant air, between 600 and 1200°C.

Mass changes of the specimens were measured by Thermo Gravimetry Analyses (TGA) using an automatic "SARTOTIOUS M 25 D-V" thermobalance (sensitivity ±0.001 mg) which was connected with computer.

All kinetics data were collected and approximated with Computer operated data on line acquisition system. Samples were cooled down in air and were observed using Scanning Electron Microscope (SEM), Jeal JSM - 35.

C/C composites materials BB 7655 used in this study were made from SCHUNK, Germany. Samples were preprotected with Si, which was deposited into the graphite matrix ("Kapillarizilziert").⁸

Samples with average dimensions 20 x 20 x 1.7 mm, the average density 1.64 g/cm³ and the average porosity 8.2% were oxidized between 400° and 800°C.

Oxidized samples were cooled down in air and tensioned by GLEEBLE 1500 (DUFFERS SCIENTIFIC) at room temperature in air at a rate of 0.1 mm/sec.

5. Results and Discussion

5.1 Oxidation behaviour of uncoated graphite

Oxidation of the graphite appeared to occur at specific active sites, leading to pitting, degradation and porosity at the surface.

Figure 2 shows the relative weight loss for oxidized samples per unit of calculated geometric area (dm/A₀) as a function of time at 600°C and 1000°C.

Due to the presence of porosity, the effective surface area over which reaction can occur is possibly 10 to 100 times higher than the geometric area. This is consistent with the high porosity of the C/C composites.

Oxidation process of graphite results in the erosion of the structure (Figure 3). Because of higher erosion the oxidation rate for uncoated graphite samples (Figure 2.b-A) at 1000°C is higher than rate at 600°C (Figure 2.a-A).

The low temperature rate - limiting step is probably a surface reaction - desorption of oxidation products (CO, CO₂) from the carbon network.

At higher temperatures the release of the oxidation products becomes easier and leaves defects in the carbon network. The rate is then probably controlled by oxygen diffusion into pores.

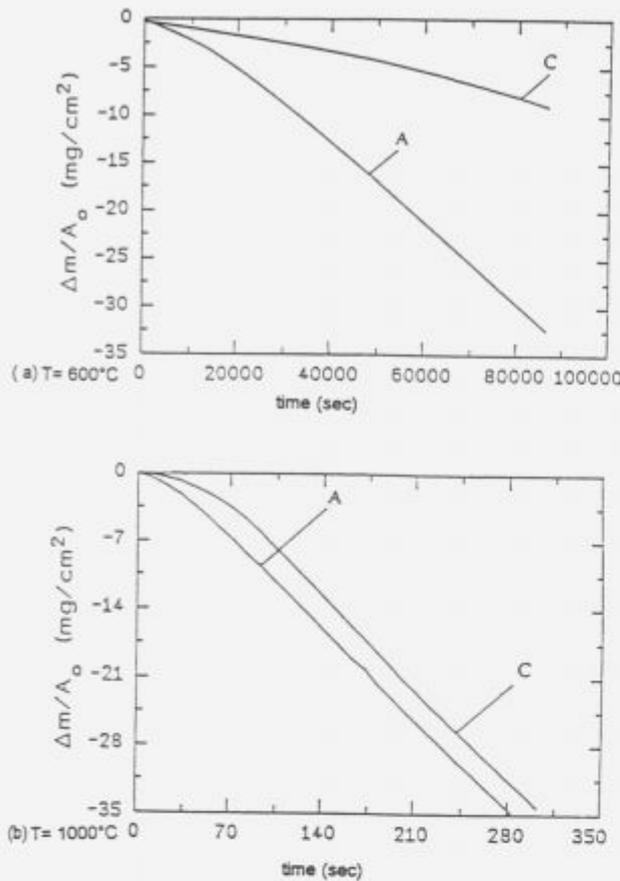


Figure 2: Relative weight loss per unit of calculated geometric area ($\Delta m/A_0$) as a function of time at 600°C (a) and 1000°C (b).

A ... uncoated graphite

C ... graphite, coated with SiC and B_2C protective coating

Slika 2: Relativna izguba mase na enoto izračunane geometrične površine ($\Delta m/A_0$) kot funkcija časa pri 600°C (a) in 1000°C (b).

A ... nezaščiten grafit

B ... grafit, zaščiten s SiC in B_2C zaščitno plastjo

With continued oxidation the porosity and active surface area increased resulting in the increase in the oxidation rate.

An important question is whether oxidation of C/C composites proceeds more readily along the carbon fiber axes or in the less well crystallized matrix of the composite.

Because of the higher incidence of reactive edge sites, amorphous carbons tend to be more susceptible to gasification than crystalline graphite.

Oxidation of the graphite occurred simultaneously at specific active sites (vacancies, pores). Burn off of oxidation products leads progressively to formation of pores in the matrix (Figure 4.a), followed by the propagation of longitudinal channels along the fiber axes (Figure 4.b). Facile oxygen diffusion along such channels allowed a rapid excavation of material and growth of larger pores between the fiber bundles.

Gasification also occurred rapidly at the exposed ends of the fibers, leading to diffusion of oxygen along the fiber axes.

5.2 Oxidation behaviour of coated graphite

In the temperature range 600°C – 1000°C samples covered with SiC and B_2C coating (Figure 2.a,b-C) showed better oxidation resistance and reduction in the oxidation rate compared with uncovered graphite samples (Figure 2.a,b-A).

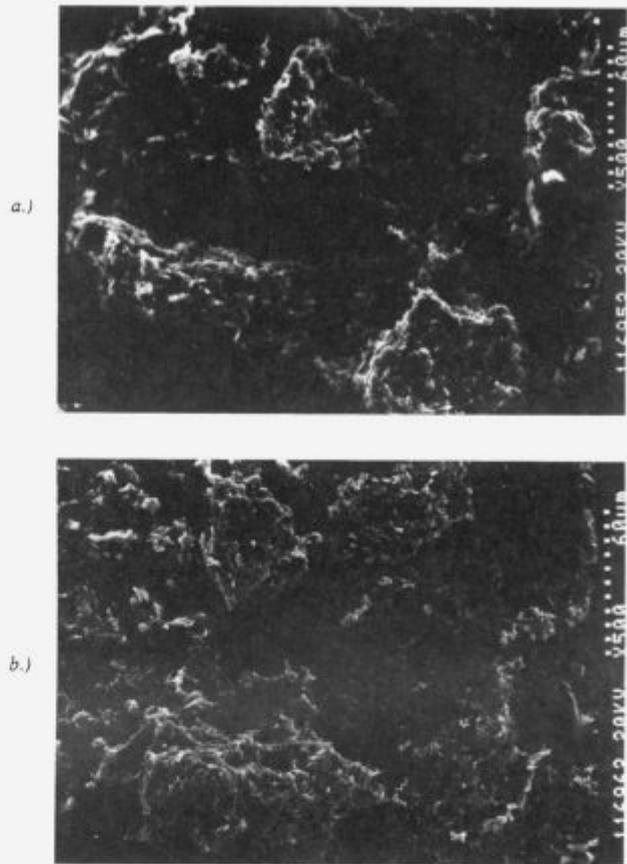


Figure 3: Surface of uncoated graphite after oxidation at 600°C (a) and 1000°C (b)

Slika 3: Površina nezaščitenega grafita po oksidaciji pri 600°C (a) in 1000°C (b)

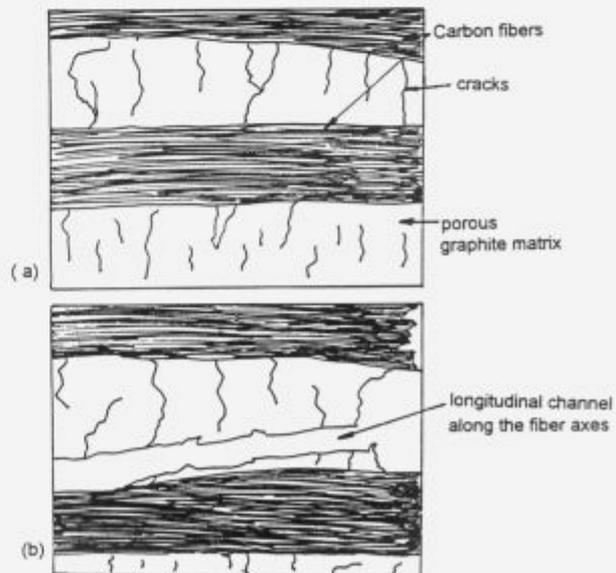


Figure 4: Oxidation of the graphite occurred simultaneously at specific active sites, appeared to lead progressively to the formation of pores in the matrix (a), followed by the propagation of longitudinal channels along the fiber axes (b) and growth of larger pores between the fiber bundles (c).

Slika 4: Oksidacija grafita prične simultano na specifičnih aktivnih mestih, kar vodi do tvorbe por v matrici (a), podolžnih kanalov vzdolž osi vlaken (b) in rasti večjih por med vlakni (c)

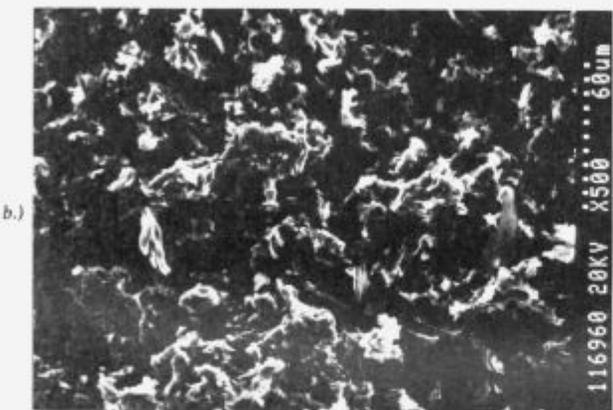


Figure 5: Surface of coated graphite after oxidation at 600°C (a) and 1000°C (b)

Slika 5: Površina zaščenega grafita po oksidaciji pri 600°C (a) in 1000°C (b)

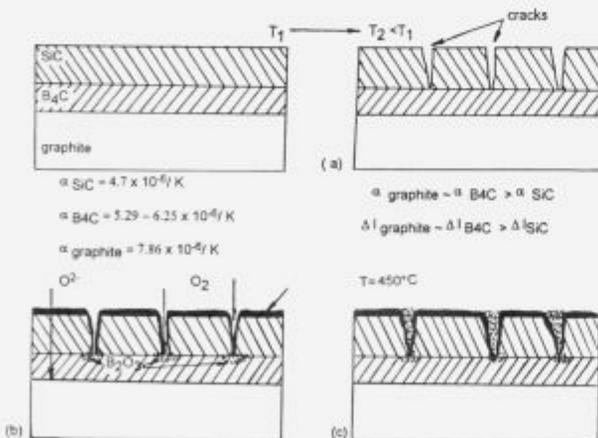


Figure 6: Cooling composite leads to cracking in the coating as a result of thermal expansion mismatches (a). Oxygen diffuse through cracks and causes oxidation of underlying carbon (b). B_2O_3 flows to fill thermal expansion mismatch cracks in the outer SiC coating and in the matrix (c).

Slika 6: Pri ohlajanju kompozita se v zaščitnih plasteh pojavijo razpoke zaradi razlik v temperaturni razteznosti zaščitnih plasti grafita (a). Kisik difundira skozi razpoke in povzroča oksidacijo spodaj ležečega ogljika (b). B_2O_3 , ki se tvori med oksidacijo, zapolni razpoke v SiC plasti in v grafiti matrici (c)

Oxide films formed during oxidation prevent direct contact between oxygen and underlying graphite and reduce numbers of specific active sites and presence of porosity over which oxidation can occur (Figure 5).

Examination of the B_4C plus SiC coated specimen on removal from the furnace suggested that oxidation was initiated at the corners and edges of the sample.

Bonding of the coating at these sites was probably poorer than on the faces and that local mismatches caused microcracking in these regions.

SiC prevent direct oxygen attack on the carbon matrix. Cooling composite from relatively high deposition temperatures leads to cracking in the coating as a result of thermal expansion mismatches (Figure 6.a).

Upon exposure to oxygen SiC becomes an oxide SiO_2 , which is an excellent oxygen barrier so oxidation by diffusion through SiO_2 layer is not the limiting factor.

Porous structure of SiC and cracks in the coating degrades the oxidation resistance of graphite. Oxygen diffuse through cracks and causes oxidation of underlying carbon. (Figure 6.b). That is the reason why SiC coating offered only limited protection of oxidation.

The use of B_4C gave good protection at temperatures up to 1000°C. B_4C forms borate glass B_2O_3 on oxidation which has surface energies less than 100 mJ m^{-2} for carbon wetting and viscosities of 10^1 to 10^2 dPa s (in the 600 to 1100°C range).

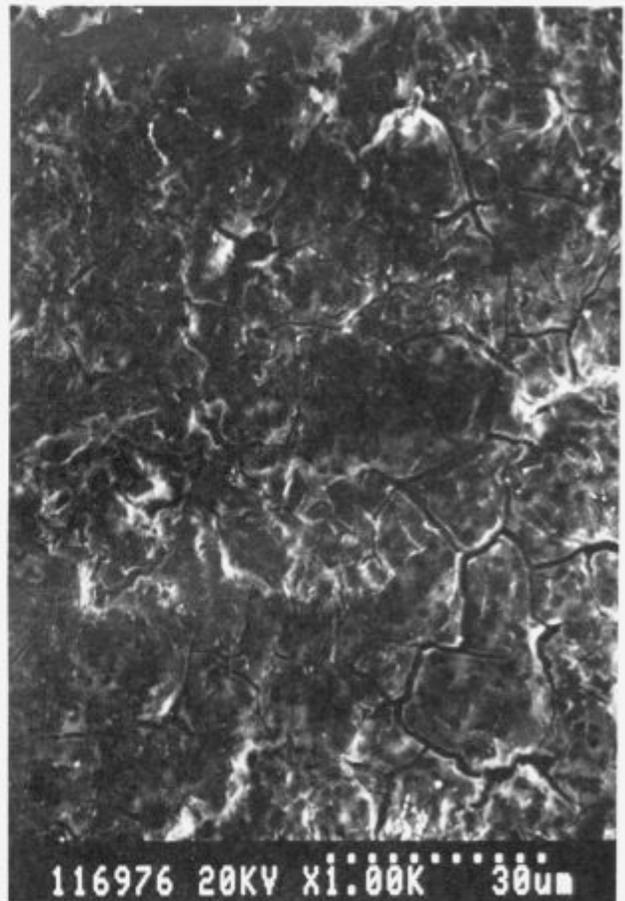


Figure 7: After removal from the furnace we noticed that B_4C plus SiC coating resinate from graphite matrix and cracked.

Slika 7: Po oksidaciji smo ugotovili, da je zaščitna plast B_4C plus SiC odstopila od grafite matrice in razpokala.

Above the melting point of B_2O_3 ($450^\circ C$) it flows to fill thermal expansion mismatch cracks in the outer SiC coating and in the matrix (Figure 6.c) providing a diffusion barrier in the composite. B_2O_3 is segregated in clusters at the active sites on the graphite surface where oxidation normally occurred and blocks these active sites.

The use of borate coating is limited by the volatility of the borate. Volatilization of the coating leaves the underlying material exposed. Rapid oxidation and a 250% volume increase at the conversion of B_2C to B_2O_3 are essential features of these coatings.

After removal from the furnace we noticed that B_2C plus SiC coating resinate from graphite matrix and crack (Figure 7). Hydrolysis of B_2O_3 produces orthoboric acid and a 125% volume increase:



Heating releases water and produces a mixture of boric oxide and metaboric acid. Under dry conditions the complete conversion H_3BO_3 back to B_2O_3 completed at about 450° .

5.3 Mechanical properties of oxidized C/C composites

Because of cracks and erosion of microstructure of C/C composites oxidized samples have lower mechanical properties.

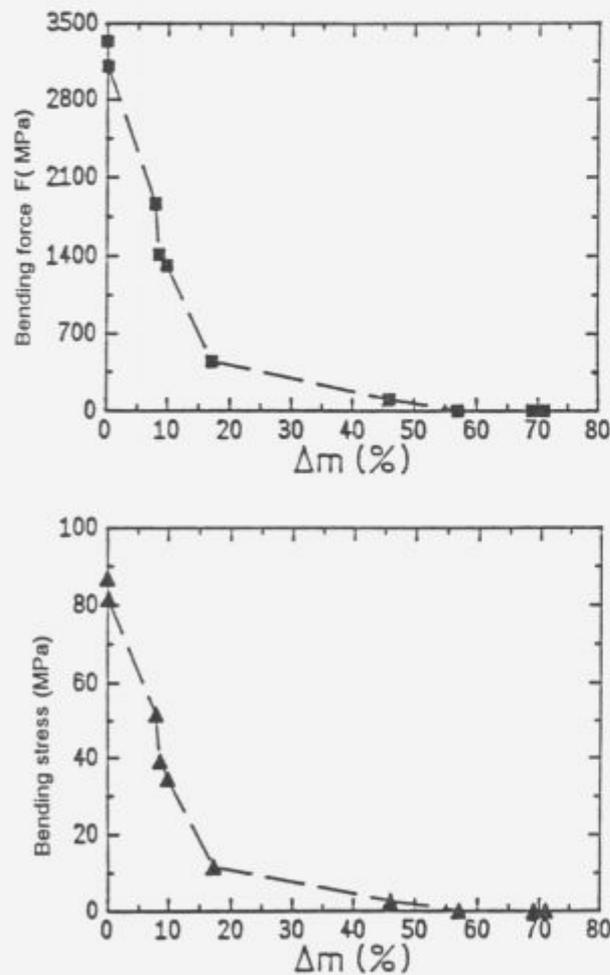


Figure 8: Bending forces and breaking stresses (up to 90 MPa) for less oxidized C/C composites as for well oxidized samples (minimal bending forces and stresses).

Slika 8: Pri manj oksidiranih C/C kompozitih so za porušitev potrebne manjše upogibne sile (do 3300 N) oz. napetosti kot pri zelo oksidiranih vzorcih, kjer so potrebne minimalne upogibne sile oz. napetosti.

Figure 8 shows that bending forces (up to 3300 N) and stresses (up to 90 MPa) for less oxidized C/C composites (at 0.036% mass loss) are much higher than those for well oxidized samples (minimal bending forces and stresses).

Relationship between breaking force (F) and mass loss (C) can be represented as following equation:

$$F = a + b(\text{sqrt}(C))^2,$$

where coefficients are $a = 58.2238$ and $b = -7.1752$.

6. Conclusions

1. The main problem for C/C composites is use of such materials in oxidizing environments (hot flowing gases). Carbon rapidly reacts with oxygen at temperatures as low as $500^\circ C$, forming gaseous products (CO , CO_2). Gasification leads to a rapid degradation of the composite.
2. Many protective coatings are being considered to prevent oxygen from reaching carbon. Most of these coatings rely on oxide films formed during oxidation as oxygen diffusion barriers. Coatings with less permeability for oxygen and temperature expansion coefficient similar to those of substrate shows efficient protection of oxidation, so layers could be mechanically stable during cooling and heating processes.
3. Graphite samples in approximately cube form, side $0.7+0.01$ mm were covered with multilayer protective coating, which was composed of an outer coating of SiC and of an inner B_2C coating.
4. SiC and B_2C coatings of various thicknesses were deposited by Physical Vapor Deposition (PVD) process with High Frequency (HF) Sputtering.
Measurements of the oxidation kinetics of all graphite samples were carried out in a vertically open - ended furnace in stagnant air, between 600 and $1200^\circ C$.
5. Comparison between uncovered graphite and graphite, covered with SiC and B_2C protective coating shows reduction in the oxidation rate resulting from protective coating.
6. After removal from the furnace we noticed that B_2C plus SiC coating resinate from graphite matrix. Because of cracks and erosion of microstructure shows oxidized C/C composites lower mechanical properties. Bending forces (up to 3300 N) and stresses (up to 90 MPa) are much higher for less oxidized C/C composites (at 0.036% mass loss) than those for well oxidized samples (minimal bending forces and stresses).

Reference:

1. J. L. Figueiredo et al: Carbon Fibers Filaments and Composites NATO ASI series, 177, 1989
2. H. V. Johnson: US Patent 1, 948,382 (1934)
3. M. S. Dresselhaus: Graphite Fibers and Filaments, Springer Verlag, London 1988, Chapter 1-5
4. K. Luthra: Carbon 26, 1988, 52, 217-224
5. J. E. Sheehan: Carbon, 27, 1989, 5, 709-715
6. T. M. Wu, C. Wei, S. E. Hsu: Ceramics International, 18, 1992, 167-172
7. G. C. Grimes: ASTM, 10, 1992, 1120
8. V. Nardin: Izdelava, lastnosti in oksidacija ogljikovih kompozitov, Diplomsko delo, Univerza v Ljubljani, 1992
9. L. E. Jones, P. A. Thrower: Carbon, 29, 1991, 522, 251-269
10. T. M. Wu, W. C. Wei, S. E. Hsu: Carbon, 29, 1991, 8, 1257-1265
11. S. M. Gee, J. A. Little: Journal of Material and Science, 26, 1991, 1093-1100
12. D. W. McKee, C. L. Spiro, E. J. Lamby: Carbon, 22, 1984, 6, 507-511
13. D. W. McKee: Carbon, 25, 1987, 4, 551-557
14. W. J. Tomlinson, J. C. Whitney: Ceramics International, 18, 1992, 207-211