

MICROSTRUCTURE AND PROPERTIES OF CARBON-CARBON COMPOSITES FROM LOW COST CLVD PROCESS

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Introduction

New rapid CLVD process is a low cost densification technique for the fabrication of carbon-carbon composites, which reduces the processing time from 100 days to several hours and achieve high density, compared with conventional densification processes---liquid impregnation and chemical vapor deposition or infiltration. For its fast deposition rate and well performances of carbon-carbon composites □ CLVD process is employed by more and more researchers and companies[1] [2].

CLVD process allows rapid densification of various substrates and liquid carbon source to obtain C/C, and can overcome some limitations of the traditional process. The main advantages of such technique include reducing the cost of C/C significantly.

We adopt resistant-radiation and induce-heating method at the same time to prepare C/C materials with density of 1.7 g/cm³, compression strength of 70MPa and bend strength of 122MPa. The microstructure of such C/C composites is analyzed in this paper.

Experimental

KEE(kerosene) and CYH(cyclohexane) are chosen in this study due to their chemical and physical characteristic and low cost. Several kinds of carbon preforms including carbon felt are used in this work. The carbon felt preforms with the density of 0.12g/cm³ are placed around a heater mandrel which is connected to AC power, and are immersed in the liquid precursor. 1K Carbon cloth adapted is wound around the heater when winding thickness is up to 5mm. The densification process is performed within the temperature range from 900°C to 1300°C.

In resistant-radiation heating device, the material of the heater mandrel is the SiC cylinder, fixed in the middle of the reactor, is connected to the electric power. The heating rate is controlled by adjusting the working electric current and voltage of electric power which can supply 10~15KW. In induce-heating equipment, the preform is surrounded on graphite mandrel, the heating power is

controlled by adjusting frequency. The temperature gradient within the preform is measured by at least three thermocouples placed along the radial direction of preforms. The densification occurs in a deposition chamber in the reactor with a cooling system which condense the vapor caused by liquid boiling and reaction.

Results and microstructure

Properties

C/C materials with density of 1.7 g/cm³ are obtained within less than 3 hours. Table 1 summarizes the mechanical properties---compression strength and tensile strength. Table 1 shows that compression strength of carbon felt composites with the density of 1.74g/cm³ is 100MPa, while for carbon cloth composites, the value is up to 222 MPa. Table 2 gives the character coefficient of deposited carbon. The XRD patterns of composites from two carbon sources exhibit broad 002 reflections. For KEE carbon source, the values of d_{002} and L_c of composites are 0.3477nm and 2.3nm, which is very similar to that of composites from CYH carbon source and are similar to the value reported in reference [2].

microstructure

The microstructure of the deposited carbon under polarized-light microscopy is that rough-laminar and smooth carbon deposit exist at the same time in preform (see Figure 2). Under crossed polarizers, the fibers (systematically dark and isotropic) are surrounded by optically anisotropic domains (bright) which appear rough, and the carbon deposited on the fibers is generally close to 35-40μm in thickness within 0.7 hour. The part of rough-laminar pyrocarbon was less than that of smooth carbon deposit, because of the low deposition temperature in present study. The carbon deposits on fiber surface under SEM display a kind of knob and knobs links each other and stack like hills. The formation mechanism of knob deposits is directly connected with chemical reactions producing pyrocarbon during deposition processing.

For the reactions among three phases and the concentration difference of carbon source exiting in depositing region, the microminiature liquid-drops

are formed heavily which comes from pyrolytic carbon of polymeric molecules and then drops on fibers surface little by little. Therefore, the knob deposits are formed from all directions.

Conclusion

Chemical liquid-vapor infiltration densification technique allows preparing low cost carbon-carbon composites with good properties and microstructure within several hours, it is no doubt that CLVD will lead to have a good future in the fields of C/C.

References

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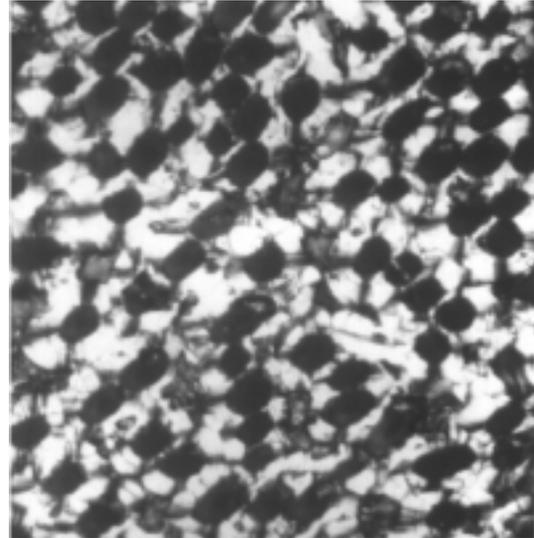


Fig 2 The microstructure of C/C composites prepared by CLVD process

Table 1 Compression strength of carbon felt C/C composites

Density, g/cm ³	1.71	1.57	1.59	1.68	1.70
Strength, MPa	70.4	52.9	54.9	63.6	68.7

Table 2 Bend strength of carbon cloth C/C composites

Density, g/cm ³	1.48	1.58	1.56	1.59	1.64
Strength, MPa	76.9	88.9	81.9	95.0	122

Table 3 the XRD patterns of C/C composites

Carbon source	Material	D ₀₀₂ /nm	Lc/nm
CYH	Carbon felt	0.3477	2.3
KEE	Carbon felt	0.3441	3.4

INVESTIGATION OF HIGH TEMPERATURE ADHESIVE FOR BONDING CARBON-CARBON COMPOSITES AND GRAPHITE MATERIALS

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Introduction

Bonding of C/C composites has become increasingly important as new applications require larger and more complex geometry parts and components, which allows reducing the processing cost significantly.

Several methods for joining of graphite to itself have been developed. These methods may also be suitable for bonding C/C composites. It has been reported that brazing alloys are used for joining graphite which are suitable for relatively low-temperature applications because of their low solidus temperature.[1]

Besides brazing method, diffusion welding of graphite specimens from 2300°C to 3000°C using interlayers of carbide forming refractory metals and Solid-state diffusion bonding with borides and carbides have also been reported[2], the later appears to be more suitable for bonding C/C composites below 2000°C and higher joint strength (interlaminar shear strength) may be obtained at high temperature. But these methods require adding higher processing pressure (pressure great than 6MPa) on specimens while bonding and retaining, which is unsuitable for most practical applications.

The present work is to employ a new method called reaction-diffusion bonding (RDB) for C/C composites using phenolic resin with high carbon yield as matrix and mixing B₄C and Ti, Si powders as reaction agent, and to investigate the ILSS of joints produced using C/C and graphite materials.

Experimental Procedure

Materials

The specimens are made of available 2D-C/C composites and commercial graphite materials. The 2D-C/C specimens are cut off from worn C/C brakes, whose density, ILSS strength, compression strength are 1.75g/cm³, 4.5MPa and 83MPa respectively. The graphite materials is general electrical heater application, with the density of 1.60g/cm³ and compression strength is greater than 16MPa, and is made of JiLingTansu Plant.

The C/C samples consists of two specimens, one

is small and its dimension is 8mm×10mm×10mm, the other is larger with the dimension of 20mm×10mm×8mm, and the joint area is 8mm×10mm. Adhesive matrix include thermalset phenolic resin with high carbon yields (HCPR) and low molecular. B₄C, Ti, Si powders as reaction agents. The purity and particle size of the powders are given in Table 1, some of physical.

Reaction-Diffusion Bonding Procedure

Reaction-Diffusion bonding of C/C composites and graphites are investigated with interlayers of slurry mixtures of HCPR solution and B₄C, Ti, Si powders which are the main components of high temperature adhesive (HTA). There is five formulas consisting the different mole ratio of the mixtures. Three of them are formula A, B, C, respectively (Table 2).

Five specimens are prepared for each formula at least. There is three groups of specimens for three formulas. The lap joint area is 8mm×10mm, and the surface of two pieces of specimen are both coated with HTA, the two pieces of specimens are bonded each other and put 0.1 MPa on pressure on the joint for 30 min, then four groups of specimens are heated in drying box and cured within temperature range of 150°C-180°C for 4 hours which is determined by the chemical properties of resin. The cured samples are heated in a graphite vacuum furnace with inert gases of N₂ and Ar₂ and chamber pressure is less than 0.09MPa. The heat treatment process of samples include four temperature stages, they are 1000°C, 1200°C, 1500°C and 1800°C, the time of above heat treatment stages is 1h, 1h, 0.5h, 3h respectively. During heating treatment process, no pressure is put on the joint, but inner gases must be injected consistently through out the processing. The heat schedule for the specimens bonded with formula C is designed to produce well-bonded joint.

Joint ILSS Determinations

The ILSS of joint of all samples was tested at Instron 4505 test device with special fixture according with GB1450-83. The geometry of shear specimens and testing mode are shown in Figure 2. In this way, a more realistic measure

of the actual bonding strength is expected for this method because of a uniform distribution of shear stress on the plane of maximum shear stress. The test is performed at room temperature and five groups for each kind of samples.

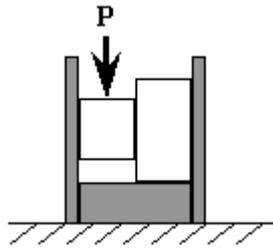


Figure 2 The geometry of specimens and testing method

Result and Discussion

Joints Produced Using HCPR

The processing strength of joint is provided by HCPR as the matrix of HTA at room temperature while at high temperature (>1000°C) the high joint strength is produced by the chemical characteristic of HCPR, in other words, the high carbon yield of HCPR is essential for HTA to produce high ILSS of joint interface. High molecular, low curing temperature and viscosity are considered for the processing properties of HCPR. The properties of resin used in this work is listed in table 4.

Joint produced using graphite materials

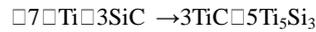
Graphite materials is chosen for bonding to screen out appropriate formula of HTA. It is found that all the samples is destroyed and graphites matrix materials is fractured in testing. The testing result is shown in Table 5. The maximum ILSS is obtained by using formula B of HTA. The value of ILSS of the formula A is similar to that of formula C.

Joint produced using c/c materials

Carbon-carbon samples are cured at 25°C then are heated at 1500°C for 0.5h. Table 6 shows that the formula 5 is adopted to bond C/C materials compared with the other formula of HTA.

The influence of heating treatment temperature on ILSS of joints

The properties of HTA is connected with temperature intensively and the heating treatment temperature is the key factor of bonding processing for HTA. The joint interface is formed at room temperature and is strengthened by proper process of high temperature treatment which allows stronger chemical bond force produced at the bonding interface because of chemical reaction at high temperature heating. The bonding strength of HTA is up to maximum value at 1500 °C, which is contributed to the following reactions.



It is these reactions that the C-Ti-B system is produced from carbon atoms in bonded materials reacted and HTA at high temperature, which strengthen the joint and caused high ILSS.

Conclusion

The HTA can be used for bonding carbon-carbon composites and graphite materials, but C/C is more difficult to bond compared with graphite using HTA because of the different stage of surface and inter of two. The highest joint strength is 5.17Mpa produced using carbon-carbon materials at 1500°C (see table 7). To obtain higher bonding strength, the bonding process will be modified by the way of proper surface treatment and high temperature treatment under pressure.

Reference

- [1] Parviz Dadras and Gopal M. Mehrotra □ Joining of Carbon-carbon composites by Graphite Formation □ J. Am. Ceram. Soc □ 77[6]1419-24 □ 1994 □
- [2] Parviz Dadras and Gopal M. Mehrotra □ Solid-state diffusion Bonding of Carbon-carbon composites with Borides and Carbides □ J. Am. Ceram. Soc □ 76[5]1274-80 □ 1992 □

Table 1 Purity and particle size of powders

Material	Purity, %	Particle size, mesh
B ₄ C	99.7	250
Ti	99.7	300
Si	99.9	250

Table 2 Formula system of HTA

No.	A	B	C
Formula.	PR+B ₄ C+Ti	PR+B ₄ C+Ti+Si	PR+B ₄ C+Ti+Si
Mole ratio	2:1:1	4:1:2:1	4:2:2:1

Table 4 Main properties of resin matrix for bonding

Carbon yield □%	Average molecula	Dynamic viscosity	Curing temperature
65 □	400	25mpa.s	150-180 □

Table 5 ILSS of graphite specimens with different temperature and formula

Formula No.	A	B	C
□ 25°C □ ILSS/MPa	4.88	5.36	4.97
□ 1000°C □ ILSS/ MPa	3.63	5.22	4.54

Table6 ILSS of C/C specimens with different temperature and formula

Formula No.	A	B	C
□ 25°C □ ILSS/MPa	3.5	2.04	3.59
□ 1500°C □ ILSS/ MPa	4..31	3.47	5..17

Table 7 ILSS of HTA for bonding C/C materials

Heat treatment temperature	1000°C	1500°C	1800°C
*ILSS/MPa	3.31	5.17	3.48

*Adopted formula C