Journal of the European Ceramic Society 36 (2016) 2443–2452

Contents lists available at www.sciencedirect.com

Journal of the European Ceramic Society

journal homepage: www.elsevier.com/locate/jeurceramsoc

Advanced silicon oxycarbide-carbon composites for high temperature resistant friction systems

M. Alejandra Mazo*, Aitana Tamayo, Juan Rubio

Instituto de Cerámica y Vidrio (CSIC), C/Kelsen 5, 28049 Madrid, Spain

ARTICLE INFO

Article history:
Received 7 August 2015
Received in revised form 9 March 2016
Accepted 13 March 2016
Available online 19 March 2016

Keywords:
Silicon oxycarbide
Tribological properties
Mechanical properties
High temperature properties
Spark plasma sintering

ABSTRACT

Highly densified bulk silicon oxycarbide—carbon composites (SiOC-C) reinforced with carbon black (CB), active carbon (AC) or graphite (GR) have been obtained through spark plasma sintering. Structural, mechanical, tribological and thermal properties of SiOC-C composites were researched. The SiOC-C composites reinforced with GR and CB tended to give β-SiC. Wear behavior at room temperature under dry conditions was determined by using a ball on plate configuration and stainless steel balls as counter bodies. The coefficient of friction of the composites decreases down to 40% and the wear rate is also reduced by 1 in the order of magnitude when compared to SiOC. A graphite-like carbon tribolayer is probably formed in the composites; this layer could be responsible for the observed enhancement of such tribological properties. These SiOC-C composites are promising candidates for use in harsh enviroments where an adequate tribological response is required at high temperatures.

1. Introduction

The study of friction, wear, and lubrication has long been of enormous practical importance as the operation of many mechanical, electromechanical, and biological systems depend on the appropriate friction and wear values. Multiple industrial applications such as brake valves, clutches and other similar motion-controlled mechanisms require good wear properties and low friction coefficients. The reciprocating motion, typical of many real world devices, also implies low friction coefficient in both forward and backward movement.

Silicon oxycarbides (SiOC) are versatile materials composed of a mixed network of silicon, tetrahedrally bonded to oxygen and carbon atoms leading to four different silicon sites (SiO_4, SiO_3C, SiO_2C_2, $SiOC_3$ and SiC_4) and also a segregated phase of sp^2 carbon (C_{free}) which is formed during the pyrolysis process. Generally, at temperatures higher than 1200 °C, the SiOC materials undergo a phase separation into amorphous SiO_2 and SiC phases and, as the annealing temperature increases, the amorphous SiC phase can crystallize into β-SiC although it is interesting to note that the SiO_2 remains amorphous due to the above mentioned C_{free} phase. At higher temperatures the carbothermal reaction of SiO_2 with the C_{free} phase produces β-SiC and gaseous species [1,2]. Additionally, the C_{free} phase can experience reorganization from highly disordered carbon to more ordered graphite-like carbon.

The study of tribological behavior of SiOC derived materials is motivated by the presence of the C_{free} phase embedded within the matrix which plays an important role in promoting an enhancement of both friction coefficient and wear rate values when compared to SiC or SiO_2 materials [3]. Following on from this idea, the incorporation of carbon reinforcements within the SiOC matrix could lead to SiOC-carbon (SiOC-C) composites with further improvement of the tribological properties due to the well-known lubricating properties of carbon materials (low wear and friction). These advantages when taken with the intrinsic properties of SiOC materials, [1,2,4] such as high temperature stability, corrosion resistance in harsh environments, good mechanical properties and their light weight compared to metal alloys make these composites appropriate for a wide range of potential tribological applications.

In precedent works polysiloxane resin derived SiOC materials were used in friction systems as binders for brake pads [5]. Siloxane based derived ceramics were developed as brake rotors, displaying slightly better tribological properties than higher cost carbosilane derived ceramics, which made them suitable for automotive, brake rotor applications [6]. On the other hand, SiOC films were studied in terms of the mechanical and tribological response showing potential applications as bio-tribological coatings [3]. Other related systems such as silicon carbonitride (SiCN) [7,8] and silicon oxycarbonitride (SiOCN) [9] have displayed promising results

---

* Corresponding author.
E-mail address: sandra@icv.csic.es (M.A. Mazo).

http://dx.doi.org/10.1016/j.jeurceramsoc.2016.03.012
0955-2219/

for applications in the field of tribology as coatings for silicon-micro electro mechanical systems (Si-MEMS) and protective low friction coatings for metal-forming processes.

Although several synthetic strategies can be followed to obtain bulk dense SiOC—derived composites [10–12], the spark plasma sintering (SPS) technique has proved to be the most suitable for obtaining such materials as SiOC-C, as it preserves the integrity of the reinforcing carbon phase after the sintering treatment. Different authors have used SPS to sinter advanced materials where the matrix [13,14] or the reinforcements [15,16] containing carbon characteristics (carbon nanofibers [17,18], carbon nanotubes [19,20], graphene [21,22], etc.). The SPS technique allows for high densification degrees without any carbon structure degradation. This non-conventional sintering technique simultaneously applies a high intensity current pulse and uniaxial pressure, thereby producing high heating rates (up to 600 °C min^{-1}) reducing both sintering temperatures (almost 100–200 °C lower) and dwelling times (a few minutes) and developing novel materials which cannot be obtained by conventional sintering techniques [23,24]. In previous works we successfully employed SPS to sinter pure SiOC powders [25] and SiOC composites with different ceramic reinforcements [26].

In this sense, the purpose of this work is to present novel SiOC-C composites sintered by SPS with an emphasis on their mechanical, tribological and thermal behavior compared with pure SiOC. We have used different types of carbon, i.e. carbon black (CB), active carbon (AC), and graphite (GR), which also present different particle sizes, surface areas and crystallinity degrees, so the raw carbon materials used as reinforcement are going to profoundly affect the properties of the sintered SiOC-C composites.

2. Experimental

SiOC powders were obtained from the pyrolysis at 1100 °C of tetraethylorthosilicate (TEOS) and polydimethylsiloxane (PDMS) hybrid materials as described elsewhere [12,27]. SiOC-C composites were prepared from different carbon raw materials: Carbon Black (CB, Ensaco^{TM} E250G, Timcal; surface area = 80 $m^2\,g^{-1}$, mean particle size d_{50} = 4.4 μm, Imerys Graphite & Carbon, Bodio, Switzerland), Active Carbon (AC, generously supplied by Canal Isabel II, Madrid, Spain; surface area = 636 $m^2\,g^{-1}$, mean particle size d_{50} = 35.6 μm) and Graphite (GR, Natural graphite Timrex 80 × 150 grade; surface area = 0.7 $m^2\,g^{-1}$, d_{50} = 124 μm, Imerys Graphite & Carbon, Bodio, Switzerland). In order to minimize the differences of particle size all the carbon materials were attrition milled for 2 h in isopropanol medium using stainless steel balls. The mixtures were dried at 50 and 120 °C to remove the isopropanol and then they were sieved below 100 μm to avoid agglomerates. After this, the SiOC powders were mixed with the different carbon materials in a constant 10% weight ratio. Each mixture was attrition milled using the same procedure described above. 2 g of each mixture was placed in a 20 mm cylindrical diameter graphite die and, afterwards incorporated into an SPS device (SPS, Dr. Sinter, SPS-510CE, SPS Syntex Inc., Kanagawa, Japan) which was heated at 1500 °C under an uniaxial pressure of 40 MPa and low vacuum (4 Pa). A heating rate of 100 °C min^{-1} and a holding time of a few seconds were also used. Bulk dense SiOC-C composites were obtained. Pure SiOC powders without additional reinforcements were similarly processed for comparative purposes.

Particle size distributions of the raw materials were determined through He-Ne laser diffraction of the powders dispersed in an alcohol medium (Mastersized S, Malvern Instruments Ltd., Malvern, UK). N_2 adsorption isotherms were collected in an adsorption analyzer (Tristar 3000, Micromeritics Instrument Corporation, Norcross, USA). From these N_2 isotherms the corresponding surface areas and pore volumes were determined. The specific surface area (S_{BET}) was evaluated by Brunauer, Emmet and Teller analysis (BET), which employs the adsorption data in the relative pressure range from 0.05 to 0.35 [28]. The pore size distribution in the mesoporous range was obtained from the adsorption branch of the isotherm using the Barrett, Joyner and Halenda analysis (BJH) [29]. In order to estimate the micropore volume, the t-plot method was used. [30]. The t-plot method represents the volume of gas adsorbed as a function of the standard multilayer thickness (t) of a reference non-porous material at the corresponding P/P_o. These t values are calculated employing the Harkins-Jura equation [31]. Mesopores are considered to be between 2 and 50 nm in size while micropores are those whose size are <2 nm. The structural characterization of raw materials, SiOC-C mixtures and sintered monolithic pieces was carried out by means of Fourier Transform Infrared Spectroscopy (FT-IR) (Spectrum BK, Perkin Elmer Corporate, Waltham, USA) and X-ray diffraction (XRD) using a diffractometer (D8 Advance, Bruker Corporation, Karlsruhe, Germany) employing the Cu Kα radiation (λ = 0.154178 nm) in the range of $10 \le 2\theta \le 70$ by steps of 0.05°.

The total carbon amount expressed in weight% was determined by an elemental analyzer (CS-200, LECO Corporation, Michigan, USA). Polished surfaces of the sintered SiOC-C composites were analyzed by Scanning Electron Microscopy (SEM, TM1000, Hitachi High-Technologies Corporation, Tokyo, Japan). Real density values were determined with a Multipycnometer (Quantachrome Instruments, Boynton Beach, USA) using He and apparent densities were measured by immersion into water by applying the Archimedes method. Porosities were calculated employing both apparent and real densities values following (1):

$$\text{Porosity} = 1\text{–}(\text{Apparent density}/\text{Real density}) \quad (1)$$

The mechanical characterization was performed through a micro-indentation unit (Apex, CETR-Bruker, Campbell, USA), equipped with a Vickers indenter calibrated with a fused silica standard. The curves corresponding to the applied indentation load as a function of penetration depth were obtained with a constant strain rate of 0.05 s^{-1} during both charge and discharge cycles. A maximum load of 5 N was used. Oliver-Pharr's method [32,33] was also used to evaluate the hardness (H) and the elastic modulus (E) of the samples. E values were calculated by fitting the unloading segment of a load-displacement curve to an empirical power-law relation,

$$P = a(h\text{-}h_f)^m \quad (2)$$

where P is the load (mN), h is the displacement (nm), a and m are the fitting parameters. The final indentation depths (h_f) and the maximum indentation depths (h_{max}) were deduced from the corresponding plot.

The contact stiffness (S) was evaluated from the derivative of the Eq. (2) at P_{max}. From S, the true contact depth (h_c) was evaluated from the relation,

$$h_c = h_{max} - 0.75(P_{max}/S) \quad (3)$$

The true contact area (A) was evaluated, taking into account the tip defects by the use of an area function calibration employing a standard fused silica sample. H and the reduced elastic modulus (E_r) were determined through the following equations,

$$H = P_{max}/A \quad (4)$$

$$E_r = (\pi½/2A½)S \quad (5)$$

E_r is related to both E and Poissonís ratio (ν) of the indented material and those of the tip (E_i,ν_i respectively) by the expression;

$$1/E_r = (1\text{-}\nu^2)/E + (1\text{-}{\nu_i}^2)/E_i \quad (6)$$

Tribological experiments were conducted with a tribometer (UMT3, CETR-Bruker, Campbell, USA) at a rotating speed of 10 Hz,