Journal of the European Ceramic Society 37 (2017) 2209–2218

Contents lists available at www.sciencedirect.com

Journal of the European Ceramic Society

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

Rheological behaviour and thermal dilation effects of alumino-silicate adhesives intended for joining of high-temperature resistant sandwich structures

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ARTICLE INFO

Article history:
Received 4 August 2016
Received in revised form
22 December 2016
Accepted 26 December 2016
Available online 6 January 2017

Keywords:
Sandwich
Inorganic adhesive
Si–O–C ceramics
Ceramic foam
Ceramic fibre

ABSTRACT

The study is concerned with inorganic adhesive layers located between the CMC composite skin and the Si–O–C ceramic foam core of sandwiches intended for high-temperature use. Two types of alumino-silicate adhesives (mastics) were tested for use as the bonding layer. The rheological properties of adhesive and its dimensional changes during high-temperature curing play a key role in terms of successful manufacture and subsequent use at high temperatures. In order to characterise these properties, specimens consisting only of the dried adhesive were subjected to compression tests conducted at increasing temperature from 300 to 1000 °C. These experiments were carried out via the application of two loading modes using both the static pre-load and cyclic loading methods. The above results were compared with thermal expansion records determined from fully-cured adhesives. In addition to the above investigation, the mechanical properties of the adhesive joint were measured employing both the DCB and shear tests.

1. Introduction

Sandwich structures consisting of refractory materials are potentially attractive for several industries, including aerospace and automotive [1]. Commonly used sandwich structures mainly provide considerable weight reduction, which is undoubtedly a great benefit. In the case of structures consisting exclusively of ceramic materials, such sandwiches offer an opportunity to resolve two additional important problems of advanced ceramics: First is the product price reduction by reducing the amount of very costly ceramic fibres which are used in the production of ceramic matrix composites (CMC). The second opportunity is more academic and involves the quest for improved fracture toughness and impact resistance of ceramics. Impact-resistant sandwich materials combining a polymer matrix laminate or metal with ceramics can be an inspiration for analogical solutions in the field of ceramic materials [2,3].

In view of the above facts, it is at first glance surprising, that sandwich structures consisting solely of ceramic materials are rarely discussed in scientific journals, in contrast to CMC which are still being further developed and which are being frequently discussed [4–17], similarly like ceramic foams [18–30] or porous ceramics [31–37]. The probable reason is, that the design and production of ceramic sandwich materials is quite a complicated problem, which requires the knowledge of several disciplines of materials sciences. In terms of structure, two basic varieties of ceramic sandwich core have been investigated: corrugated ceramic core [38] and ceramic foam core [39].

The interface between the ceramic core and the ceramic skin is a key problem for design and production of ceramic sandwiches. One possible solution is bonding with high-temperature inorganic adhesive. Joining of basic types of ceramics by using high-temperature adhesives is described e.g. in [40,41] for SiC and in [42,43] for Al_2O_3. High temperature inorganic adhesives for fixing of ceramics are currently often discussed in the context of solid oxide fuel cells, where they are used for joining the ceramic electrolyte with the frame of the fuel cell [44–56]. Unlike in case of structural sandwiches, the joints in fuel cells must be gas-tight. The operating temperatures of these joints reach up to 800 °C. Similar

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http://dx.doi.org/10.1016/j.jeurceramsoc.2016.12.046
0955-2219/

Table 1
Properties of the Si–O–C foam obtained from the MPS precursor.

elemental composition	average pore size	bulk density	apparent density	elastic modulus	compressive strength
$SiO_{1.4}C_{2.4}$	0.41 mm	1.81 g cm^{-3}	0.43 g cm^{-3}	1.5 GPa	9.8 MPa

demands are placed on high-temperature adhesives for fixing and sealing of perovskite membranes [57].

Bonding of CMC skin on a ceramic foam core is a separate and very challenging task. The adhesive connection between skin and foam core must meet several essential requirements:

1) The thermal expansion of all components of the sandwiches should be as similar as possible throughout the whole temperature range of the intended use.
2) The thermal expansion of the binder during its high-temperature curing should differ as little as possible from the expansion curve of fully cured binder.
3) The cured binder should have good adhesion to the skin as well as to the core in the whole temperature range of the intended use.
4) The non-cured binder should have a certain adhesion to the core and to the skin in the entire range of the high-temperature curing during the production of the sandwich.
5) When using a foam core, the binder should fill to some extent the pores, in order to increase the adhesion area. For this reason, it is advisable to use mastics with optimal filler grain size as binder.
6) None of the sandwich components should be affected by creep in the entire temperature range of the intended use. In particular, this demand applies to the high-temperature adhesive.

The aim of our study is to present a development and production process of a ceramic sandwich structure, with special focus on dilation and on rheological behaviour of the inorganic adhesive during its high-temperature curing process. These properties were studied in several types of compression experiments, using either cyclic load or static pre-load in the range from 300 to 1000 °C. The strength of the adhesive bond was tested in double cantilever beam (DCB) and in shear tests.

2. Material

The material investigated in this study is a high-temperature sandwich intended for use up to 1000 °C. The face sheet layers (skins) are made of a ceramic matrix composite (CMC) with a matrix based on pyrolyzed polymethylsiloxane resin (MS). The sandwich core is formed by a Si–O–C foam, which was prepared by pyrolysis of the polymethylphenylsiloxane resin (MPS). The skins and the core are bonded by an alumino-silicate adhesive (alumino-silicate mastic).

2.1. Skins

As an outer supporting layer, two variants of the fabric-reinforced CMC which differed in fibre type were used. The first type was Nextel 720 – a fibre having the alumina-mullite nanocristaline structure. The elastic modulus of these fibres is 190 GPa and its maximum service temperature is 1300 °C. The second type was Nextel 610 – a fibre with pure alumina nanocristaline structure which possesses improved creep resistance, elastic modulus of 300 GPa and a maximum service temperature of 1400 °C. Both types of composites have been produced by manual lamination of woven satin fabric which has been impregnated with the polymethylsiloxane (MS) resin. Plate-shaped samples were moulded and cured at a temperature/pressure controlled mode (up to 0.8 MPa and 250 °C). Subsequently, the composite plates were pyrolyzed at a slow heating rate up to 1100 °C (from 20 to 250 °C with 50 °C/h and from 250 to 1100 °C with 20 °C/h, followed by a 6 h dwell time at this temperature).

Structural changes in the MS precursor resin during the pyrolysis are described in [58,59]. The composite reinforced with Nextel 720 fibres (hereinafter N720) has a strength of 58 MPa, Young's modulus of 66 GPa and apparent density of 2.24 g/cm^3. The composite reinforced with Nextel 610 fibres (hereinafter N610) has a strength of 67 MPa, Young's modulus of 92 GPa and density of 2.45 g/cm^3.

2.2. Core

The foam core of the sandwich was produced by foaming the polymethylphenylsiloxane (MPS) resin with 12 wt.% of added starch. Foaming and curing of the preceramic foam took place simultaneously at 230 °C for 2 h. Subsequently, the foam was pyrolyzed at a slow heating rate up to 1100 °C using same temperature program as in the case of the skin plates (see 2.1). This foam has good mechanical properties, combined with good oxidation resistance at high temperatures, and its amorphous structure displays a high thermal stability. The low density of this foam is the key advantage for the use in sandwich structures. The production process and the properties of the foam are described in [26] and in [28]. The basic properties of the used foam are summarized in Table 1.

2.3. The adhesive layers of the studied sandwich structure

As a binder between the skins and the foam core, two types of high-temperature adhesives based on alumino-silicate mastic, which differ in their technological properties, were used. These two adhesives were selected in preliminary experiments among the six initially studied inorganic binders.

The initial intention of the authors was to produce a sandwich during foaming and curing of the core, without any adhesive layer, but significant differences in the shrinkage of the foam core and of the composite skins during pyrolysis did not allow implementing this intention. Second possibility of skin/core joining is the use of MS or MPS resin as adhesive after completed pyrolysis of the CMC skins and of the foam core. However, this method does not provide sufficient bonding strength after the pyrolysis of the adhesive resin layer.

Gluing of Si–O–C foam core and CMC composite skin by alumino-silicate adhesive was found to be successful and the adhesive provides a strong bond even where the bonded surfaces are separated by some distance – for example in a pore. The adhesive, however, forms an autonomous region with a thickness between ca. 0.1 and 1 mm, and therefore it must be considered as a separate layer which, by its mechanical properties, affects the entire sandwich.

The alumino-silicate adhesive with the trade name HT Silicate Adhesive (hereinafter SA) produced by Techniqll (Poland) is designed for the use at temperatures up to 1200 °C. The composition determined by EDS is: 55 wt.% of SiO_2, 40 wt.% of Al_2O_3, 0.3 wt.% of Fe_2O_3 and 2.5 wt.% of $Na_2O + K_2O$. SA has a density of 2.22 g/cm^3. The alumino-silicate adhesive adhesive Rudokit NT1350 (hereinafter Rk – the manufacturer uses the term “mastic”) produced by P-D Refractories CZ a.s. in the Czech Republic is certified for the use up to 1350 °C. The chemical composition provided by the man-