Ceramics in Energy Applications

NEW OPPORTUNITIES

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CERAMICS IN ENERGY APPLICATIONS

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and associated societies overseas:

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Australian Institute of Energy
Canadian Institute of Energy
L'Institut Francais de l'Energie
Fuel Society of Japan
Verein Deutscher Ingenieure (GET)

and in association with

The Institute of Ceramics
British Ceramic Research Ltd
The Institution of Refractory Engineers
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CERAMICS IN ENERGY APPLICATIONS

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Paper presented at Conf. on Ceramics in Energy Applications, Sheffield, April 1990
Session 1

The performance of materials used for ceramic radiant and immersion tubes

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ABSTRACT: The past 5-10 years has seen a number of developments in indirect gas-fired heating systems. Two such systems, namely radiant (700-1250°C) and immersion tubes (450-900°C) have recently exploited the higher temperature capabilities of ceramics. The tubes are fabricated from silicon nitride bonded silicon carbide (SNBSC), however, during field trials of both applications initial problems were encountered with variable tube lives. Laboratory studies and examination of used tubes confirmed that the principle cause of failure was oxidation of SNBSC. Service performance is a function of the tube manufacturing route and further work is concentrating on adjusting the base material to achieve a more consistent product with improved oxidation resistance.

1. INTRODUCTION

In many applications of industrial gas heating, there is a requirement to control the furnace atmosphere in order to preserve or modify the properties of the material being heated. At the same time there is a need to maximise the thermal efficiency of the heating process to minimise operating costs. To meet these demands gas fired radiant tubes with waste heat recovery have been developed. In many low temperature applications, metallic tubes are used, but at higher temperatures and in more hostile environments ceramic tubes are required.

The Midlands Research Station of British Gas has developed ceramic radiant tubes for the indirect heating of furnaces with controlled atmospheres and ceramic immersion tubes to heat molten zinc and aluminium with the tube immersed in the molten metal. After initial development, licensees have produced and marketed commercial versions. The introduction of the technology into a number of different applications (Table 1) was conducted via production field trials during which the performances of all aspects of the technology could be monitored and any problems identified and rectified. During two of these field trials, initial problems were encountered with variable tube life. This paper describes the identification of the cause of these failures and the improvements which have subsequently led to economically and technically acceptable tube lives being obtained in these applications.

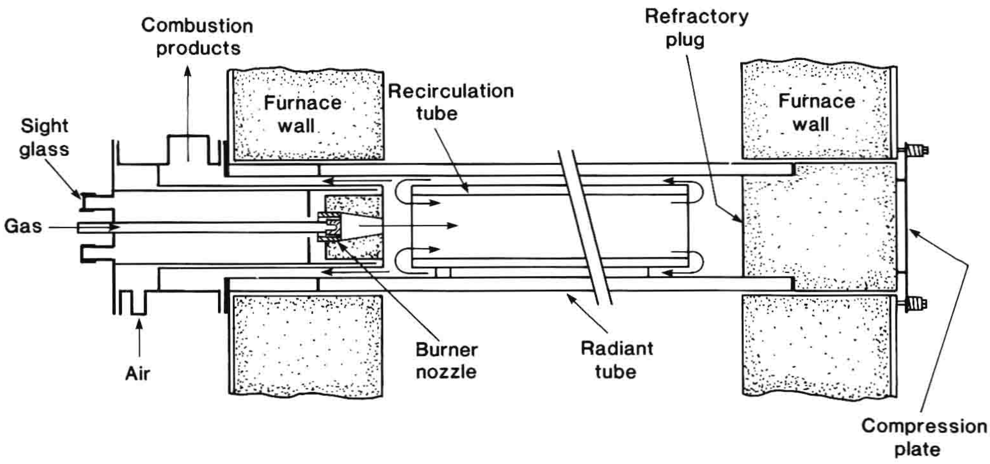

FIG. 1. SCHEMATIC OF CERAMIC RADIANT TUBE

2. TUBE DESIGN AND OPERATION

The gas fired ceramic radiant tubes have been developed primarily for operation in the temperature range 900°C to 1250°C. The tube design, Figure 1, consists of an open ended outer (radiant) tube and an inner (recirculation) tube fitted with a small recuperative burner at one end and a ceramic plug at the other. Each end of the tube is supported in the furnace wall using robust mounting techniques which accommodate thermal expansion and reduce tensile stresses in the material. The recuperator pre-heats the incoming air prior to mixing with the fuel gas at the burner nozzle. Combustion takes place inside the tunnel which is designed to provide a high velocity jet of combustion products to promote recirculation around the inner tube. This gives a uniform temperature along the outer tube.

The outer tube, which has a diameter of 170 mm and working length of 1.4 metres, can dissipate up to 40 kW/m^2 of heat from the radiating surface with the outer tube surface temperature upto 1350°C and the inner tube at a higher temperature of up to 1450°C. The inner tube and the inside surface of the outer (radiant) tube are therefore exposed to the combustion flue gases (72%N_2, 17%H_2O, 9%CO_2, 2%O_2) whilst the outer surface of the radiant tube is exposed to the furnace atmosphere. The thermal efficiency based on the gross calorific value of the fuel is 50 to 55% with the use of a recuperative burner. In practice this resulted in improvements of between 25% and 50% of the thermal efficiency of the plant compared to the previous equipment.

The ceramic immersion tube is of a similar design, except that a closed end tube is used. The burner is mounted vertically facing downwards into the tube. The tube is immersed in the molten metal and the outside surface of the radiant tube is exposed to three environments, air in the upper portion, a zone incorporating a flux/melt/air interface and a zone of molten metal.

3. TUBE MATERIAL SELECTION

Since tubes were intended for use in range of corrosive and oxidising environments, there were limitations on types of material which could be considered. The combination of these external conditions and the high operating temperatures required the careful selection of a non-oxide ceramic with a high thermal conductivity in order to maximise thermal efficiency and thermal shock resistance. The strength of the material was not a major consideration. Finally the material had to be capable of being formed into large, tubular components at an acceptable cost.

The material selected as most closely meeting these specification requirements was silicon nitride bonded silicon carbide, SNBSC.

4. TUBE MANUFACTURE

The tubes are manufactured from a controlled mixture of coarse, medium and fine silicon carbide grains together with a controlled size of silicon metal powder and green and permanent binders. The mixture is then shaped into the green tube. The method of shaping varies with manufacturer; two manufacturers have provided the vast majority of the tubes using specific processing routes of either manual pressing (Manufacturer 1) or isostatic pressing (Manufacturer 2). After drying, the "green" tube is hand ground to produce a relatively smooth surface finish. The final stage of manufacture involves firing the tube in a nitrogen atmosphere at around 1400°C. The silicon metal reacts with the nitrogen to produce a continuous bonding phase of silicon nitride.

The finished material from both manufacturers contains about 75% SiC, 23% Si_3N_4 with a residual porosity of around 15%.

5. LABORATORY STUDIES

Two investigational routes were followed. A programme of laboratory testing of sample materials was initiated and studies were also made on materials from used radiant and immersion tubes.

5.1 Comparison of Unused Material

An examination of the unused material shows differences in the microstructure of the materials produced by Manufacturers 1 and 2. In both cases the major phase is silicon carbide. The distribution of the fine, medium and coarse silicon carbide grains is reasonably even although agglomerations of similarly sized particles have been observed in both materials. The bonding phase of Material No. 1 is a mixture of silicon and cristobalite, SiO_2, whereas the bond of Material No. 2 consists of silicon nitride and silicon oxy-nitride, Si_2ON_2. The cristobalite present in Material No. 1 has been measured at levels of 5% to 8% in an unused sample (Fig 2). Optical microscopy shows that it is present principally around pore sites. It is less easy to distinguish between silicon nitride and silicon oxy-nitride in Material No. 2. There are small pockets of unreacted silicon metal in the bonding phase of both materials. The mean density of each material was determined (from fifty, one centimetre cubes). A value of $2.63gcm^{-3}$ was obtained for both materials, but the standard deviation of the cubes from Material No. 1 was three times that of Material No. 2. The crush strengths of the unused materials are very similar at around 220-240MPa.

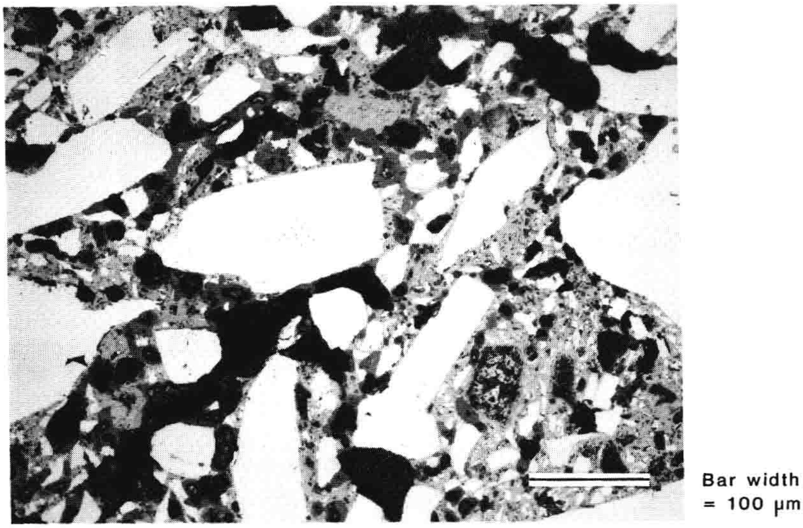

FIG. 2. MATERIAL No. 1; AS RECEIVED

5.2 Oxidation Studies

Test cubes ($1cm^3$) were cut from unused tubes produced by Manufacturers 1 and 2. The materials were exposed to air and combustion product environments for 500 hours at temperatures in the range 800°C to 1200°C (ten cubes for each test condition). The material property changes were examined in terms of weight and volume changes, x-ray diffraction (XRD), fourier transform infrared spectroscopy (FTIR), optical microscopy, scanning electron microscopy (SEM) and cold crush strength. In addition some limited Thermo-gravimetric analysis (TGA) scans were conducted on the material.

5.3 WEIGHT CHANGE

Isothermal oxidation tests (Table 2) show that in both air and combustion products Material No. 2 experiences significantly higher weight gains than Material No. 1. This holds for every test condition. Material No. 2 also shows markedly higher weight gains in combustion products (900-1150°C) compared to air. The same effect is observed in Material No. 1 above 1000°C. Weight changes were estimated from ten samples thus a spread of individual weight gains was obtained. In general the weight gains for Material No. 1 were subject to quite a large scatter particularly, for example, at 950°C in air. The effect of temperature on weight change (Fig. 3) reveals quite different behaviour in Materials No. 1 and 2. At the lowest temperature, 800°C the weight changes are only significant in Material No. 2. As the temperature is increased, however, the weight gains gradually rise, and in the case of Material No. 2 peak at 900°C in air and 1000°C in combustion products. Beyond these temperatures the mean weight gains fall off. The oxidation behaviour of Material No. 1 is not characterised by such readily discernible peaks. Instead the weight gains are seen to increase steadily throughout the range of temperatures investigated.

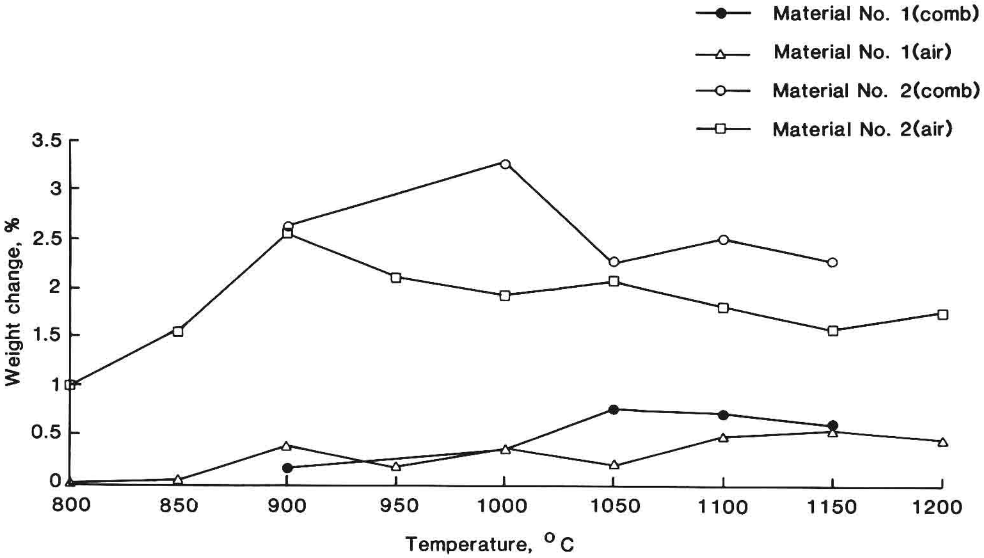

FIG. 3. WEIGHT CHANGE VS. TEMPERATURE
LAB TESTS IN AIR AND COMBUSTION PRODUCTS

5.4 Volume Change

Contrary to the weight change data the volume changes (Table 2) are much the same for both materials. Oxidation to silica is accompanied by a volume expansion which occurs because the silica has a lower density, $2.20 gcm^{-3}$ than the silicon carbide/silicon nitride, $3.20 gcm^{-3}$. However, measurements would be influenced by surface irregularities, e.g. scales and protrusions. In particular above 1100°C material No. 2 was covered in a surface glaze which affected the measurements. Material No. 1 was also covered in a surface deposit, but this was quite different in nature to a glazing effect.

5.5 FTIR Analysis

FTIR analysis (Table 2) was carried out on one cube from each test regime. This technique has been specially adapted to provide a quantitative assessment of cristobalite, SiO_2 in samples of SNBSC. As cristobalite is the principal oxidation product the degree of oxidation can be defined by this technique. Tests on the unused material indicate that whilst Material No. 2 does not contain any cristobalite, Material No. 1 contains quite significant quantities (5-8%). The levels of cristobalite production in Materials No. 1 and 2, as a result of oxidation, are reasonably similar, although there is greater variability in Material No. 1. The cristobalite content of Material No. 2 increases with the test temperature between 800°C and 1050°C. Above 1050°C the cristobalite levels fall off slightly.

5.6 XRD Analysis

XRD results (Table 2) confirm that cristobalite is produced in both materials over the range of test temperatures. It is not clear which species (Si, SiC, Si_3N_4, Si_2ON_2) have been oxidised as there are only very minor phase differences between samples. The technique is semi-quantitative and can therefore only differentiate between unoxidised and oxidised samples.

5.7 Crush Strength

In these tests oxidation appears to strengthen the material (Fig. 4). All of the test samples are stronger than the unused material. There is an increase in strength as the test temperature increases from 800°C in air. The strength peaks at 900°C (Material No. 1) and 1050°C (Material No. 2). These effects are less prominent after tests in combustion products.