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# THE EFFECT OF LONG-TERM EXPOSURE TO HIGH TEMPERATURE ATMOSPHERE ON THE MECHANICAL PROPERTIES OF $Al_2O_3$-BASED CERAMIC MATERIALS

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*Two corundum-based ceramic materials (C799 and C795) and one type of mullite ceramics (C610) have been tested for the production of components of technological circuits working with high-temperature helium and supercritical water. The materials were exposed to an atmosphere of high-temperature helium (900 °C), air (900 °C) and supercritical water (577 °C; 24 MPa) for 1000 hours and subsequently tested for bending strength at temperatures up to 1400 °C. The highest bending strength was exhibited by the corundum ceramics C799 (more than 300 MPa at 25 °C); for a significant decrease in the strength, it was necessary to use temperatures higher than 1000 °C. This material also exhibited relatively good stability during exposure to high-temperature helium, hot air as well as supercritical water; after 1000-hour exposure, its tensile strength decreased by maximally 11 %. Therefore, the pure corundum material has been evaluated as the most suitable among the tested materials for the production of components of the mentioned technological circuits.*

## INTRODUCTION

For more than ten years, research organisations, industrial enterprises and universities in the Czech Republic have participated in a research program focused on advanced gas-cooled nuclear reactors and other such systems operating at high temperatures of working media (600 - 900 °C, in some cases even higher) [1, 2]. Among other things this program involves the construction of unique experimental devices, technology development and testing, and material resistance research. The group of materials for high-temperature systems comprises both special types of steel and other metal alloys on the one hand [3, 4] and non-metallic materials on the other [5, 6]. Non-metallic materials also include high-temperature ceramic materials based on oxides, nitrides or carbides [7, 8]. Oxide-based ceramic materials ($Al_2O_3$, $SiO_2$) are characterised by relatively low strength, especially in tension (< 10 MPa); in the case of nuclear reactors, they are thus considered for use as construction, or thermal insulation, materials [9, 10].

$Al_2O_3$-based ceramic materials have been included in the experimental program focused on advanced nuclear reactors for two reasons. The first of them is the use of these materials for components of actual advanced reactors and the resulting need to verify the properties and resistance of these materials under the operating conditions of the reactors. Nevertheless, the implementation of advanced reactors is only expected in the long term – it may take more than ten years to prepare the first prototypes. The second reason is the use of the mentioned ceramic materials for key components of large research facilities – technological circuits – intended for research on advanced energy systems. One of the applications of ceramic materials for the components of technological circuits is e.g. the isolation of the heating elements of high-temperature helium experimental loops or supercritical water (SCW) loops [2, 11]. Several of these experimental technological circuits have recently been built in the Czech Republic. For maximum reliability of these devices, it was necessary to optimise their design, to design optimal materials for components subjected to tension and, last but not least, to verify the properties of the proposed key component materials in an environment simulating long-term operation of these devices.

Since $Al_2O_3$-based ceramic materials are generally very resistant to high temperatures, they are used for various high-temperature applications [12, 13]. For this reason, they have been considered as one of the construction materials for the new experimental circuits.

The key properties of the materials that needed to be verified and compared in more types of materials included mechanical strength and the influence of high temperature; further the long-term effect of SCW, high-temperature helium and hot air on the strength and stability of ceramic materials.

## EXPERIMENTAL

### Materials and production of specimens

The research was mainly focused on ceramic materials based on $Al_2O_3$, and $SiO_2$–$Al_2O_3$. Since these materials are readily available, they are currently used for the production of various components of special experimental devices. Their use for producing insulation of the heating elements in high-temperature helium experimental loops has been experimentally verified [11, 14]. An overview of the tested materials and their basic properties is provided in Table 1.

The ceramic materials were made from chemically prepared $Al(OH)_3$, which was calcined to a temperature of approximately 1400 °C to convert all $Al_2O_3$ into α-form (corundum). From such ceramic materials, samples were prepared in the shape of cylinders (by calendering) with a diameter of 6 mm and a length of 160 mm.

### Exposure of the specimens

Tests have been performed on selected materials, focusing on their resistance to high-temperature helium, SCW and hot air.

The exposure to high-temperature helium was carried out in a reactor in a horizontal tube furnace at a gas pressure of 0.85 MPa. The experiment was performed with a gaseous mixture prepared in advance. Its composition corresponded to the composition of the primary coolant of a high-temperature graphite moderated reactor [15]. The gas also contained some moisture, whose amount was monitored throughout the experiment using an optical hygrometer. The composition of the gas atmosphere is shown in Table 2. The samples were placed in a holder in the middle of the furnace (Figure 1), which ensured a constant temperature

Figure 1. Placement of the samples of ceramic materials in a holder before exposure to high-temperature helium.

Table 2. Composition of the gas atmosphere during the exposure of the samples of ceramic materials to high-temperature helium.

| Component | Composition [vol. %] |
|---|---|
| CO | 0.05 |
| $H_2$ | 0.01 |
| $CH_4$ | 0.01 |
| $H_2O$ | 0.002 – 0.006 |
| He | balance |

Table 1. Overview of the tested materials and their basic properties.

| Material designation | C 799 | C 795 | C 610 |
|---|---|---|---|
| Type of ceramics | corundum | corundum-mullite | mullite |
| Composition [wt. %] | | | |
| $Al_2O_3$ | 98.860 | 96.010 | 63.750 |
| $SiO_2$ | 0.674 | 1.880 | 32.350 |
| $K_2O$ | > 0.003 | > 0.003 | 1.740 |
| $Na_2O$ | > 0.003 | 0.019 | 0.235 |
| CaO | 0.165 | 1.180 | 0.203 |
| MgO | 0.251 | 0.849 | 0.235 |
| $Fe_2O3$ | 0.024 | 0.043 | 0.904 |
| $TiO_2$ | > 0.003 | > 0.003 | 0.450 |
| Body characteristic | | sintered (fully densified) | |
| Porosity | | nil | |
| Water absorption [%] | | 0 | |
| Bulk density [$kg\cdot m^{-3}$] | min. 3800 | 3750 | 2500 |
| Bending strength at 20 °C [MPa] | 300 | 375 | 120 |
| Thermal shock resistence [K] | min. 150 | min. 140 | min. 150 |
| Mean coefficient of thermal expansion [$K^{-1}$] | $7 – 8.10^{-6}$ | $6 – 8.10^{-6}$ | $5 – 6.10^{-6}$ |
| Specific dielectric strength [$kV\cdot mm^{-1}$] | min. 17 | min. 25 | min. 24 |
| Resistivity [Ω·cm] | min. $10^{12}$ (200 °C)<br>min. $10^{8}$ (600 °C) | min. $101^{2}$ (200 °C)<br>min. $10^{8}$ (600 °C) | min. $10^{9}$ (200 °C)<br>min. $10^{5}$ (600 °C) |

on the entire sample surface and even access of the gas atmosphere to the samples. At the beginning of the experiment, the temperature in the furnace was uniformly increased at a rate of 1 °C per minute until the temperature of 900 °C, after which this temperature was maintained for 1000 hours. Subsequently, the temperature was gradually reduced again at the rate of 1 °C per minute to ambient temperature (approximately 25 °C), when the exposure was terminated. The gas flow through the reactor was around 0.1 $l \cdot min^{-1}$.

The exposure to SCW was carried out in a special autoclave at a temperature of 577 °C and at an overpressure of 24 MPa. The water used had been demineralised and degassed using argon to dissolved oxygen concentrations below 10 $\mu g\ kg^{-1}$; before the experiment, the conductivity of the demineralised water was below 0.1 $\mu S \cdot cm^{-1}$. At the beginning of the experiment, the temperature in the autoclave was continuously increased at a rate of approximately 1 °C per minute up to 577 °C. At this temperature, the exposure was done in the autoclave for 1000 hours. The flow through the autoclave was set to 150 $ml \cdot hr^{-1}$. The samples were placed in a holder similar to the one used in the case of the exposure to high-temperature helium – see Figure 2.

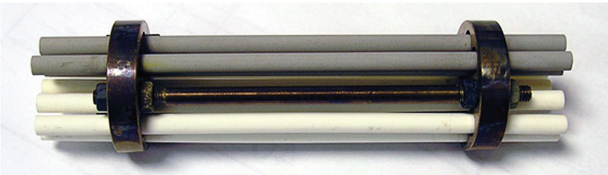

Figure 2. Placement of the samples before their insertion into the autoclave for testing in SCW.

The exposure to air, whose relative humidity was ca 50 - 80 %, was carried out in a horizontal tube furnace with the reactor open. The temperature was first increased at a rate of 1 °C per minute until 900 °C, which was maintained for 1000 hours, after which the temperature was reduced to ambient temperature at a rate of approximately 1 °C per minute and the experiment was terminated. The samples were placed in the same holder as in the case of the exposure to high-temperature helium (Figure 1).

## Bending strength testing

The dependence of bending strength on temperature was tested in air as well, specifically on cylindrical samples (with a diameter of 6 mm and a length of 160 mm) following the procedure described below at temperatures of 20, 600 and 800 - 1400 °C.

Bending strength was tested on samples without and with exposed in all three atmospheres. Three identical samples were usually tested to provide one value of bending strength. The samples were heated to the test temperature, at which they were kept until a uniform temperature distribution was achieved. Bending strength tests on unexposed samples were performed at the same temperature as the exposure, i.e. in the cases of the samples exposed to high-temperature helium and to air at 900 °C and the samples exposed to SCW at 577 °C.

For the testing of strength using the method of three-point bending at high temperatures, a special device was created through the modification of a superkanthal furnace with four heating loops (see Figures 3 and 4). A lever loading mechanism was inserted through an opening in the furnace roof; it enabled a continuous increase of the load applied on the sample during a strength test at high temperatures. A body on two supports was evenly loaded in the middle with the stress increasing at the rate of 0.15 $MPa \cdot s^{-1}$ until breakage.

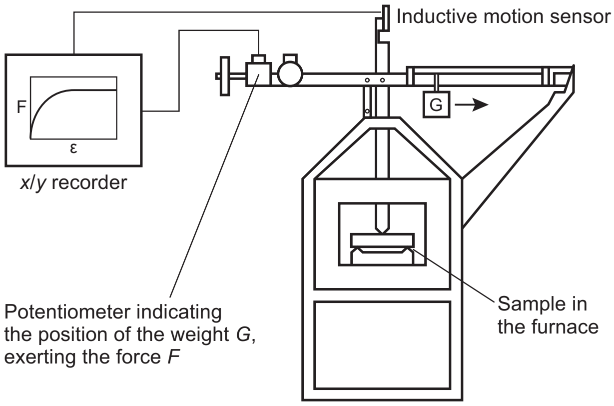


Figure 3. The high-temperature device used for the bending test [16].

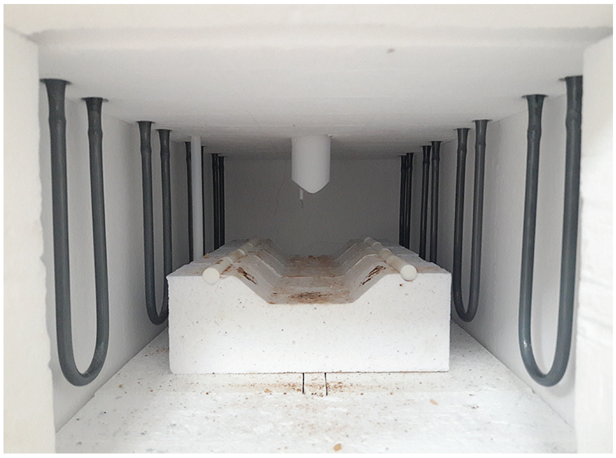

Figure 4. Detail of the interior of the device for the measurement of three-point bending.

## RESULTS AND DISCUSSION

First, changes in sample weight after the exposure in the mentioned media were compared. The results are summarized in Table 3.

Table 2. Change in the weight of the ceramic samples after 1000-hour exposure expressed in % of the initial weight.

| Material | Change in the weight after exposure [%] | | |
|---|---|---|---|
| | Air 900 °C | Helium 900 °C | SCW 577 °C |
| C 799 | 0.005 | 0.005 | 0.005 |
| C 795 | 0.014 | 0.013 | 0.014 |
| C 610 | 0.015 | 0.015 | 0.013 |

In most of the cases, the exposure caused a very slight increase in the weight in the order of hundredths to thousandths of a percent. The smallest changes in the weight after exposure to all of the mentioned media have been recorded in the material 1 (corundum ceramics). This indicator implies log-term stability of this material even after prolonged exposure to different media.

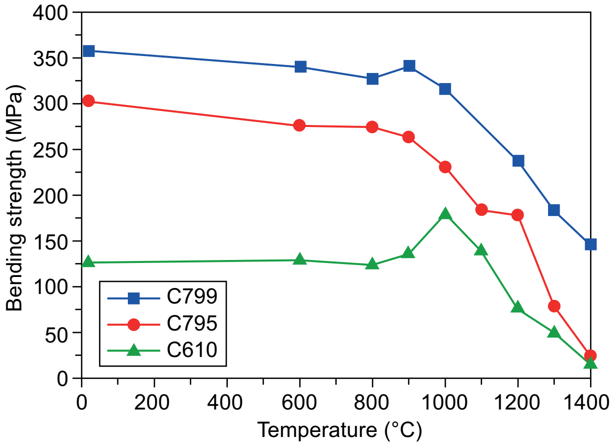


Figure 5. Bending strength determined for the unexposed materials in dependence on temperature.

The results of the tests of bending stress in dependence on temperature are summarized in Figure 5. On the basis of these results, the following information has been obtained:

- The highest bending strength among the three tested materials in the temperature range of 25 - 1400 °C was exhibited by the corundum ceramics C 799. On the contrary, the bending strength of the mullite ceramics (C 610), mainly in the temperature range of 25 - 900 °C, was considerably lower than the bending strength of both corundum-based ceramic materials tested.
- In the temperature range of 25 - 900 °C, the bending strength of all three tested materials did not change much. At temperatures above 900 °C, the bending strength of the corundum ceramics C 799 and C 795 significantly decreased. In the case of the mullite ceramics C 610, the bending strength increased in the temperature range of 800 - 1000 °C, reaching its maximum at 1000 °C; at higher temperatures, the strength subsequently decreased. This is because the refractory ceramic, as a heterogeneous material, contains a number of microcracks from the production, which reduce its mechanical strength. Once heated to temperatures when melt begins to form, the material begins to soften and these microcracks are healed. With even higher temperatures and thus higher amounts of melt and its decreasing viscosity, bending strengths decrease like in corundum ceramics [17, 18].

The results of the tests of the effect of long-term exposure to air and helium at the temperature of 900 °C and to SCW at the temperature of 577 °C and the pressure of 24 MPa on the bending strength of the tested materials are summarized in Figure 6. Based on these results, the influence of the long-term exposure on the strength of the tested ceramic materials is not essential, but it is evident in almost all cases. The bending strength decreased by more than 10 % with respect to the initial state in the case of the material C 799 exposed for 1000 hours to helium and air at 900 °C and in the case of the material C 795 exposed to SCW. On the other hand, the material C 610 exhibited only a small decrease of the bending strength (by approximately 1.5 % with respect to the initial state) after the exposure to helium; after its exposure to air, its bending strength even increased by approximately 3 %.

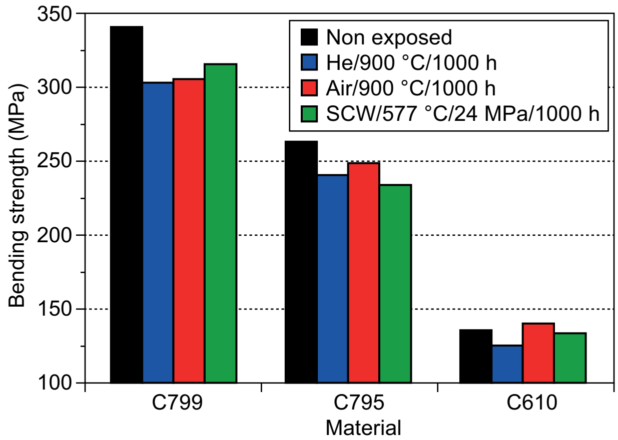


Figure 6. Influence of the 1000-hour exposure of the tested materials to air, helium and SCW on their bending strength.

The above-mentioned results imply that among the materials tested, the most suitable material for ceramic components of technological circuits working with high-temperature helium and supercritical water as well as for other similar applications are ceramics based on pure corundum (C 799). The bending strength of this material reached the highest values among the materials tested; after long-term exposure to high-temperature environments, this value decreased by a maximally 10 %. After the exposure to high-temperature environments, the weight of this material did not change much either, which indicates its good stability. The maximum temperatures should be around 900 °C in the case of helium technologies and around 600 °C in the case of SCW technologies [15]. At these temperatures, the bending strength of corundum ceramics or the other tested materials does not decrease much yet.

## CONLUSION

In order to find a suitable material for the components of technological circuits working with high-temperature helium and supercritical water, three types of relatively easily available ceramic materials intended for high-temperature applications have been tested. These included two types of corundum-based ceramic materials (the material C 799, containing more than 98 % of $Al_2O_3$, and the material C 795 with approximately 96 % of $Al_2O_3$) and one type of mullite ceramics (C 610), with the main components being $Al_2O_3$ (63.7 %) and $SiO_2$ (32.3 %). In these materials, the dependence of bending strength on temperature up to 1400 °C was studied along with the influence of long-term exposure to high-temperature helium (900 °C), air (900 °C) and SCW (577 °C; 24 MPa) at increased temperature on the bending strength and weight of the samples. Based on the results of the tests, the highest bending strength was exhibited by the corundum ceramics C 799 (more than 300 MPa at 25 °C). On the other hand, the lowest bending strength was exhibited by the mullite ceramics C 610 (more than 100 MPa at 25 °C). The bending strength of the tested materials significantly decreased at temperatures higher than 1000 °C; in the case of the mullite ceramics C 610, the bending strength exhibited a maximum in the temperature range of 900 - 1000 °C. In most of the cases, the exposure of the tested materials to the mentioned media decreased their bending strength by 1.5 - 11 %; in the case of mullite ceramics, the exposure of the material to air increased its bending strength by approximately 3 %. The lowest weight loss was measured in the case of the corundum ceramics C 799, which may prove its high stability in the media tested. Based on these results, the most suitable material for the ceramic components of technological circuits with high-temperature helium, SCW and some other similar applications is the material based on pure corundum – C 799.

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