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NON-OXIDE CERAMICS – CHANCES FOR APPLICATION IN NUCLEAR HYDROGEN PRODUCTION

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ABSTRACT

Research and development are increasingly focusing on the provision and utilization of heat in the high-temperature range above 900 °C, in particular under the aspect of resource-saving energy technologies. On the one hand, the exploitation of the high-temperature range helps to improve the efficiency of energy conversion processes; on the other hand, the provision of high-temperature heat makes it possible to utilize innovative thermochemical processes, which in turn represent environmentally compatible processes. An example to be quoted here is the thermally induced production of hydrogen by the iodine-sulfur process. The high temperatures alone place extremely high requirements on the materials to be used so that metallic materials soon reach their limits of application. If additionally chemically aggressive process media are used, as in the iodine-sulfur process, basically only ceramic materials can be considered as construction materials. In this application, notably silicon carbide (SiC) is favored owing to its excellent high-temperature properties. The possible technical fields of application of such high-performance ceramics can be broadly extended provided that suitable, highly efficient joining methods are available for these ceramics. In addition to its use as a constructional ceramic, SiC can principally also be used as a functional ceramic. For this purpose, the basic ceramic is modified with different additives, providing it with electrical properties that permit its application as a full ceramic heat conductor or sensor. In this case, it also holds true that a suitable joining method for making electrically conductive joints will extend the fields of application considerably. Laser-based joining technologies are being developed for both applications at the Dresden University of Technology. The research work presented here notably focuses on laser joining of electrically conductive SiC ceramics. In addition to a CO_2 laser, a diode laser has been used. Basically, electrical connection has been made in two ways. In the first variants, graphite pins are inserted into the joining zone as electrically conductive bridges. In an alternative concept, the oxidic glass filler itself is made electrically conductive with additives. Like that a full ceramic heating conductor joined by means of laser radiation has been tested. The temperature resistance and functionality of the laser-joined heating conductor could be fully demonstrated.

INTRODUCTION

International efforts to accelerate the development of selected nuclear reactor concepts under the Generation IV Program also include the development of innovative high-temperature reactors ((V)HTR). These reactors supply nuclear-generated heat in a temperature range above 900°C. This heat can either be used for high efficiency generation of electrical energy or used as process heat for thermochemical heat treatments. However, the extension of the utilization parameters

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above 900 °C poses extremely high requirements on the construction materials to be used. The high temperature range alone makes metallic materials insufficient for the stable long-term operation of such plants. Ceramic materials, and notably non-oxide ceramics, offer a good alternative to metallic alloys. If high temperatures are accompanied by the utilization of chemically aggressive or abrasive process media, basically only ceramic materials can be used. Non-oxide ceramics such as silicon carbide (SiC) or silicon nitride (Si_3N_4) have excellent high-temperature properties. They can be used above 1,200 °C, even in oxidizing environments; they are stable against a large number of chemical substances, in particular acids; they are radiation resistant and due to their great hardness can be used under abrasive conditions whilst maintaining long-term stability. Presently, SiC is favored for many fields of application. The possibility to modify this ceramic material with additives so that its electrical conductivity varies in a wide range, permits the use of SiC as a functional ceramic, in addition to its use as a construction material for parts such as pipes, containers or heat exchangers. This opens up the possibility to produce electrically heated SiC elements or, reversing the electro-thermal effect, to produce fully ceramic sensors for temperature measurements. By combining both functions of a constructional and functional ceramic a wide range of practical applications is opened up. The extent to which this potential of applications can be exploited in practice highly depends on whether suitable joining methods for these ceramics are available. Research and development at the TU Dresden has shown that joining methods based on high-temperature laser brazing are well suited to make high temperature stable, chemically resistant and electrically conductive joints between ceramic materials.

1 THE IODINE-SULFUR PROCESS

The iodine-sulfur process is one possibility for the industrial thermochemical production of hydrogen and oxygen. Figure 1 shows a graph of the chemical process. It can be seen that there are two cycles coupled in this process, with only water and process heat to be supplied at two different temperature levels (approx. 400 °C and approx. 900 °C, respectively) in order to produce hydrogen and oxygen. Additionally, waste heat of approx. 100 °C is generated. Combined with a high temperature reactor, the process heat can be provided at the required temperature level and at moderate costs. However, it is also obvious that the highly aggressive media (H_2SO_4, IH) need to be kept under control at high temperatures during the thermochemical process.
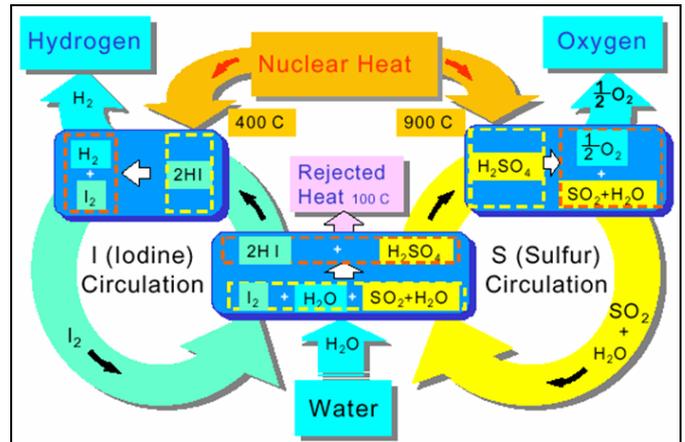

Figure 1 I-S process for hydrogen production [1]

Any experience gained so far has been based on laboratory or small-scale configurations [2], primarily using glassware. For industrial plants, ceramic materials would be of greater advantage as their thermomechanical properties and long-term stability in contact with acids are better. Besides the necessity to control the process parameters during normal operation, the start-up and shut-down procedures with the temperature gradients that occur need to be controlled in materials engineering. Although SiC, among ceramic materials, provides excellent thermal shock resistance, load change processes are a great challenge. Assuming that a quick shut-down of the heat source may become necessary, the task is to design a technological plant as for the iodine-sulfur process that is thermically conditioned to be safely changed to break or rest mode. One possibility to minimize thermally induced stress due to load-change processes is to fit sensitive plant areas with an additional electrically operated heating unit. A good option is to design the SiC-based equipment (pipes, containers, heat exchangers) fully or partially for direct electrical heating. An optimal solution may be to combine SiC with varying electrical conductivity with non-conductive SiC. Furthermore, electrically heated plant components can prevent the freezing of reactants in break mode.

2 LASER BEAM JOINING TECHNOLOGY

The research work presented here aims at joining the non-oxide ceramic material SiC by means of a laser beam. The material and the joint are to be electrically conductive and be used as a heating element in the temperature range of approx. 1,000 °C.

2.1 Heating conductor material LPS-SiC

Liquid phase sintered silicon carbide (LPS-SiC) is distinguished from other SiC material types by its high content of oxidic additives. The electrical resistance of SiC can be changed by targeted modification of the material and by modifying the sintering parameters as fit

for the purpose [3]. A specific electrical resistance < 20 Ωcm at room temperature allows the use of SiC as a heating conductor.

2.2 Brazing fillers
The SiC ceramic has a high proportion of co-valent bonds of more than 88 % that accounts for the absence of a melting phase. This makes it necessary to develop a suitable brazing filler for joining this ceramic material. The selection of fillers depends largely on the desired utilization temperature.
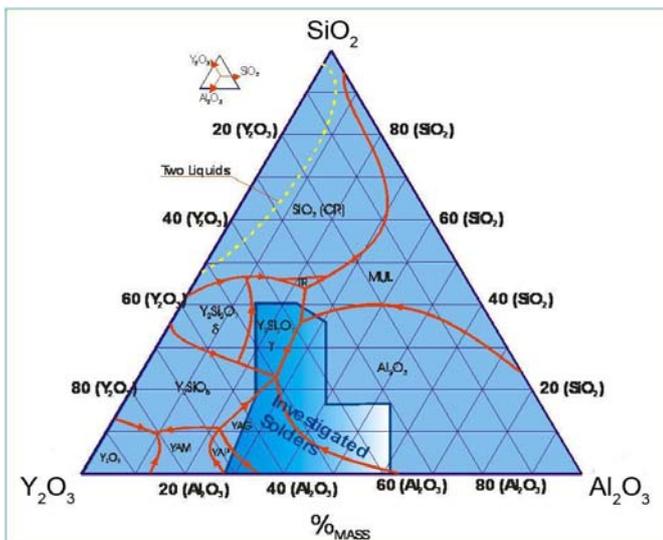

Figure 2 Ternary phase diagram of brazing fillers [4]

Special attention must be paid to the thermal expansion coefficient of the brazing filler. This must largely correspond over the full temperature range to the expansion coefficient of the ceramic material to be joined (utilization temperature up to flow temperature of the brazing filler). Furthermore, good wetting of the ceramic surface by the filler is indispensable.
Previous research work on laser beam joining of SiC components has yielded oxidic brazing fillers of the Y_2O_3-Al_2O_3-SiO_2 system (Figure 2) that ensure the thermal stability of the joint at temperatures well above 1,000 °C. The fillers used are mostly in the low SiO_2 area (framed in dark blue in Figure 2).
The filler can be applied to the faces of the ceramic elements to be joined as a suspension. However, the favored method is the use of a film that ensures an even, reproducible and very thin distribution of the filler on the surfaces to be joined. (Thickness of brazing filler film: approx. 50 μm) [5].

2.3 Laser technology used
The Chair of Hydrogen and Nuclear Power Engineering of the TU Dresden has a laboratory with two high-performance lasers. In addition to a CO_2 laser (wavelength: 10.6 μm, continuous wave (cw) beam power: 2.0 kW), it has a diode laser (wavelengths: 808 nm and 940 nm, cw beam power: 3.1 kW) (see Figure 3).
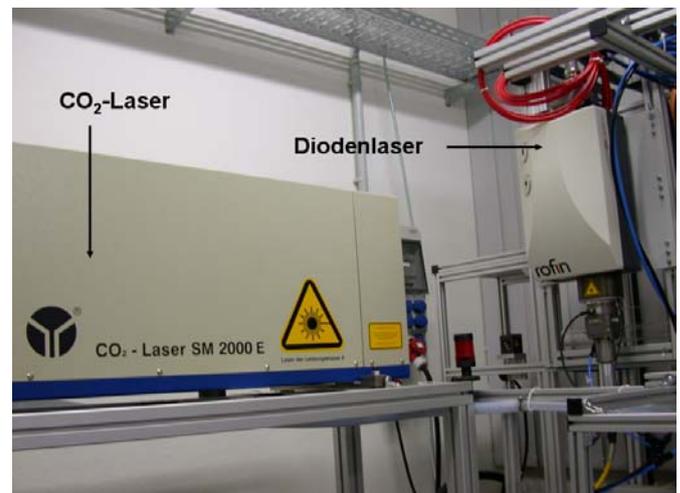

Figure 3 Laser laboratory of the TU Dresden

The wavelengths of the diode laser can be set separately so that laser-material interaction can be investigated separately for both wavelengths. The radiation emitted by both laser systems is absorbed by the non-oxide ceramics primarily at the surface [6]. The energy is brought deep down into the components by heat conduction processes. Extensive investigations have demonstrated that both lasers are equally suitable for joining non-oxide ceramics. Since, beside the time-dependent laser power, the only technologically relevant variable to be controlled is the laser beam direction to the component in the cases described, the coordinated control of these two variables is of major importance. Laser process optimization must therefore aim at heating the ceramic material in the joining zone up to the temperature required for melting the filler without damaging the components by thermally induced stress and without affecting the materials thermochemically.
The laser beam can produce the most diverse images on the sample, using beam guiding and forming systems. The optical scanner unit used to guide the beam is shown in Figure 4 at the top left. It allows the beam to trace virtually any two-dimensional shape on the sample surface at extremely high speed, so that the image created can be considered as quasi-stationary. The laser beam impinging on the sample to be joined is illustrated schematically at the bottom left of Figure 4.

In the samples investigated here, the laser beam rotates on the ceramic surface, tracing two ellipses, thus inducing an optimal amount of energy. The right part of Figure 4 shows a real photo of the laser joining process.
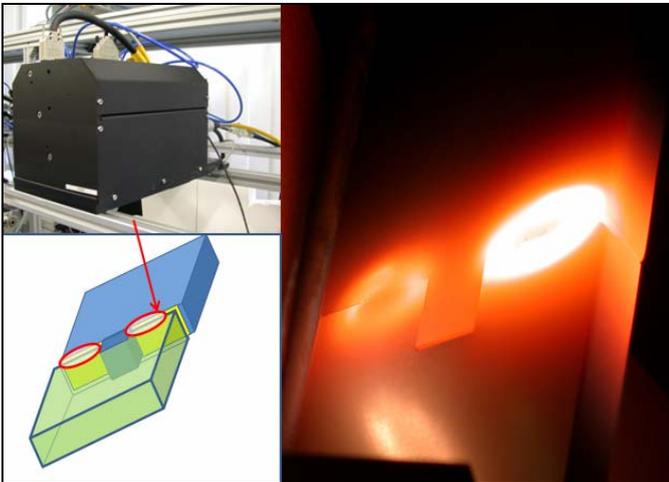

Figure 4 Laser joining process of SiC heater

The different regions of intensity of energy induction are distinctive. The central region with an adapter piece carries a minor load of laser radiation in order to reduce the (undesirable) thermomechanical stress peaks in this region.

Investigations have shown that the image quality of the scan shapes has a considerable effect on joint seam quality. Therefore the geometry and speed parameters need to be matched exactly with the ceramic material and the joint seam geometry.

2.4 Electrically conductive joints
The necessity to join ceramic heating conductor elements results essentially from two reasons:
- On the one hand, it is technologically demanding to produce relatively large ceramic heating conductors of intricate shape in one piece, i.e. in one technological sintering process step. This is why several small heating segments must be joined into one larger functional assembly.
- On the other hand, the ceramic heating conductor cannot be connected directly by metallic cables if the utilization temperatures are too high. In this case, it is necessary to fit in an intermediate ceramic segment that has a lower electrical resistance than the heating conductor and therefore does not heat itself up to the same degree.

Basically, electrical connection can be made in two ways. In the first variants, graphite pins are inserted into the joining zone as electrically conductive bridges. Figure 5 shows such a configuration with two graphite pins before joining.

Figure 5 Graphite bridges in SiC-body

The challenge to the joining process performed in free atmosphere is to prevent graphite oxidation during the joining process and later during application by directed application of the filler. Furthermore, it is important to ensure long-term mechanical stability of the joint and to provide a sufficiently large contact area for electric current flow.

Investigations carried out so far have shown that this method is successful in producing electrically conductive joints of the required quality. The graphite pins were fully integrated into the brazing filler, ensuring electrical contact of the segments.

Since, however, the intermediate graphite has less electrical resistance than the filler and also than the SiC ceramic, electric current tends to flow through the graphite pins in the joint region, resulting ultimately in a locally reduced heating of the joint region. With a mathematical simulation it is possible to confirm this effect. The FEM-Code COMSOL Multiphysics carries out numerical simulations. The software is based on partial differential equations, which can be calculated by using high-capacity solvers based on the finite-element-method [7]. The result of the calculation is displayed in Figure 6 and shows this effect as a mathematical simulation. This can be an undesirable effect for certain purposes, e.g., when a very homogenous temperature field is required.
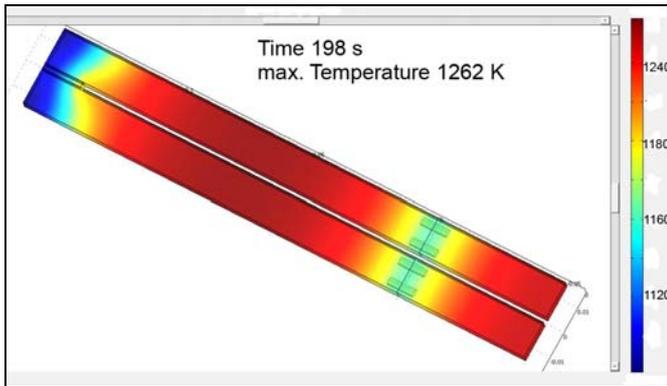
Figure 6 Mathematical simulation of electrically induced temperature field in a laser joined SiC heater

In an alternative concept, the oxidic glass filler itself is made electrically conductive with additives. Current investigations aim at determining an optimal filler composition, besides suitable additives, in order to ensure the desired long-term stability of electrical conductivity and to achieve the important flow and wetting characteristics of the filler without reducing the mechanical strength of the joint. First test results have shown that joints produced with such fillers can reach the expected electrical and thermomechanical properties.

2.5 Process and parameter control

The laser joining process is controlled thermographically. This contactless measurement procedure captures and represents the instationary temperature fields on solid-state surfaces. It uses a bolometric camera [8] that captures the heat radiation emitted from the body surface. The camera measures infrared radiation in the wavelength range from 8.0 to 13.0 µm. A special filter protects the sensor chip from the laser radiation, preventing erroneous temperature measurements caused by scattered radiation of the laser. A crucial factor for the thermograms is the temperature-dependent emission coefficient of the samples to be investigated. Since this coefficient can vary strongly, depending on ceramic modification, it needs to be determined separately for every ceramic material over the full temperature range. The temperature range of interest for non-oxide ceramics is generally from room temperature to 1,800 °C. Since the joining process takes place within the component volume, the temperature field must be simulated mathematically to establish the relationship between surface and volume temperature. This can only be achieved by creating a mathematical model of the total process. Modeling is carried out with the finite element code COMSOL.

Besides the determination of the temperature field for the laser joining process, it is important to know the temperature fields that are produced during electrical heating. In particular, the stress generated in the joining zone by thermal gradients during the heating and cooling phases can put the integrity of the heating conductor at risk. In order to assess these transient process loads, simulation calculations are performed for these cases in addition to experimental investigations.

3 RESULTS

Figure 7 shows a full ceramic heating conductor joined by means of laser radiation. In a test experiment, this conductor was heated up at a start voltage of 230 V to an operating temperature of more than 1,000 °C. During the heating process, the voltage applied must be continuously reduced as the electrical resistance of the ceramic falls as temperature rises (SiC behaves like a semiconductor). The electrical power of this heater was about 460 W in the temperature range between 800 and 1,050 °C. The temperature resistance and functionality of the laser-joined heating conductor could be fully demonstrated in this experiment.
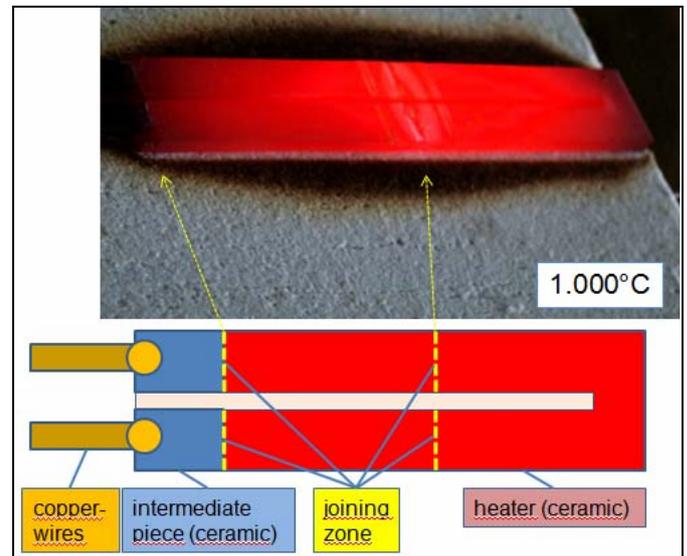

Figure 7 Test of electrically heated SiC heater

For a further characterisation of the joints scanning electron microscope (SEM) micrographs were taken. Figure 8 displays details of the joining zone of the heating element.

The micrograph on the right was taken with a magnification of 100 diameters. The micrograph indicates many miniature glass blisters and an accumulation of the electrically conductive remunerating substance in the marginal area of the joining zone. A typical glass fracture structure is seen in the left micrograph outside of the red marked area. This micrograph was taken with a magnification of 48 diameters.
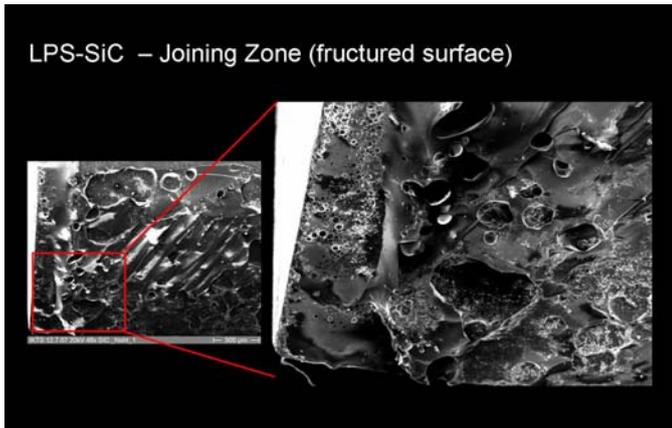
LPS-SiC – Joining Zone (fructured surface)

Figure 8 SEM micrograph of the joining zone

The brazing filler has a regular structure covering the entire joining zone. It is also completely melted.

4 SUMMARY

Modern high-performance ceramics such as SiC or Si_3N_4 are an interesting alternative to metallic materials for a great number of innovative technical applications. In particular in the field of high-temperature power engineering, these ceramics – both constructional and functional – are often the only option for the implementation of thermally demanding processes. The combination of their excellent mechanical and thermochemical properties with further functional properties such as selectively adjustable electrical conductivity extends the range of applications for this group of materials considerably. In the past the effort to join these ceramics to gain high temperature resistance properties was problematical and complex. The laser joining technology presented here offers an attractive possibility to join ceramic bodies in free atmosphere with a justifiable effort. In particular, the feasibility of joining SiC heating conductors to maintain their electrical conductivity opens up a wide range of technological applications. Considering the technological challenge of the development of modern high-temperature reactors and related technologies, the practical use of constructional and functional ceramics combined with an efficient joining technology can make a significant contribution to the solution of a number of problems.

ACKKNOWLEDGMENTS

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