

HIGH DENSITY INFRARED SINTERING PROCESS

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INTRODUCTION

Solid oxide fuel cells (SOFC) have been under development for more than 30 years and are on the verge of commercialization. The projected initial costs for the fuel cell stack are approximately \$1000/kW while the allowable fuel cell installed cost ranges from \$700/kW to more than \$1500/kW, depending on the market segment and size [1]. The largest contributors to the cost of the SOFC stack are materials costs, the fabrication method, and heat-treatment (sintering) time. When and if low-cost materials and fabrication methods are used, the amount of time required for heat-treatment becomes the dominant factor in the cost of the fuel cell.

A new method has been developed for densifying coatings on both planar and tubular metallic and ceramic supports. This process called high-density-infrared (HDI) transient-liquid coating (TLC) process has been developed to produce wear- and corrosion-resistant coatings on a variety of surfaces that are of commercial interest [2,3]. Infrared technology is used in a wide range of industrial applications. It is used in the electronics industry for drying solder resists, in food processing for browning and sterilization, in finishing for stoving and curing, in textiles for drying and sealing, in plastics for softening, in printing for drying, and in engineering for preheating and shrink fitting [4]. These types of equipment for the above applications are typically limited to 537 to 760 °C.

Infrared heating has many advantages over other heating techniques. Infrared heating provides 1) an inherently clean non-contact heating method; 2) rapid response energy fluxes capable of heating rates in excess of 500°C/s (state-of-the-art equipment provides excellent spatial and tempered control which allows sample-only heating uni-directionally over large areas), 3) rapid power level changes [no thermal mass (plasma lamp)], and 4) rapid cooling rates due to the “cold wall” nature of the process in which only the sample is heated. The plasma lamp technology provides controllable temperature gradient processing due to flux densities of up to 3500 W/cm². Thus, infrared provides a versatile and flexible answer to heat transfer problems throughout the industrial spectrum [4] and it has recently been used to sinter YSZ on an anode support with the complete cycle time (heat-up, sintering, cool down) being reduced to less than 5 minutes. It is the purpose of this paper to briefly discuss this work.

HIGH DENSITY INFRARED (HDI) PROCESS

The HDI process utilizes a unique technology to produce extremely high-power densities of up to 3.5 kW/cm² with a single lamp, which is currently the most powerful one in the world (Figure 1). Instead of using an electrically heated resistive element to produce radiant energy, a controlled and contained plasma is utilized.

The lamp consists of a 3.175-cm-diam quartz tube, which can be 10.16, 20.32, or 38.1 cm long. The lamp is sealed at the ends where the cathode and anode are located. Deionized water mixed with argon or nitrogen gas enters at the cathode side through high-velocity jets impinging at a given angle. Due to the high velocities and pressure, the de-ionized water is impelled to the wall of the quartz tube and spirals down the length of the tube in a uniform 2- to 3-mm-thick film. This water film serves two purposes: 1) to cool the quartz wall and 2) to remove any tungsten particulate that may be expelled from the electrodes. The gas moves in a spiral fashion through

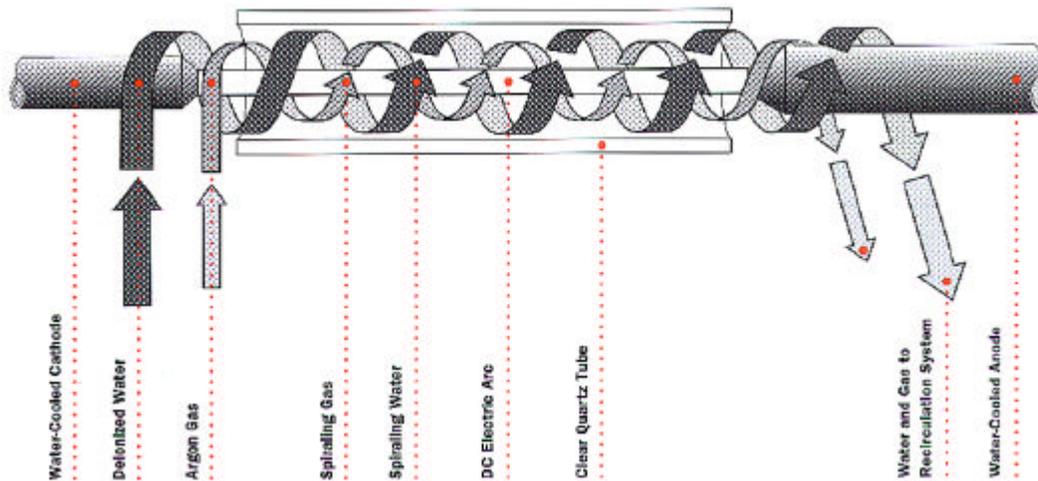


Figure 1. Schematic of a high-power density plasma-arc lamp and the principles of operation.

the center of the tube, and a capacitive circuit initiates the plasma. The plasma, which has a temperature in excess of 10,000 K, is stable and produces a radiant spectrum from 0.2 to 1.4 microns. The spectrum is primarily in the infrared (0.78 to 1.00 μm), although substantial energy is released in the visible wavelength, similar to the appearance of natural sunlight in energy distribution and color rendition. In contrast, the spectrum at a CO_2 laser with wavelengths near 10.6 microns is absorbed with much lower efficiency. The powder coatings discussed here are highly absorbing because the open areas act like black bodies.

The lamp has a typical life of approximately 1200 hours, and failure occurs in the anodes and cathode, which are inexpensive and can be changed in approximately 15 min. Furthermore, the lamp has a consistent spectral output independent of lamp life and power level. The lamp is typically configured with a reflector to produce a line focus or an area of uniform irradiance.

The HDI lamp is mounted on a large six-axis robotic manipulator. A state-of-the-art PC based robotic controller is utilized for precise lamp movement. This controller is capable of using computer-aided drawing data files of large parts to generate instructions to manipulate the source over a complicated geometry in a predetermined systematic way.

Test sample processing is performed in an environmentally controlled box, which has a quartz window cover to permit processing of materials in a controlled atmosphere. The infrared reflector has a focal length that extends through the quartz and onto the material being processed. A lathe to rotate parts while heat treating or fusing coatings is also included in the processing facility. Another feature of the plasma lamp for this facility is a water window. This water window device passes a thin film of water over the quartz glass covering the elliptical reflector. This feature protects the lamp when operating in harsh environments. This window has a 3-mm water film that continuously cools the lamp quartz window. The water clings to the quartz window due to surface tension and stream momentum. The water is introduced on one side of the lamp across an air knife and removed on the opposite side through a vacuum orifice. This water window, shown in Figure 2, protects the lamp from harmful effluent and hot-spalled material.

EXPERIMENTAL PROCEDURE

Anode substrates were prepared by ball milling NiO (Baker) and YSZ (Tosoh TZ8Y) with an appropriate organic pore forming agent. After milling, the powder was uniaxially pressed into disks (2.54 cm in diameter) at 33 MPa and then isostatically pressed at 130 MPa. The green bodies were sintered for 2 hours at 1400°C in air. A slurry was prepared by dispersing YSZ in

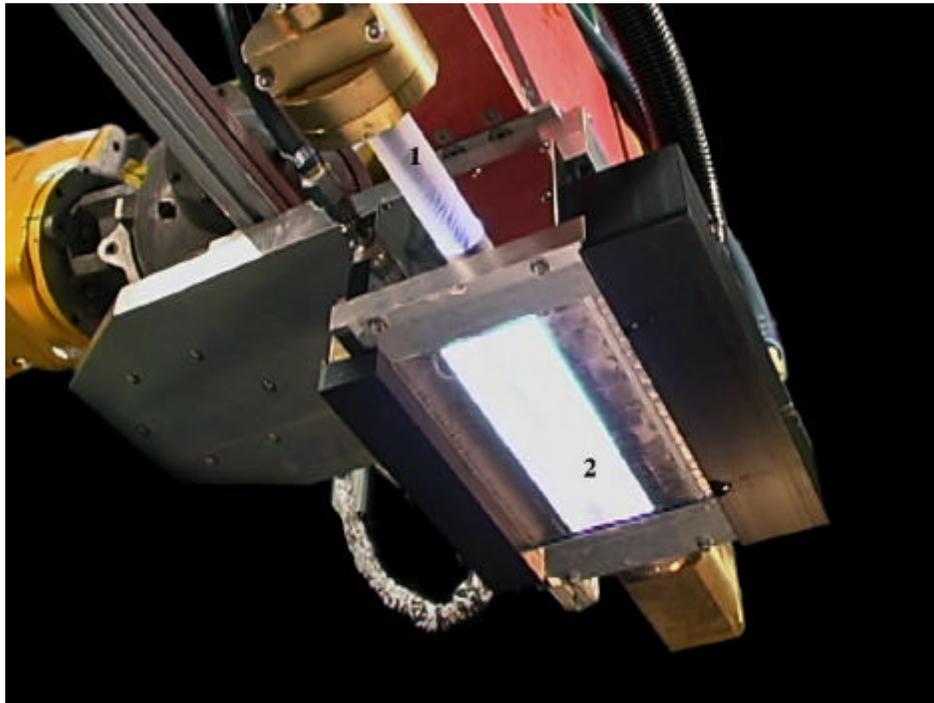


Figure 2. Infrared plasma-arc lamp showing (1) internal and (2) external water walls.

deionized water/ethanol solution. A YSZ coating was deposited onto the surface of the sintered anode supports by spraying an aqueous slurry using a gravity feed spray system.

Coated samples were placed on a stainless steel support under the HDI source. Samples were preheated by rastering the HDI source set at lower power densities across the sample surface at approximately 10 mm/sec. After preheating the power density was increased density (700 to 1200 W/cm^2) and the samples were heat-treated by rastering the focus plasma over the sample at rates ranging from 5 to greater than 20 mm/sec. Selected samples were analyzed by both optical and electron microscopy to evaluate microstructural development.

RESULTS AND DISCUSSION

The use of the HDIC process for fuel cell materials has only been in development for a short period and is still in the early development stages. The HDIC process, however, shows potential for use to rapidly sinter YSZ. In the initial samples, the scan rate was fixed at 10 mm/sec and the power density was varied between 800 and 1000 W/cm^2 . In this set of experiments it was found that the scan rate was too slow and in most cases NiO in the anode melted (1984°C) and infiltrated the porous zirconia, forming reacting to form a eutectic microstructure. Figure 3 shows a SEM micrograph of the surface of YSZ showing significant densification in the YSZ coating heat-treated for less than 3 seconds. This sample was heat-treated at 800 W/cm^2 with a scan rate 10 mm/sec. The total cycle time from preheat to cool down on this sample was 5 minutes. The grain size of the partially sintered grains (Figure 3) is approximately the same size as the starting powder, indicating the rapid heat-up and cool down of the material during processing.

In subsequent trials, the power density was fixed at 800 and 1000 W/cm^2 and the scan rate was increased from 10 mm/sec to 50 mm/sec in small increments. At 14 mm/sec the heat transfer was reduced whereby NiO did not melt and the YSZ started to sinter. However these samples are still undergoing analysis and micrographs were unavailable for this paper.

The plasma unit is currently being upgraded to increase its power density by a factor of 3. This will allow for higher power densities to heat the YSZ surface without melting the under laying NiO. Coupled with a fast scan rate it will be possible to melt and quench the YSZ with minimal

heat transfer to the anode support. The very high-power densities achievable with the arc lamp permit the coating of almost any material. This almost instantaneous on/off capability of the high-power density arc lamp system allows for excellent controllability. The solid/liquid phase reactions which occur on processed surfaces can be modeled as well as the effects of the process on the base material.

These early experiments indicate that the HDIC process is promising for rapid sintering of YSZ. This, and the fact that an industrial HDI unit costs less than \$500K makes this process a potential method to reduce the sintering cycle time for solid oxide fuel cell materials.

REFERENCES

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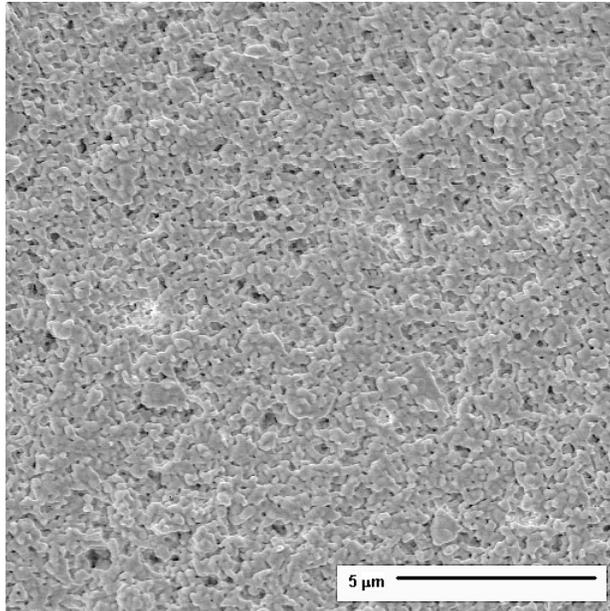


Figure 3. SEM micrograph of HDIC processed YSZ thick film on anode support. Total heat-treatment time was 2 seconds at 800 W/cm².