Economical Thermal Processing of Solid Oxide Membrane Materials

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Abstract

Substantial progress has been made in the development of an innovative rapid thermal processing method for manufacturing solid oxide membrane components. Previous work has shown that conventional furnace sintering of a tape cast, nickel oxide (NiO) precursor material, which had been screen-printed with a thin yittrium stabilized zirconia (YSZ) coating (<9um), can reliably produce thin dense films of YSZ electrolyte on a NiO porous anode support. In the present work, a new processing method has been developed using a focused plasma-arc-lamp IR heating source to sinter specimens, instead of a conventional furnace. The objective of this approach is to reduce the furnace processing time from 36 hours to less than 20 hours, while producing thin dense films of YSZ electrolyte on a NiO porous anode support. Experimental results indicate that by taking advantage of the high power density and precise control capability of the plasma-arc-lamp to heat only the sample without having to also heat a furnace mass will allow more rapid heating profiles. Preliminary results, using samples identical to those used to develop the furnace sintering profiles, have resulted in virtually identical results with respect to the microstructure of the membranes. Processing times have been shortened to one hour and have the potential to be further reduced to minutes. The production of samples that have consistent flatness is currently being developed.

EXPERIMENTAL PROCEDURE

A unique thermal processing facility at the Oak Ridge National Laboratory, Figure 1, has been used to investigate the feasibility of developing rapid heating methods for manufacturing solid oxide membrane components. The 300 kW plasma-arc-lamp used in this facility, Figure 2, is capable of focusing a beam of incoherent light, 0.2 to 1.4 microns, on an area as small as 10 cm^2 at a power density of 3500 W/cm^2. At these power density levels the lamp provides a capability to initiate melting in any substance in fractions of a second. The utility of this facility is not just limited to the high power and high power density capability of the 300kW plasma-arc-lamp. Precise control of the lamp is essential for practical industrial processing applications. In this regard, note in Figure 2 that the plasma lamp is coupled to a robotic manipulator. This robot has, state-of-the-art, 6-axis capability and provides the lamp capability to scan complex surfaces, with a prescribed heat flux. Other facility attributes allow the arc lamp to be configured with a variety of different reflectors, two of which are shown schematically in Figure 3. Other reflectors are available at our Plasma Arc Lamp Facility that provide focused, rectangular beam profiles measuring: 3 cm by 20 cm and 3 cm by 35 cm, which produce power densities of 1200 W/cm^2 and 600 W/cm^2, respectively. A uniform irradiance reflector shown in Figure 3 (right) will

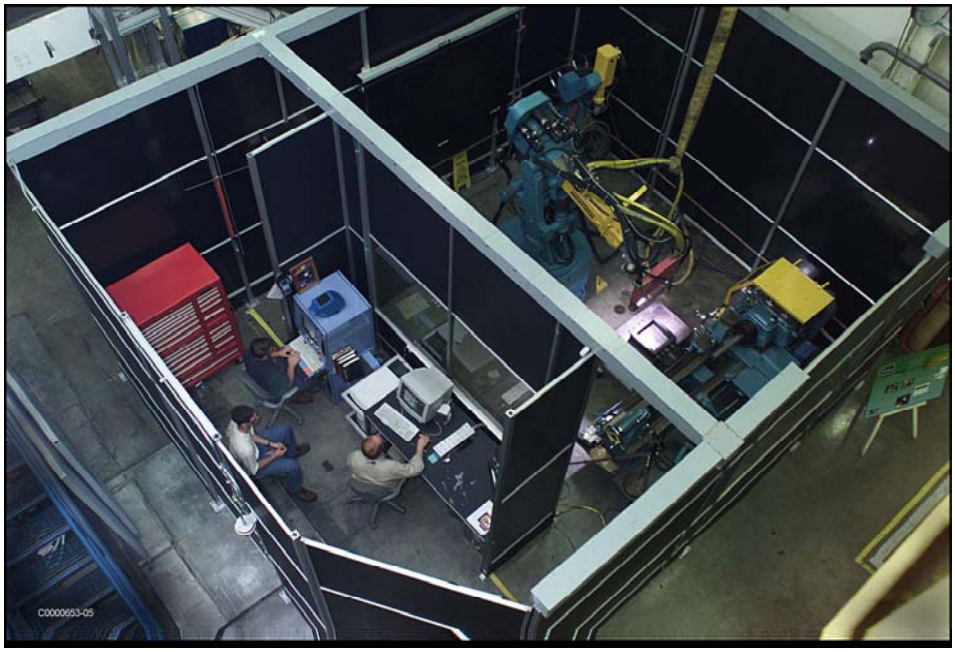

Fig. 1. The Plasma-Arc-Lamp Processing Facility at the Oak Ridge National Laboratory

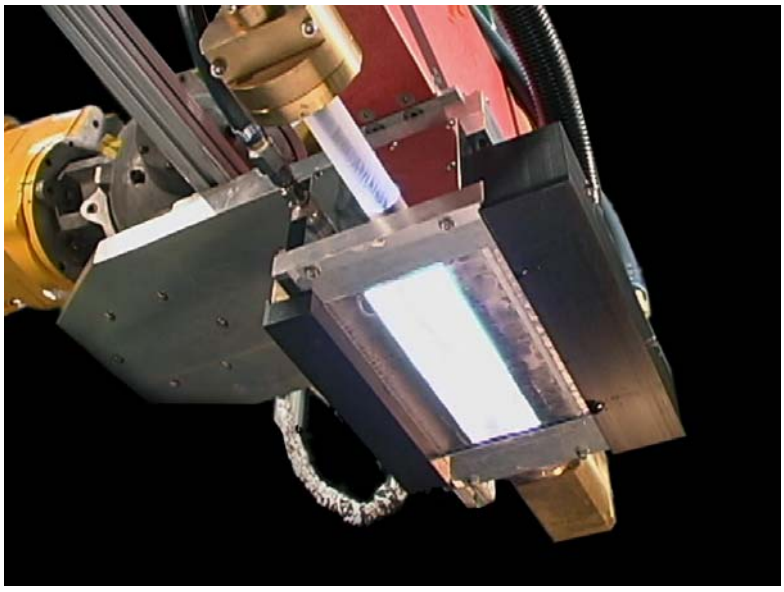

Fig. 2. A view looking into the exit aperture of the 300 kW plasma-arc-lamp installed in the ORNL test facility.

provide a uniform heat flux over a 20 cm by 20 cm area at 200 W/cm^2. Control of the lamp power output is essential for the thin film processing applications described in this paper. In this regard, the lamp is capable of continuously varying power levels, accurate to within 0.1%, in either a pulsed or DC mode. Power levels are PC controlled and can be precisely incremented in 0.001sec intervals from idle to full power.

Shown schematically in Figure 4, are the basic electrical/mechanical attributes of the arc lamp that allow very rapid and precise modulation of the power output. Our arc lamp source is configured as a simple quartz tube, 4 cm ID, into which a mixture of deionized water and argon are injected (Figure 4). The mixture is injected tangentially into the quartz tube's interior at one end of the tube. The resultant helical flow down the length of the tube produces a thin film of water against the tube wall, which effectively cools it. The argon gas flows in a similar fashion down the core of the tube and provides the medium into which a high-pressure plasma arc can be formed for passing up to 1200 A. These sources are able to operate continuously for up to 1000 hours. Power output is continuously variable from near 1 kW to full power and requires only 0.001 sec. to ramp up or be extinguished.

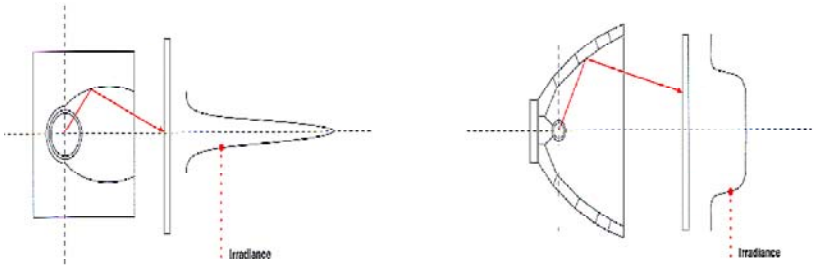

Figure 3. Typical Plasma-Arc-Lamp reflector configurations.

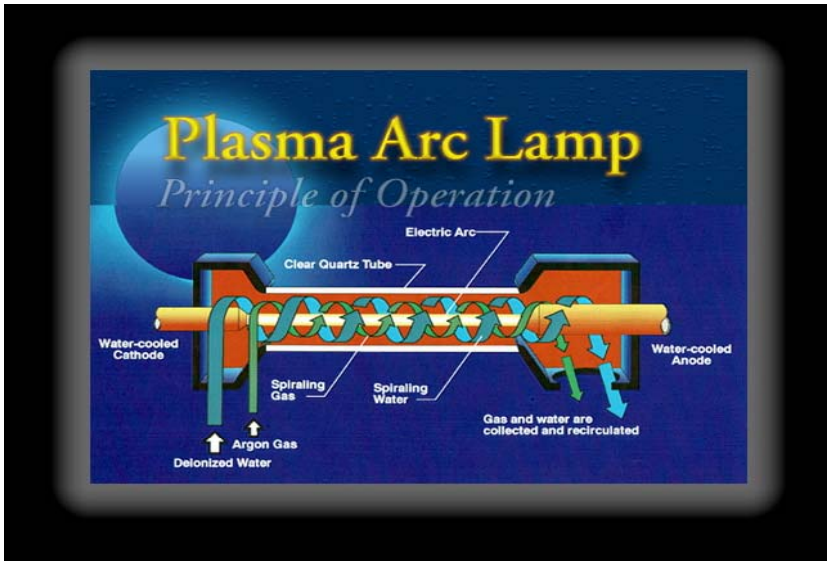

Figure 4. Plasma-arc-lamp operating principal schematic

Other ancillary equipment that is useful for IR lamp processing includes: (1) a variety of processing boxes that are available for the heating of specimens in different atmospheres when using the plasma arc lamp (Figure 5), (2) on-line video cameras for monitoring and recording of experiments, and (3) PC-based data acquisition and control is available in the facility to record and control: temperature, heat flux, lamp head position/kinematics parameters and lamp electrical operating characteristics.

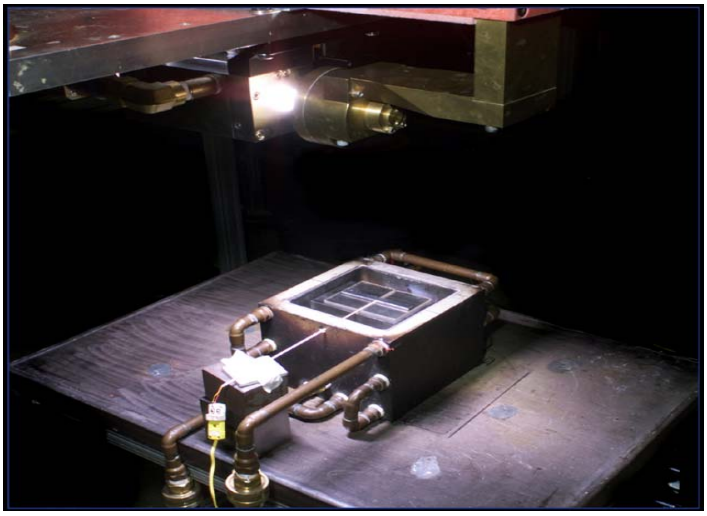

Figure 5. Water-cooled chamber processing chamber used to provide vacuum or special gaseous atmospheres during processing by plasma-arc-lamp. Specimen chamber has a Quartz cover that is transparent to the lamp IR beam.

Initial experiments were carried out on solid oxide fuel cell membranes consisting of a 10μ yttria stabilized electrolyte (YSZ) supported on a 1 mm thick NiO/YSZ anode. Anode substrates were prepared by tape casting. The resulting dried tape was laminated together to produce a substrate of desired thickness, (1.0mm) and cut to size by a hot knife (i.e. 25.4mm diameter disc or 25.4 mm square wafer). The YSZ coating was applied to the anode by screen printing using a proprietary binder developed at ORNL. The coated substrates were then bisque fired for 2 hours at 1000°C in air.

INFRARED PROCESSING

Initial considerations that motivated the study of high density infrared (HDI) solid oxide fuel cell membranes was the drive to considerably reduce the sintering time to reduce cost and increase productivity. The current solid state sintering process can be simply described as requiring a slow and uniformly heated source (i.e. furnace) that increases the sample temperature at an average rate of 4°C/min to 1400°C. The samples are held at 1400°C for two hours and slowly cooled to room temperature at the 0.33 °C/sec rate. Other details of the process involved selectively covering the samples with inert covers to eliminate thermally induced distortions. This process nominally required 48 hours and would constitute the most significant cost in the manufacture of commercial components.

Other research at the HDI processing facility at the ORNL has been successful in processing coatings with dissimilar thermal properties. In many ways, HDI processing is similar to laser flash heating technology in that very high power heat fluxes can be precisely applied to surfaces. HDI, however, can illuminate substantially more surface area at comparable flux densities and does not result in convective mixing.

A basic strategy of HDI processing in brittle materials is to gently and very precisely preheat the substrate/coating system to a temperature close to where the desired processing outcome of melting or sintering will occur. Once this point has been reached, the application of a small increment in heat flux of the correct duration is all that is needed to produce the desired outcome. This can often be accomplished much more quickly with HDI, compared to a furnace, as the components are directly heated with a uniform surface heat flux. In addition, by having very precise control of the heat flux intensity and duration, it is often possible to optimize a heating cycle with respect to minimizing mechanical stresses due to: temperature gradients, sintering or other phase and material property changes. In the discussion below, two initial attempts for HDI processing of the YSZ/NiO system are described even though they were largely unsuccessful. Their inclusion however, may be of interest as the techniques used demonstrate the processing flexibility possible with the infrared lamp and led to a third process that was very successful for obtaining membranes with the desired microstructure.

The first attempt to process samples were placed on a quartz plate, which was supported by a steel block and preheated with the HDI source set at low power (10 to 300 W/cm^2) by scanning across the sample surface at approximately 10 mm/sec. Following a series of preheating scans, the lamp power was increased, 700 to 1200 W/cm^2, and the samples again scanned at rates ranging from 5 to greater than 20 mm/sec. In these runs, no sample was produced that did not experience severe mechanical damage. Selected samples fragments were analyzed by both optical and electron microscopy to evaluate microstructural development. Dense, but fractured YSZ coatings were observed on some samples. As a result of this first series of experiments, it became obvious that a less severe thermal cycling approach would be required. In addition, better diagnostics would be required in order to observe the densification process of the screen-printed YSZ coating.

In the second series of experiments, a number of samples (Figure 6) were prepared. These samples had a type S thermocouple attached to the backside of each of the samples. The thermocouple weld bead was milled to a flat surface in order to mate with the anode substrate and attached with a ceramic adhesive. These samples were run with the HDI lamp in a fixed position with the sample positioned at the 1cm wide focal point of the lamp. An additional visual diagnostic was included in the new set-up by a shuttered video camera. The camera was able view the samples with a 50X telephoto lens at full lamp power and provided real time feed back on the condition of the sample during processing.

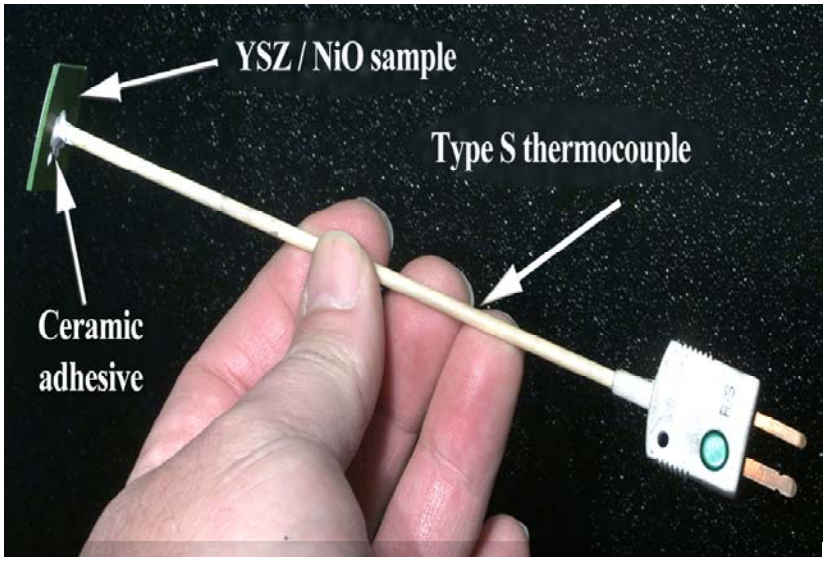

Figure 6. Type S thermocouple attached to backside of a YSZ/NiO processing sample

Experiments that were carried out with this series of samples were focused on determining the lamp power and rear face sample temperature that coincided with densification of the YSZ coating. Because the focused beam width was 1.0 cm wide at the surface of the 2.5 cm wide sample, we were able to visually observe a range of sample responses due to the temperature gradients that were present in the sample. A plot of the temperature as a function of power is shown in Figure 7.

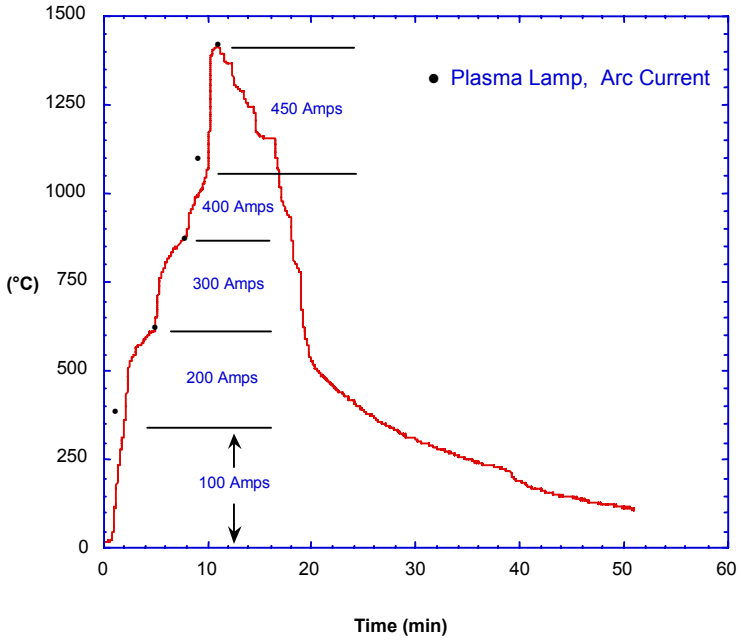

Figure 7. Rear face temp. Response, YSZ/NiO 1cm wafer, at the focus of the HDI lamp.

For the sample that was processed to the profile shown in Figure 7, three distinct material responses were observed in the sample: (1) the center of the hot surface over sintered (this region was distinctly black in color indicative of melting of the NiO), (2) in a 0.5 cm band around the central spot, the YSZ densified (become transparent), and (3) In a third region around the periphery of the sample, a narrow band of the YSZ remained as the original the screen-printed coating before processing. During the course of the processing run, each of the different regions were clearly visible on the real-time video monitor.

After a series of runs as described above, a new processing strategy was formulated. The main features of this new approach resulted in the elimination of the thermocouple as a necessary diagnostic tool in favor of the real-time video monitor. The effectiveness of the ceramic adhesive in insulating the backside of the sample resulted in the setting of samples on an aluminum oxide setter. This allowed concurrent heating of the sample from both sides as the base heated up in the HDI beam. Also observed in the earlier sample runs were severe mechanical deformations of the sample that occurred coincident with the sintering interval of the process. This deformation was virtually eliminated by covering the sample with a 3mm thick sapphire disc.

After updating the process as described above, new samples were run with the lamp positioned in the divergent region of the HDI beam that provided uniform heating of the complete sample. Figure 8 shows the before and after processing appearance of the YSZ/NiO sample clearly showing the transition to the transparent YSZ coating and the sintering shrinkage.

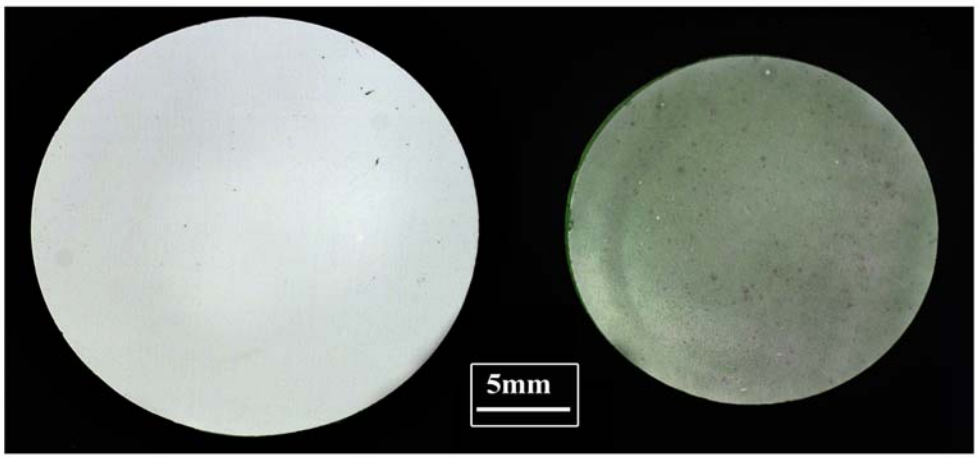

Figure 8. YSZ/NiO sample, before and after HDI processing

The heating profile used to produce the results shown in Figure 8 is shown in Figure 9. The sample was placed on an aluminum oxide wafer and covered with a 3mm thick 10 mm diameter sapphire cover during process. The sapphire cover helped to keep sample flat during the process. The aluminum oxide wafer provided an insulating boundary on the rear face of the sample and the wafer edges also absorbed radiation from the HDI beam. These factors provided a more

uniform heating of the sample with respect to its thickness, which in-turn decreased the temperature gradient through the sample and therefore the thermally induced bending stresses.

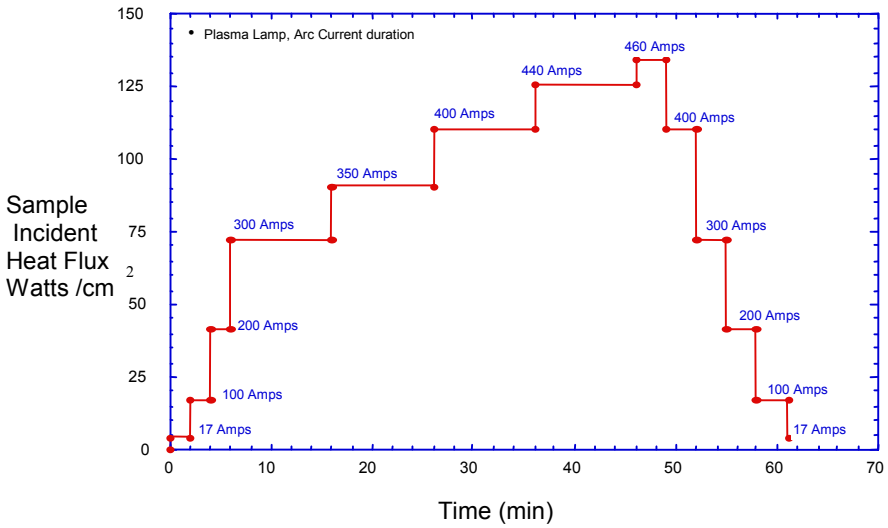

Figure 9. HDI, arc current profile and resultant sample heat flux used to sinter the sample shown in Figure 8.

Other interesting features of the process described above are shown in Figure 10 as a sequence of still photographs taken from the processing run videotape. In the upper left photo, the sample is 35 minutes into the processing sequence and was slowly heated with an incremental heat flux from 5 W/cm^2 to 110 W/cm^2. Note that the sample is still flat and virtually unchanged from its room temperature appearance. In the next photo, taken at 39 minutes, the sample has been at 125 W/cm^2 for three minutes and the early stages of YSZ coating densification are apparent. In the last two photos taken at 42 and 50 minutes respectively, the sample has completed densification after the last heat flux increase to 135 W/cm^2 at 39 minutes and is already cooling down.

CONCLUSIONS

A new processing method has been developed using a focused plasma-arc-lamp IR heating source to sinter solid oxide fuel cell membranes. The new IR technique is able to reduce conventional furnace processing time from 36 hours to 18 hours. The new method is able produce equivalent samples with thin dense film of YSZ electrolyte on a NiO porous anode support. Further development of the HDI processing technique for this application may lead to a better understanding of methods to optimize both the conventional furnace sintering process as well the HDI process.

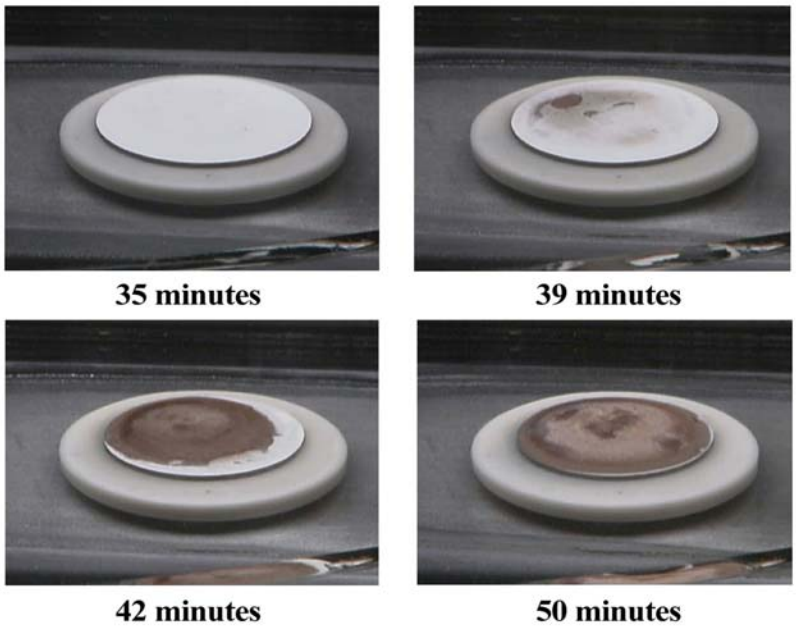

Figure 10. Densification sequence of the YSZ/NiO sample when subjected to the heat flux profile indicated in Figure 9