Hard glass-ceramic coating by microwave processing

S. Das [a,*], A.K. Mukhopadhyay [a], S. Datta [a], G.C. Das [b], D. Basu [a]

[a] *Central Glass and Ceramic Research Institute, 196, Raja S.C. Mullick Road, kolkata 700032, India*
[b] *Department of Metallurgical and Material Engineering, Jadavpur University, Kolkata 700032, India*

Abstract

Microwave processing was employed in the present work to obtain hard glass-ceramic coating on nickel based superalloy substrate. The glass-ceramic coatings were developed from a glass based on $MgO–Al_2O_3–TiO_2$ system. The coatings were characterized through X-ray diffractometry (XRD), scanning electron microscopy (SEM), image analysis, surface roughness measurement and hardness evaluation by depth sensitive indentation (DSI) technique. Surface and cross-sectional SEM examinations of the polished and etched samples revealed that under identical combination of heat treatment temperature and time, the microwave processed coating contained finer crystallites than the sizes of the crystallites obtained in the conventionally processed coating. The microwave processed glass-ceramic coating exhibited surface roughness (R_a) value much lower than that of the conventionally processed glass-ceramic coating. DSI results confirmed that the microwave processed coating possessed much higher hardness ($\sim$6 GPa) compared to that of the conventionally processed coating.
© 2007 Elsevier Ltd. All rights reserved.

Keywords: Microwave processing; Glass-ceramics; Microstructure-final; Hardness; Coatings

1. Introduction

Ceramic and glass-ceramic coatings are used in modern gas turbine engines to protect various hot zone components from oxidative, hot corrosive, thermal and thermo-mechanical degradation and thus extend the service life of these expensive strategic materials. Recently, energy efficient microwave processing has been utilized for sintering of various ceramics,[1–4] glazing of alumina–titania ceramic composite coatings, reaction bonding of silicon nitride, sol–gel processing, powder synthesis and joining of ceramic composites.[5–9] Microwave has also been successfully employed in our laboratory for the development of oxide coating on aluminium and of $Al–Al_2O_3$ composite.[10–12] Crystallization of sol–gel derived barium aluminosilicate glass was studied by Cozzi et al. in a 2.45 GHz microwave field.[13] Microwave energy decreased the processing time required to produce the monoclinic celsian phase at 1300 °C with the addition of 10%CuO as a seed material. Siligardi et al. investigated microwave effect on sintering, crystallization and

other related phenomena of glassy powders belonging to the $CaO–ZrO_2–SiO_2$ system.[14] Their work revealed that presence of different crystalline phases affects the final microstructures and the hardness properties of the glass-ceramic materials.

High temperature and abrasion resistant glass-ceramic coatings have been already developed in our laboratory for a nickel based superalloy substrate.[15] The motivation behind that work was to develop suitable glass-ceramic coatings for possible end applications in different hot zone components of gas turbine engine. In that work, $MgO–Al_2O_3–TiO_2$ based glass coating was formed on the metal substrate and subsequently heat treated in a muffle furnace to develop different crystalline phases such as magnesium aluminium titanate, magnesium silicate and aluminium titanate in the glass coating. The objective of the present work was to obtain hard glass-ceramic coating on a nickel based superalloy by microwave processing.

2. Experimental procedure

The approximate oxide composition of the coating system was as follows: SiO_2 30–35; Na_2O 1–3; K_2O 4–6; TiO_2 12–15; B_2O_3 9–11; MgO 12–15; CaO 1–2; Al_2O_3 20–25 in wt.%. The coating material was prepared by melting the glass-forming batch at 1400 °C for 3 h. Subsequently the molten glass was

* Corresponding author. Tel.: +91 33 2473 3469/76/77/96;
fax: +91 33 2473 0957.
E-mail address: sumana@cgcri.res.in (S. Das).

Table 1
Nominal composition of the Nimonic superalloy (AE 435) in wt.%

Cr	Fe	C	Si	Mn	Ti	Al	Cu	S	P	Ni
19–22	1.0	0.12	0.8	0.7	0.15–0.35	0.15	0.07	0.01	0.015	Balance

fritted and the frit was crushed to powder, which was investigated by differential thermal analysis technique (STA 409C, Netzsch, Germany) to determine the nucleation and the growth temperatures of the crystallites. The glass powder was wet milled with the mill addition of 5 wt.% clay in a porcelain ball mill for about 40 h to obtain glass particles of 3–5 μm size. A thick creamy suspension of glass was produced as slurry for application over the cleaned metal surface. The rheological properties of the coating material slurry were standardized by optimizing its specific gravity, particle size distribution and viscosity.[15] Nickel based superalloy was selected as the substrate material (Nimonic—AE 435, 15 mm × 12 mm × 2 mm). The nominal composition of the superalloy is given in Table 1. The thermal expansion coefficient of the nimonic alloy from room temperature to 600 °C is 13.85×10^{-6}, which is quite high compared to that (7.60×10^{-6}) of the coating material. However, very good adherent coating is obtained when thin coating (<150 μm) is applied.[15] The metal surface was thoroughly prepared by thermal degreasing and sand blasting followed by ultrasonic cleaning with acetone to achieve proper bonding of the coating with the metal surface. The coating material was applied on the cleaned metal substrate by conventional spraying technique using a spray gun (PILOT spray gun, type 68-S with a 0.14 L gravity feed cup, Manik Machinery Manufacturers Pvt. Ltd., Mumbai, India).

The glass powder coated substrates were dried at 100 °C for 45 min prior to firing at a fusion temperature of 1170 °C for 5 min in air in a muffle furnace. The fusion temperature (1170 °C) of the coating material was determined by trial and error method.[15] A small amount of powdered frit was heated in a muffle furnace in an oxidizing atmosphere at different temperatures in the range of 1150–1200 °C. The selection criteria for fixing up an optimized fusion temperature were threefold e.g. the fusion temperature should be such that (a) the glass powder at that temperature can have a viscosity in the range of 0.1–1 N-s/m^2 because that helps the glass to flow in an appropriate manner so that an impervious glass coating can be obtained, (b) the coating produced would adhere to the metallic substrate and finally, (c) the coating obtained is free of macroscopic defects and has a reasonable hardness value good enough for the intended application.

Finally, the glass coated substrate was kept in a silicon carbide crucible (susceptor material), which was placed inside a thermal insulation arrangement made of alumina fibre board in the multi-mode cavity of a microwave furnace (Multilab 2.0 KW, 2.45 GHz, Linn High Therm GmbH, Germany) for suitable heat treatments at 880 °C for 30–90 min followed by 30–90 min at 1020 °C.

The power absorbed by a material inside a microwave cavity depends on the frequency of the microwave source, the loss tangent and the relative dielectric constant of the material and the magnitude of the electric field.[1]

Initially, silicon carbide absorbs the microwave energy and raises the temperature because it is a well-known absorber for microwave energy. It may be noted that at 600, 800 and 1000 °C, the loss tangent (tan δ) values of silica glass are about 0.0005, 00006 and 0.001, respectively.[1] Similarly, the values of the relative dielectric constant of silica glass are nearly 3.2, 3.6 and 3.8 at 600, 800 and 1000 °C.[1] It has been reported that beyond a critical temperature the values of the relative dielectric constant and the loss tangent of silica glass can increase with temperature whereby a sharp rise in energy absorbed and hence, the consequent rise in temperature of the sample can be expected once the critical temperature ($T_c \sim 800$ °C) is surpassed.[1]

It was therefore assumed in the present work that beyond a critical temperature of around 800 °C, the values of the relative dielectric constant and the loss tangent of the glass coating can increase significantly.[1] That would facilitate effective coupling of the microwave energy with the glass coating. The temperature of the microwave cavity was measured using an optical pyrometer with an accuracy of ±1%. For the purpose of comparison only, glass-ceramic coatings of exactly same composition and processing history, as of the ones processed through microwave processing technique, were also prepared by conventional heat treatments.[15]

The coatings processed by microwave and conventional heat treatments were characterized by X-ray diffraction analysis (PW 1710, Philips Research Laboratory, Eindhoven, The Netherlands), scanning electron microscopy (SEM, LEO S430i, LEO, UK), image analysis (LEICA Q500MC, UK), surface roughness measurement (Surtronic 3P, Rank Taylor Hobson Ltd., UK) and hardness evaluation by depth sensitive indentation technique (Fischerscope H100C XY$_p$, Fischer, Switzerland).

Extensive use was made of the scanning electron microscopy (SEM) technique for examination of the microstructural features e.g. crystallite size etc. from the top surface view as well as from the cross-sectional view of a large number of polished and chemically etched samples. All samples were polished down to a 1 μm diamond paste grit size followed by a final polishing with a 0.25 μm diamond paste grit size. The chemical etching of the polished surfaces was done with 5 wt.% HF solution. The measurement of average crystallite size from the top surface and the cross-section of the glass-ceramic coating were done by image analysis technique using at least 10 different SEM micrographs randomly taken from various locations for each sample type. The reported values for each sample are therefore average values taken from the total data pull of the sizes of a few hundred individual crystallites. However, for the sake of brevity, only representative photographs have been included in this communication.

Hardness of the glass-ceramic coating was measured by the depth sensitive indentation technique.[16] Nanoindentation tests were carried out on the flat parallel, polished material surfaces by using the depth sensitive indentation machine mentioned earlier. A four-sided diamond pyramidal Vicker's tip with a nominal radius of curvature around 130 nm was used as the indenter. The load and displacement were monitored continuously by a three-plate capacitive force/displacement transducer. The force sensing resolution was 0.2 μN. The depth sensing resolution was 0.1 nm.

The load applied was selected to be as low as 1 mN to avoid coating fracture. The loading time was 30 s and the unloading time was also selected as 30 s. The load selection was also done in accordance with the thumb rule that the maximum depth of penetration of the indenter into the coating must be well below 10% of the coating thickness to avoid influence of the mechanical properties of the substrate into the data measured for the coating. For any given sample, five specimens were examined. In the case of each specimen at least 50 individual data were taken. These large numbers of data were intentionally taken to take care of the unavoidable variations at the scale of local microstructure of the coating because these unavoidable variations usually act as the source of large scatter in the data. The hardness data were determined from the load–displacement plot following the procedure developed by Oliver and Pharr.[17]

3. Results and discussions

3.1. Differential thermal analysis (DTA) and thermo gravimetric analysis (TGA)

Fig. 1 shows the DTA and TG curves of the glass. The DTA data show that the critical temperatures, strictly speaking, are 951.4 °C for nucleation and 1046.3 °C for growth. Since the nucleation and growth temperatures were both found out to be below 1100 °C, the necessity to conduct DTA experiment beyond 1100 °C was not felt. Ideally, the heat treatment should have been done at exactly these temperatures, if, just the nucleation and subsequent growth of the ceramic crystallites in the glass coating was the only aim of this research effort. However, the actual target of the present work was to develop a glass-

ceramic coating that was not only impervious, defect free and adherent but also hard.

Therefore, guided by this requirement, a large number of trial experiments were conducted in the vicinity of the exact nucleation and growth temperatures. All samples were subsequently analyzed by XRD and hardness measurement.[18] Based on these conventional heat treatments with different combinations of nucleation and growth temperatures as well as times and analyzing the resultant glass-ceramics by XRD and hardness evaluation, the nucleation condition was selected as heating for 90 min at 880 °C and the growth condition was selected as heating for an exactly same period of time at 1020 °C; because it was found out[18] that the most hard, impervious, adherent, macro-defect free coatings were obtained for this particular combination of temperatures and times.

For the purpose of comparison only, exactly similar holding times of 90 min each at the same nucleation temperature of 880 °C and growth temperature of 1020 °C were utilized in the case of microwave processed coatings also. However, realizing that the holding time of 90 min was a really long time for the microwave treatment at both 880 °C and 1020 °C, additional experiments were also conducted with much lower holding times e.g. 30, 45 and 60 min. This was intentionally done for the microwave processed coatings to check out the idea that if a reasonably good hard glass-ceramic coating could be obtained with shorter holding time, thereby saving both time of experimentation and energy. In addition, just for the sake of comparison, conventionally processed coatings were also prepared with similar low holding times of 30, 45 and 60 min, although such coatings would not necessarily have the high hardness value.[18] Data from the TG experiment are also included in Fig. 1. This data only indicated that negligible mass gain occurred up to 1100 °C.

3.2. XRD analysis

XRD data of the glass-ceramic coatings obtained in the present work are shown in Fig. 2. As a typical, illustrative example, data from the lowest holding time e.g. 30 min and the highest holding time e.g. 90 min are only included in Fig. 2. Fig. 2a shows the XRD data of the conventionally processed glass-ceramic coating obtained by heat treatment of the glass coating for 30 min at 880 °C followed by 30 min at 1020 °C. The XRD data of the microwave processed glass-ceramic coating obtained after heat treatment of the glass coating for 30 min at 880 °C followed by 30 min at 1020 °C are shown in Fig. 2b. Similarly, the XRD data of the conventionally processed glass-ceramic coating obtained by heat treatment of the glass coating for 90 min at 880 °C followed by 90 min at 1020 °C are given in Fig. 2c. Fig. 2d shows the XRD data of the microwave processed glass-ceramic coating obtained after heat treatment of the glass coating for 90 min at 880 °C followed by 90 min at 1020 °C.

Presence of magnesium aluminium titanate, magnesium silicate and aluminium titanate phases were identified (JCPDS file nos. 5–0636, 18–68 and 19–768) in all the glass-ceramic coatings produced by the microwave heat treatments. The variation in holding time did not have a significant influence on the types
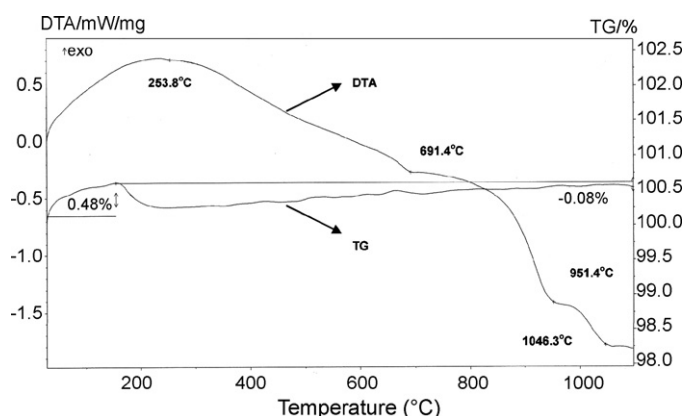

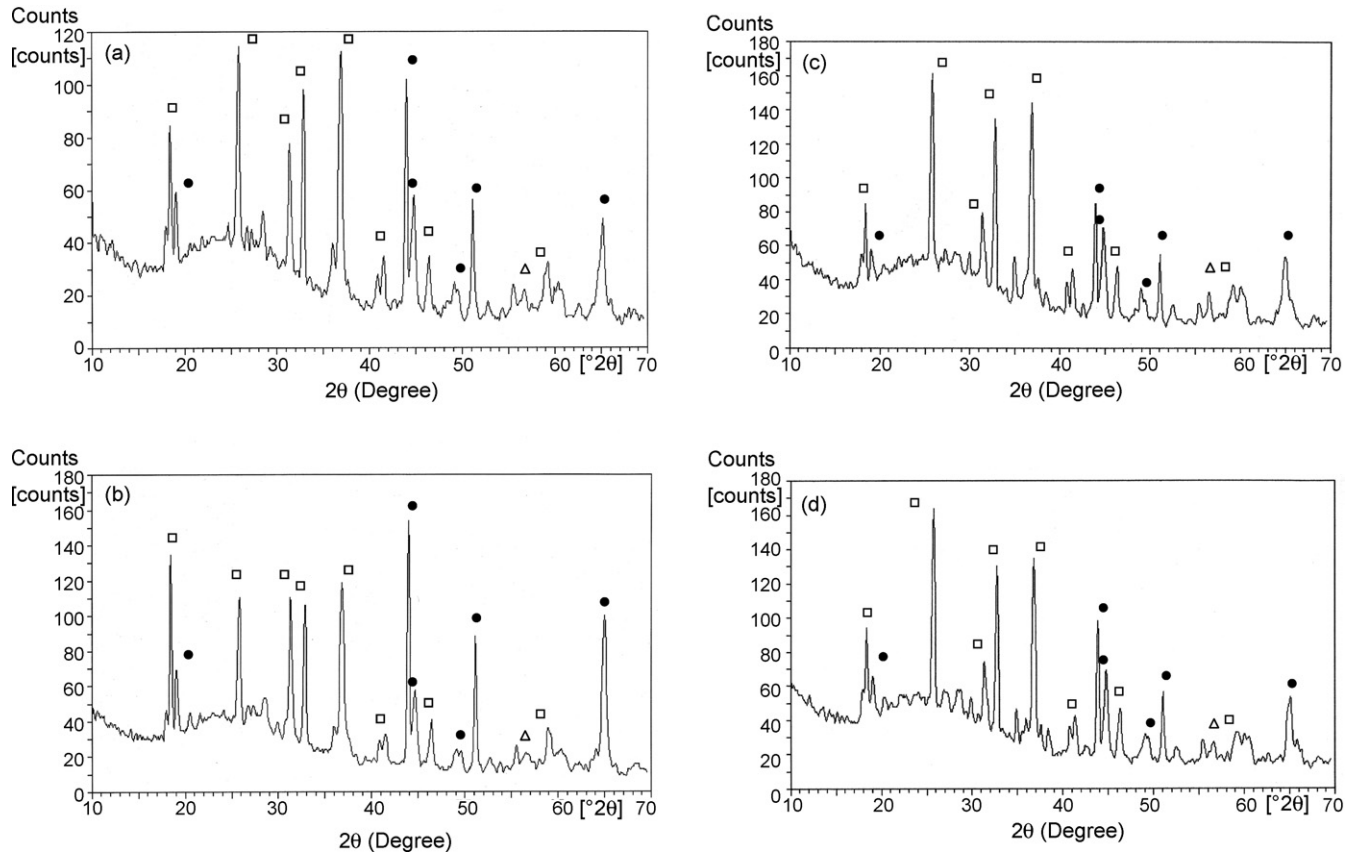Fig. 1. DTA and TG curves of the glass.

Fig. 2. Typical XRD plots of the glass-ceramic coatings obtained by heat treatments of the glass coatings for 30 min at 880 °C followed by 30 min at 1020 °C in (a) conventional furnace, (b) microwave furnace and 90 min at 880 °C followed by 90 min at 1020 °C in (c) conventional furnace, (d) microwave furnace (□—Mg–Al–titanate, ●—Mg-silicate, △—Al-titanate).

of phases obtained, Fig. 2b and d. In the conventionally processed coatings also, the presence of magnesium aluminium titanate, magnesium silicate and aluminium titanate phases were identified, Fig. 2a and c. These results were also similar to our earlier findings for the conventionally processed coatings.[15] Earlier work[13] on crystallization of barium aluminosilicate glass showed that microwave energy decreased the processing time required to produce the monoclinic celsian phase. Studies[14] on the effect of microwave exposure on crystallization of glass powders from the CaO–ZrO$_2$–SiO$_2$ system revealed that presence of different crystalline phases affects the final microstructures and the hardness properties of the glass-ceramic materials.

3.3. Microstructure

Here we present the typical microstructural features of both conventionally and microwave processed glass-ceramic coatings as obtained from the polished and etched top-surfaces (Fig. 3). However, no conclusive evidence should be drawn from only surface microstructural studies of the coatings. Therefore, thorough examination of the cross-sectional microstructures was conducted for both the conventionally and microwave processed glass-ceramic coatings. The typical data from scanning electron microscopic examination of the polished and etched cross-section of the microwave processed glass-ceramic coating are presented in Fig. 4. To make comparative assessment,

data from the polished and etched cross-section of the conventionally processed glass-ceramic coating prepared under similar experimental conditions as shown in Fig. 4 are included in Fig. 5.

Fig. 3a shows the surface microstructure of the conventionally processed glass-ceramic coating obtained by heat treatment of the glass coating for 30 min at 880 °C followed by 30 min at 1020 °C. The surface microstructure of the microwave processed glass-ceramic coating obtained after heat treatment of the glass coating for 30 min at 880 °C followed by 30 min at 1020 °C is shown in Fig. 3b. It appears from a comparison of these two SEM micrographs as if microwave processing produced slightly finer sized crystallites in the glass coating surface compared to the sizes of the crystallites in the coating surface evolved by the conventional heat treatment process. The typical average crystallite size of the microwave processed coating was about 296 ± 7 nm while that of the conventionally processed coating was only marginally higher at about 313 ± 8 nm.

Fig. 3c shows the surface microstructure of the conventionally processed glass-ceramic coating obtained by heat treatment of the glass coating for 90 min at 880 °C followed by 90 min at 1020 °C. The surface microstructure of the microwave processed glass-ceramic coating obtained after heat treatment of the glass coating for 90 min at 880 °C followed by 90 min at 1020 °C is shown in Fig. 3d. A comparison of these two SEM micrographs clearly suggests that microwave processing produced finer sized crystallites in the glass coating surface compared to the sizes of
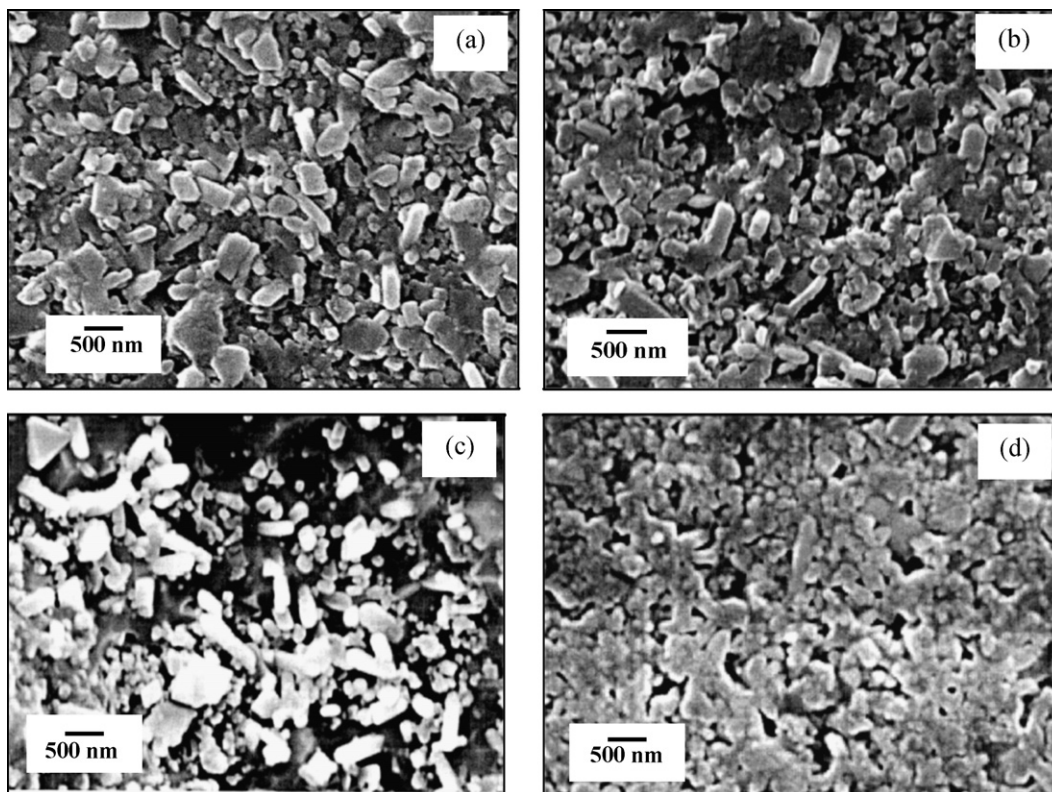
Fig. 3. The surface microstructures of the glass-ceramic coatings (etched) obtained by heat treatments of the glass coatings for (a) 30 min at 880 °C followed by 30 min at 1020 °C, conventional; (b) 30 min at 880 °C followed by 30 min at 1020 °C, microwave; (c) 90 min at 880 °C followed by 90 min at 1020 °C, conventional; (d) 90 min at 880 °C followed by 90 min at 1020 °C, microwave.

the crystallites observed in the surface of the conventionally heat treated coating. The microstructure analysis by means of image analysis technique revealed that the average crystallite size of the conventionally processed coating was about 398 ± 25 nm while that of the microwave processed coating was much lower at about 183 ± 15 nm.

Notwithstanding these results obtained from only surface microstructure examinations, additional experiments were conducted on the polished and etched cross-sections of the glass-ceramic coatings obtained by both conventional and microwave processing; to confirm whether microwave processing really produced finer sized crystallites in the glass coating compared to the sizes of crystallites obtained by the conventional heat treatment. A large number of coatings were examined in the cross-sectional direction through scanning electron microscopy followed by image analysis as mentioned earlier. However, only typical, illustrative examples from the holding time of 90 min are included here for both the microwave processed coating (Fig. 4) and the conventionally processed coating (Fig. 5).

Fig. 4a shows the cross-sectional microstructure of the microwave processed glass-ceramic coating obtained by heat treatment of the glass coating for 90 min at 880 °C followed by 90 min at 1020 °C. Please notice that the coating was about 35 μm thick along the cross-sectional direction. The common scale bar for all the other Figures e.g. Fig. 4b–e is included only in Fig. 4e for the sake of clarity only. In Fig. 4a, the region just at the surface of the coating as viewed in cross-section is indi-

cated by "S", the near surface region of the coating is marked by "NS", the region at the core of the coating is identified by "C" and the region at the interface between substrate and coating is illustrated by "I". The magnified views of all these regions are shown in Fig. 4b–e. All these SEM micrographs were taken at one and the same magnification.

Fig. 4b shows the cross-sectional microstructure just at the surface of the glass-ceramic coating (region "S" of Fig. 4a) obtained by microwave processing condition as mentioned above. Here, the average crystallite size was really very fine at about 188 ± 25 nm. However, just below the surface that corresponds to the region "NS" in Fig. 4a; a slightly larger average crystallite size was estimated e.g. 210 ± 24 nm (Fig. 4c), suggesting that during cooling the temperature gradient was possibly from the surface increasing towards the bulk, which is also otherwise expected for a volumetric heating process like the microwave heating[1] used in the present experiments.

As one moves towards the core of the coating, much larger crystallites can be seen, Fig. 4d. Image analysis revealed that the core region at the cross-sectional view of the coating (region "C" of Fig. 4a) had an average crystallite size of 321 ± 35 nm. This data provided confirmatory evidence that during cooling the temperature gradient was indeed from the surface increasing towards the bulk.

Finally, the cross-sectional microstructure was also examined at the interface region between the substrate and the coating (region "I" of Fig. 4a). Data obtained by image analysis tech-
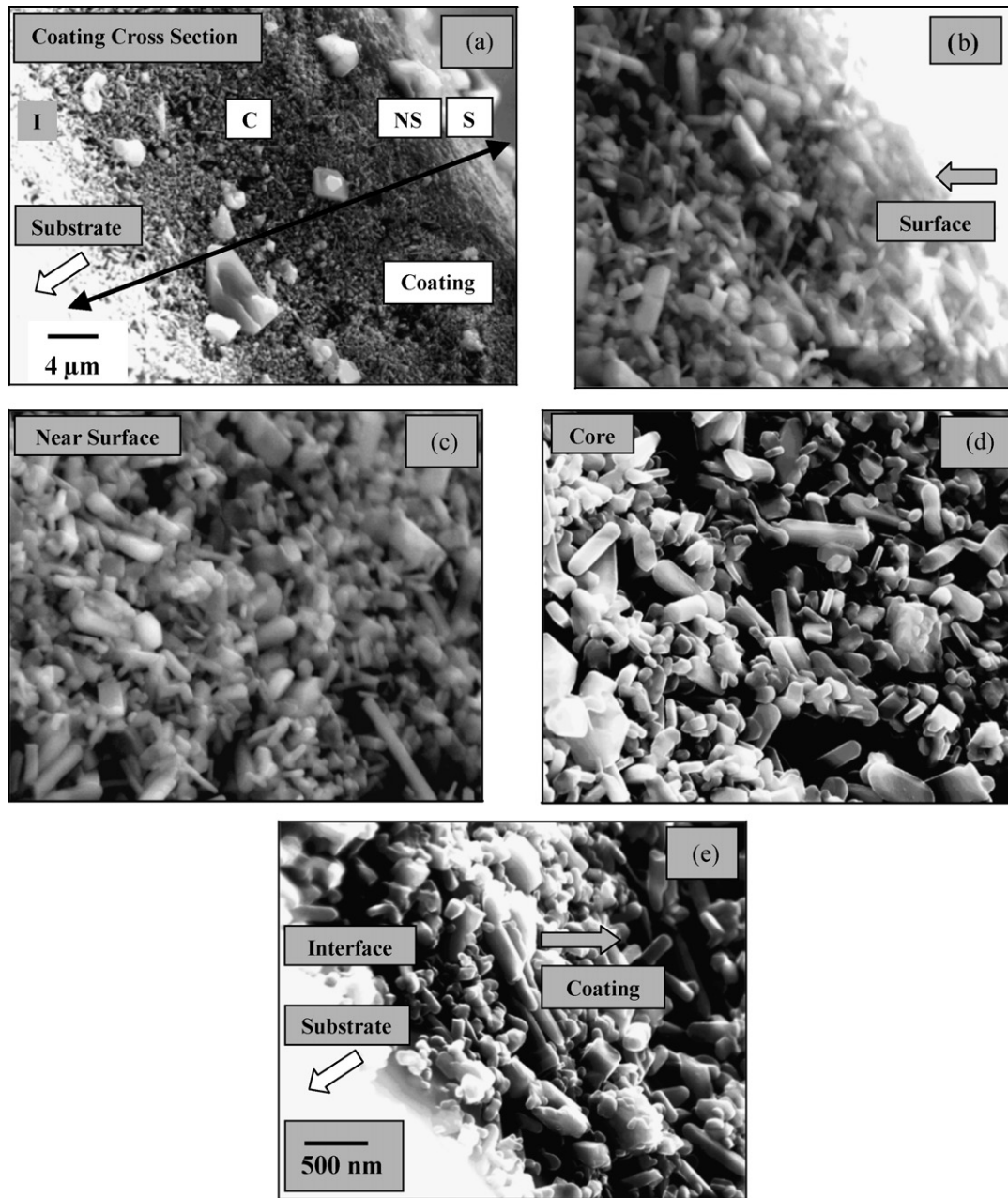
Fig. 4. Microwave processed coating at 880 °C for 90 min and 1020 °C for 90 min (a) cross sectional view; (b) surface region of the coating; (c) near surface region of the coating; (d) core of the coating and (e) coating-substrate interface.

nique revealed that here at the interface (Fig. 4e), slightly smaller crystallites e.g. 285 ± 34 nm were present than the sizes of the crystallites noted at the core of the coating (Fig. 4d). This slight reduction in crystallite size may be due to the fact that a part of the heat flux produced during microwave processing would be conducted through the metallic substrate, which has a much higher thermal conductivity than that of the glass-ceramic coating.

The comparative data for the conventionally processed coating are presented in Fig. 5a–d. The coating was about 25 μm thick along the cross-sectional direction (Fig. 5a). The region just at the surface of the coating as viewed in cross section is depicted by "S", the region at the core of the coating is marked by "C" and the region at the substrate-coating interface is indi-

cated by "I". The magnified views of all these regions are shown in Fig. 5b–d. All these SEM micrographs were taken at one and the same magnification as of Fig. 4b–e.

Fig. 5b shows the cross-sectional microstructure just at the surface of the glass-ceramic coating (region "S" of Fig. 5a) obtained by conventional processing condition as mentioned above. Here, the average crystallite size was really very coarse at about 388 ± 28 nm. At the core of the coating nearly similar sized crystallites can be seen, Fig. 5c. Image analysis revealed that the core region at the cross-sectional view of the coating (region "C" of Fig. 5a) had an average crystallite size of about 372 ± 33 nm. This data provided strong evidence that the temperature gradient, if any, had no significant influence on
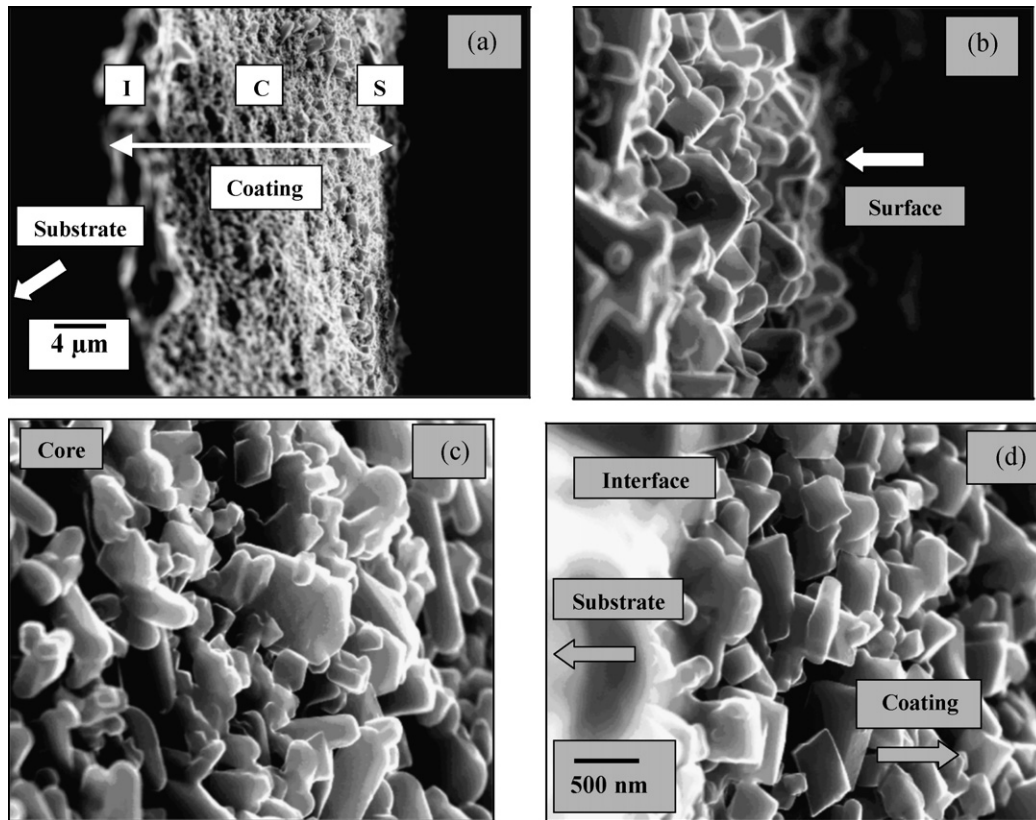
Fig. 5. Conventionally processed coating at 880 °C for 90 min and 1020 °C for 90 min (a) cross sectional view; (b) surface region of the coating; (c) core of the coating and (d) coating-substrate interface.

the crystallite size. The cross-sectional microstructure was also examined at the region of interface between the substrate and the coating (region "I" of Fig. 5a). Here, slightly smaller crystallites e.g. 362 ± 27 nm (Fig. 5d) were present. The slight reduction in average crystallite size may be due to the conduction of heat through the metallic substrate.

Cross-sectional examinations of both conventionally and microwave processed coatings strongly indicate that microwave processing produced finer sized crystallites in the glass coating compared to the sizes of the crystallites obtained in the conventionally heat treated coating. Based on the current experimental evidences, the following simplified picture is presented.

On prolonged microwave exposure, the coupling of the glass coating with the microwave field is improved.[1,19] Therefore, it seems plausible to assume that the microwave power is absorbed and hence, the rise in heat content in the bulk of the coating starts taking place at a rate faster compared to that in the near surface region of the coating. Thus, during heating, the gradient is from the bulk to the surface side of the coating. Further, as the surface cools at a much faster rate through process of radiative heat loss, the gradient from the surface to the bulk side becomes stiff for the coating. Because of the faster cooling rate and consequently lower surface temperature, the surface region as well as the near surface region of the coating can undergo microstructural refinement,[5] as observed in the micrographs obtained for the microwave processed glass-ceramic coatings (Figs. 3 and 4b,c). Coatings showed finer surface microstructure as the soak time

was enhanced (Fig. 3). With increasing the soak time, the surface temperature of the coating continued to fall resulting in stiffer temperature gradient. This was reflected in the decreased crystallite size on the surface of the coating as the time of soaking was increased (e.g. 90 min). Coarsening of the crystallite size was observed at the core of the coating (Fig. 4d) due to the slower cooling rate and the higher temperature of the core because of the volumetric heating process. However, the average crystallite size in the coating-substrate interface region (Fig. 4e) was slightly lower than the average size of the crystallites noted in the core of the coating, most likely as a consequence of conduction of heat through the metallic substrate.

In the case of conventionally processed coating (Fig. 5b–d), the effect of thermal gradient was almost negligible. As the coating was very thin ($\sim$25 μm), there was no significant difference in the temperature of the coating along the cross-sectional region. This situation possibly led to nearly similar crystallite size throughout the cross section of the coating.

3.4. Surface finish

The surface roughness data of the microwave processed glass-ceramic coatings were much lower compared to those of the coatings processed by conventional heating (Fig. 6). The microwave processed coating showed $R_a \sim 0.28$ μm whereas that of the conventionally processed coating was ~ 0.83 μm for an identical soaking period of 90 min. This means that the
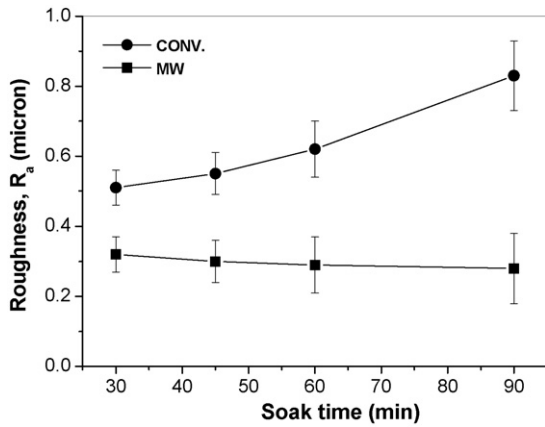
Fig. 6. Typical surface roughness of the microwave and conventionally processed glass-ceramic coatings.

microwave processed coating was much smoother than the conventionally processed coating prepared under identical holding time of 90 min at 880 °C followed by 90 min at 1020 °C.

The low surface roughness may be explained by the fact that microwave processing produced finer sized crystallites in the glass coating surface compared to the sizes of crystallites observed in the conventionally heat treated coating surface (Fig. 7). As the soak time was increased, the crystallite size increased for the glass-ceramic coating obtained by conventional processing (Fig. 7). This could lead to higher surface roughness (Fig. 6) in the conventionally processed coating. Further support to this suggestion arises from the physical appearances of the surfaces of the two coatings (Fig. 8a and b).

A very smooth featureless surface appearance was present in the microwave processed coating (Fig. 8a) and hence, a lower surface roughness that was possibly linked to the presence of finer crystallites evolved due to more microstructural refinement at higher holding times. However, it is evident from the typical example provided in Fig. 8b that the conventionally processed coating surface was very rough and thus, exhibited higher surface roughness.
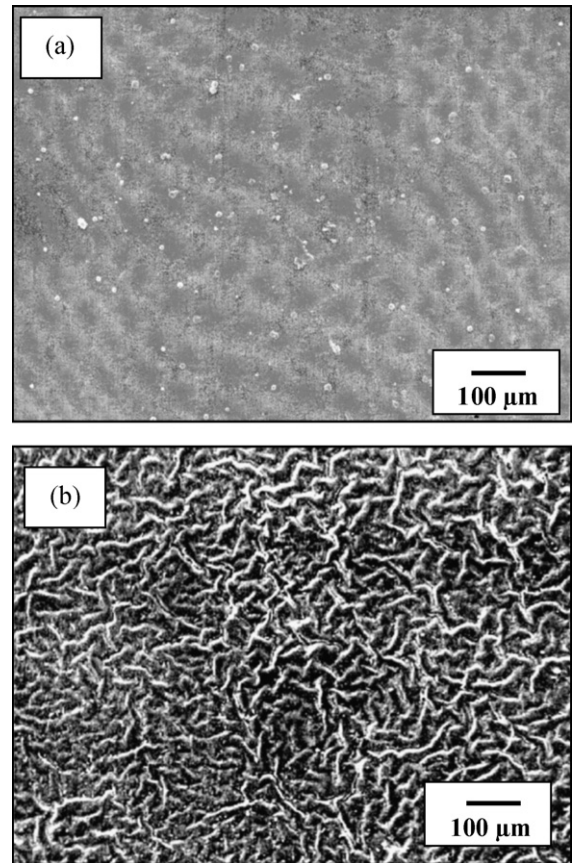

Fig. 8. SEM micrographs of the as prepared glass-ceramic coatings after heat treatments of the glass coatings for 90 min at 880 °C followed by 90 min at 1020 °C in (a) microwave furnace and (b) conventional furnace.

3.5. Microhardness

The hardness data presented in Fig. 9 illustrate that microwave processing produced glass-ceramic coating of high hardness value (~6 GPa). It is suggested that the slight increase in the microhardness values with the soak time for the microwave processed glass-ceramic coatings might be associated with the decrease in crystallite size with the increase in soak time (Fig. 7).
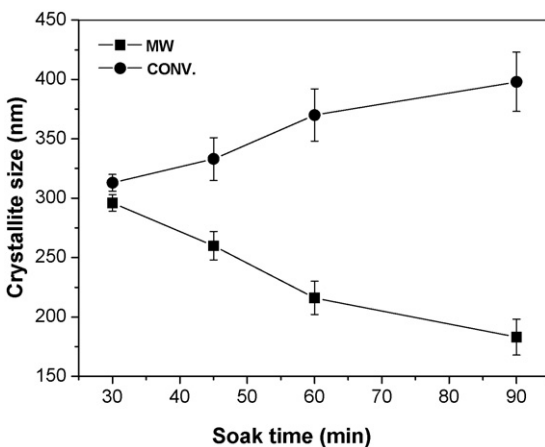

Fig. 7. Variation of crystallite size with soak time for the microwave and conventionally processed glass-ceramic coatings.
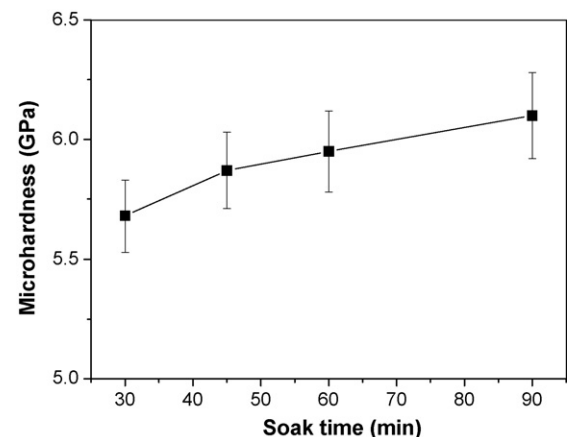

Fig. 9. Typical hardness of the microwave processed glass-ceramic coatings.

The area fraction of crystallites in the glassy matrix is expected to increase with the reduction in crystallite size as the soak time was enhanced.[14,20,21] Therefore, the extent of reinforcement to the glass matrix may increase with increasing the soak time, which should lead to the enhancement of hardness in the microwave processed glass-ceramic coatings as was observed in the present experimental data (Fig. 9).

However, it should be borne in the mind that hardness of a surface is not a unique and single valued function of the crystallite size only, although it may be recognized that it is one of the important variables that might affect the measured hardness values. For instance, presence of thermally originated residual compressive stress[20,21] on the surface might cause an apparent increase in the hardness value. If during surface finishing, the surface gets work-hardened e.g. during prolonged polishing with $0.25\,\mu m$ diamond paste grit size, there might be an apparent increase in the hardness value. Further, it may be noted that during microwave processing, the cooling takes place in a much shorter time period at the surface. The presence of stiff thermal gradient during cooling might lead to high dislocation density near the surface of the coating and hence, might affect the measured values of hardness as well.

For a soak time of 30–90 min, the hardness values of the conventionally processed coatings were measured to be much lower (4.21 ± 0.3 to 5.00 ± 0.36 GPa). In fact, it was always measured that for a given soak time the hardness of the microwave processed glass-ceramic coating was higher than that of the conventionally processed one. This can be explained by the fact that as the soak time was increased from 30 to 90 min the crystallite size also increased in the conventionally processed coating, which led to coarser and coarser microstructures with consequently lower hardness values compared to those of the microwave processed coatings.

4. Conclusions

The major findings obtained from the present work were as follows:

(a) Glass-ceramic coatings were developed on nimonic alloy substrates by both microwave and conventional processing from a glass based on $MgO–Al_2O_3–TiO_2$ system. The microwave processing was done in air at a frequency of 2.45 GHz after placing the samples in a silicon carbide susceptor in a microwave furnace.
(b) The coatings were characterized through X-ray diffractometry (XRD), scanning electron microscopy (SEM), image analysis, surface roughness measurement and hardness evaluation through the depth sensitive indentation (DSI) technique.
(c) XRD analysis identified the presence of magnesium aluminium titanate, magnesium silicate and aluminium titanate phases in all the glass-ceramic coatings produced by both microwave and conventional processing.
(d) SEM investigations on the top surfaces and the cross-sections of both conventionally and microwave processed glass-ceramic coatings (obtained by heat treatments of the

glass coatings for 90 min at 880 °C followed by 90 min at 1020 °C) strongly indicate that microwave processing produced finer sized crystallites in the glass coating surface compared to the sizes of the crystallites in the coating surface evolved by the conventional heat treatment process.
(e) The microwave processed coating showed surface roughness ($R_a \sim 0.28\,\mu m$) much lower than that ($\sim 0.83\,\mu m$) of the conventionally processed coating for an identical soaking period of 90 min at 880 °C followed by 90 min at 1020 °C.
(f) Samples obtained under identical condition of preparation by both microwave and conventional processing techniques showed that a very smooth featureless surface appearance was present in the microwave processed coating whereas a very rough appearance was present in the conventionally processed coating.
(g) DSI technique showed that the microwave processed glass-ceramic coating had high hardness (~ 6 GPa). There was a slight increase in the microhardness values with the soak time for the microwave processed coatings. However, for a given soak times in the range of 30–90 min, the hardness values of the conventionally processed coatings were measured to be much lower (4.21 ± 0.3 to 5.00 ± 0.36 GPa) than those of the microwave processed coatings.
(h) The results of the present work suggest that microwave processing can be efficiently utilized to tune the microstructure as well as properties of the glass-ceramic coating to suit a given end application.

References

1. Sutton, W. H., Microwave processing of ceramic materials. *Ceram. Bull.*, 1989, **68**, 376–386.
2. Cheng, J., Agrawal, D., Zhang, Y. and Roy, R., Microwave reactive sintering to fully transparent aluminum oxynitride (ALON) ceramics. *J. Mater. Sci. Lett.*, 2001, **20**, 77–79.
3. Mukhopadhyay, A. K., Ray Chaudhury, M., Seal, A., Dalui, S. K., Banerjee, M. and Phani, K. K., Mechanical characterization of microwave sintered zinc oxide. *Bull. Mater. Sci.*, 2001, **24**, 125–128.
4. Mandal, S., Seal, A., Dalui, S. K., Dey, A. K., Ghatak, S. and Mukhopadhyay, A. K., Mechanical characteristics of microwave sintered silicon carbide. *Bull. Mater. Sci.*, 2001, **24**, 121–124.
5. Sharma, A. K., Aravindhan, S. and Krisnamurthy, R., Microwave glazing of alumina-titania ceramic composite coatings. *Mater. Lett.*, 2001, **50**, 295–301.
6. Fisher, J. G., Woo, S. K., Bai, K., Han, I. S., Lee, K. S., Hong, K. S. and Seo, D. W., Microwave reaction bonding of silicon nitride using an inverse temperature gradient and ZrO_2 and Al_2O_3 sintering additives. *J. Eur. Ceram. Soc.*, 2003, **23**, 791–799.

7. Zhou, Y., Vander Biest, O., Groffils, C., and Luypaent, P. J. Microwave processing CaO–Al2O3–SiO2 glass using sol–gel technique. In *Microwave Processing of Materials V*, ed. Iskander M. F., Kiggans, Jr., J.O., and Bolomey, J. C. Materials Research Society Symposium Proceedings, vol. 430, Pittsburgh, Pennsylvania, Mater. Res. Soc., 1996, pp. 131–137.

8. Kumar, N., Pant, A., Sood, R. R., Ng-Yelim, J., and Holt, R. T., Production of ultra-fine silicon carbide by fast firing in microwave and resistance furnaces. In *Microwaves: Theory and Application in Materials Processing*, ed. Clark, D. E., Gac, F. D., and Sutton, W. H., Ceramic Transactions, vol. 21, The Am. Ceram. Soc., Inc. Westerville, Ohio, 1991, pp. 395–402.

9. Aravindan, S. and Krishnamurthy, R., Joining of ceramic composites by microwave heating. *Mater. Lett.*, 1999, **38**, 245–249.

10. Das, S., Mukhopadhyay, A. K., Datta, S. and Basu, D., Novel method of developing oxide coating on aluminium using microwave heating. *J. Mater. Sci. Lett.*, 2003, **22**, 1635–1637.

11. Das, S., Mukhopadhyay, A. K., Datta, S. and Basu, D., Aluminium oxide coating by microwave processing. *Trans. Ind. Ceram. Soc.*, 2006, **65**, 105–110.

12. Das, S., Basu, D., Datta, S. and Mukhopadhyay, A. K., A process of making Al–Al$_2$O$_3$ composites useful in engineering applications. *Indian Patent application*, App. No. 245/DEL/03.

13. Cozzi, A. D., Fathi, Z., and Clark D. E., Crystallization of sol–gel derived barium aluminosilicate in a 2.45 GHz microwave field. In *Microwaves: Theory and Application in Materials Processing II*, ed. Clark, D.E., and Tinga, W. R., Laia, Jr., J. R. Ceramic Transactions, vol. 36, The Am. Ceram. Soc., Inc, Westerville, Ohio, 1993, pp. 317–324.

14. Siligardi, C., Leonelli, C., Bondioli, F., Corradi, A. and Pellacani, G. C., Densification of glass powders belonging to the CaO–ZrO$_2$–SiO$_2$ system by microwave heating. *J. Euro. Ceram. Soc.*, 2000, **20**, 177–183.

15. Datta, S. and Das, S., A new high temperature resistant glass-ceramic coating for gas turbine engine components. *Bull. Mater. Sci.*, 2005, **28**, 689–696.

16. Mukhopadhyay, N. K. and Paufler, P., Micro and nanoindentation techniques for mechanical characterisation of materials. *Int. Mater. Rev.*, 2006, **51**, 1–37.

17. Oliver, W. C. and Pharr, G. M., An improved technique for determining hardness and elastic modulus using load and displacement sensing indentation experiments. *J. Mater. Res.*, 1992, **7**, 1564–1583.

18. Das, S., Mukhopadhyay, A. K., Datta, S. and Basu, D., unpublished work, 2007.

19. Katz, J. D., Microwave sintering of ceramics. *Annu. Rev. Mater. Sci.*, 1992, **22**, 153–170.

20. Fulrath, R. M., Internal stress in model ceramic systems. *J. Am. Ceram. Soc.*, 1959, **42**, 423–429.

21. Xu, C., Effects of particle size and matrix grain size and volume fraction of particles on the toughening of ceramic composite by thermal residual stress. *Ceram. Int.*, 2005, **31**, 537–542.