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Combinatorial preparation of solid-state materials by injection moulding

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Abstract

A new combinatorial technique has been developed for the parallel synthesis of multi-component solid-state inorganic materials. As an example to illustrate the utility of this new method, a phase relationship investigation for the ternary system Fe_2O_3–TiO_2–Al_2O_3, is presented with a much wider composition range in comparison with the previous investigations by conventional means. The combinatorial composition spreading in a ternary system was realized by three combined triangular pyramid-shaped layers produced by the injection moulding technique in the final shape of a triangular prism, followed by a subsequent dividing and mixing process. The consistency of the phase relationship analyzed by XRD with the previous reports proved the reliability of the new combinatorial strategy. The samples were also characterized by SEM and ICP-AES.

Keywords: Injection moulding; Pressing; X-ray methods; Microstructure-final

1. Introduction

Since the 1960s, materials scientists and condensed matter physicists have made efforts to develop more effective methods to obtain phase diagrams. Conventional methods by mechanical mixing of coarse starting materials and grinding operations at each discrete composition point are time-consuming, energy intensive, and discouraging because of the difficult technique of homogeneous milling and product contamination.[1,2] However, the improved efficiency of a combinatorial approach makes it possible to treat complex systems and interactions in a “faster, cheaper, and more convenient” way and has stimulated much progress in the past few years in studies of phase diagrams and composition–structure–property relationships.[3–10]

Various parallel synthesis strategies have been developed to produce materials libraries. For instance, the combinatorial thin film deposition technique by physical deposition processes, which utilizes natural gradient profiles followed by interdiffusion, has been developed for phase diagrams of alloys.[3–5] However, the thin films might interact with the substrate and formation of metastable structures complicates the study of equilibrium phases.[6] Diffusion-multiple approach,[7] which relies on the existence of a small interdiffusion region of tens of micrometers created by long-term annealing of intimate junctions of three or more alloys, enables effective studies of phase diagrams, kinetics, etc. The unevenly distributed phase points in the cross-section of the interface region need to be determined accurately with high spatial resolution. In addition, the highest temperature for diffusion is limited by the lowest liquidus temperature of the multicomponent system.[6] In solution-based parallel synthesis, the precursor solutions are dispensed automatically by microdispenser or inkjet delivery apparatus, followed by mixing and reaction. This method can only treat soluble compounds in the liquid starting state.[8]

Instead of homogeneous solutions from soluble compounds, high reactive nanoparticle powders could be used to prepare stable suspensions, which have been proven to be applicable in automatic microdispensers or ink-jet delivery systems to produce combinatorial libraries.[8–13] Due to the nanometric particle size of the suspension, the mixing of different precursors and the interdiffusion between the particles can be more effective than that in the homogeneous solutions, in which one precursor could be precipitated prior to others.[8] However, this method is limited to the treatment of nanoparticles and the stability of the nanoparticle suspensions has to be well-controlled to avoid sedimentation or agglomeration during operation. In ink-jet printing techniques,[10–13] the suspension of different ceramic powders has been successfully delivered to create combinatorial libraries of ceramic compositions. Interestingly, continuous gradients can

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be generated in this technique; the particle size determines the minimum gradient step size.[10] However, demixing might occur during the drying stage of the droplets of multiple powders.[11]

In this paper, we present a new method for the synthesis of material libraries by means of an injection moulding technique. Powders with a particle size range from nano- to submicrometer can be applied in this approach. The settling which is probably happening in nanoparticle suspension can be avoided. The amount of material which is obtained for each composition is sufficient to test the bulk properties. We have chosen the ternary system Fe_2O_3–TiO_2–Al_2O_3 as an example to study the applicability of this new method.

2. Experimental procedure

The basic idea to achieve a combinatorial library in a ternary system is shown schematically in Fig. 1. Three combined triangular pyramid-shaped layers (Fig. 1a), produced by injection moulding, were stacked on top of one another (Fig. 1b) and further separated by honeycomb cutting (Fig. 1c), followed by subsequent mixing and heating treatment. The detailed procedures were carried out as following.

2.1. Synthesis and combination of three layers

Starting materials used were alumina (Aluminiumoxid C, Degussa), titania (P25, Degussa) and iron oxide (1300 M, Nordic pigments) powders with average particle size about 30, 50, 200 nm, respectively. The powders were dried at 120 °C overnight prior to mixing with the binder. The low-viscosity feedstock comprised of paraffin wax-based binder, ceramic powder (Fe_2O_3, TiO_2, or Al_2O_3) and surfactant was prepared by using a kneader (Stephan, Hameln, Germany) with a 650 cm^3 bowl, and two sigmoidal, counter-rotating blades operating at 35 rpm (rotations per minute). The kneading time was 5 h. Granulation of the feedstock was performed during cooling by continuously rotating the blades as the temperature dropped from 100 to 40 °C. The as-prepared feedstock was then fed into an injection moulding machine (Allrounder 220 M, Arburg) to form triangular pyramid-shaped layers (see Fig. 1a). Three layers composed of Fe_2O_3, TiO_2, or Al_2O_3, respectively, were stacked on top of one another with a rotation of 120° to form a triangular prism with dimensions of base side 120 mm and height of 20 mm, as shown in Fig. 1(b).

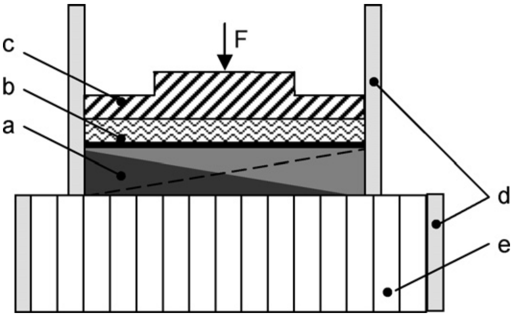

Fig. 2. Schematic experimental set-up used to separate library cells. (a) Injected three layers, (b) silicone rubber layer sputtered with graphite, (c) stainless-steel cover, (d) Frame made of aluminium alloy and (e) honeycomb.

2.2. Separation of library cells by honeycomb cutting

The stacked three layers were vertically put on top of an aluminium honeycomb (Euro-composites Co.) with a cell size of 6.4 mm (see Fig. 1b). To avoid the slipping of layers and honeycomb during cutting, an additional frame was used to stabilize the system. The frame made of aluminium alloy consists of two parts, one is to fix the honeycomb, and the other is to stabilize the three layers and their covers during cutting. The experimental set-up used to separate the library cells is shown schematically in Fig. 2. First of all, the honeycomb was fixed into the lower part of the frame. The injected three layers were directly put on top of the honeycomb, which is stabilized by the upper part of the frame. Silicone rubber (Strauch GmbH) sputtered with graphite, as an isolation to avoid the sticking of the layers to the cover, was then put on top of three layers. Flexible silicone rubber was used to protect the edges of the honeycomb after the three layers were totally pressed into the honeycomb. Finally, a hard cover made of stainless steel was added on top of the silicone rubber. Subsequent heating of the as-obtained system at 100 °C for 20 min softened the three layers. Then the cover was slowly pressed to push the three layers into the honeycomb. Thus the separated library members were obtained in the honeycomb cells (see Fig. 1c). A total of 171 compositions were achieved in this library.

2.3. Mixing and post-treatment

In order to get a homogeneous mixture of each layered piece in the honeycomb cells, each individual layered piece was

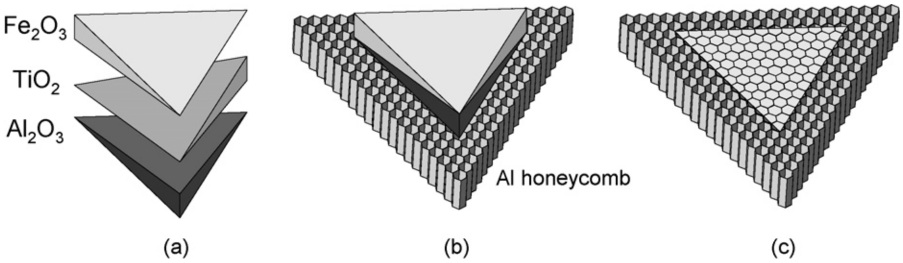

Fig. 1. Schematic arrangement for three component systems. (a) Fe_2O_3, TiO_2 and Al_2O_3 layers, in which each layer was individually produced by injection moulding from the mixtures of the corresponding solid powder, paraffin wax, surfactants; (b) the combination of three layers on aluminium honeycomb; (c) the combinatorial library made by honeycomb cutting.

manually transferred to a self-made aluminium rack with 70 parallel wells of 10 mm in diameter and 10 mm in depth. Certain amounts of decane and paraffin wax as a dilution agent were added in each well of the aluminium rack to aid the mixing. The rack was covered by a silicone rubber and then clamped between two electric heating plates. The assembled system was fixed in a red-devil painter mixer (Chameleon M & T Machines Ltd.). The system was heated up to 120 °C by electric heating plates and shaken for 0.5 h at 120 °C. In this step, the binder inside each well of the rack was melted and the contained individual layered piece was mixed in the diluted wax-based solution. After half an hour mixing at 120 °C, the whole system was cooled down to room temperature during shaking, whereas the wax-based solution became solid again. Therefore, the mixing status of the mixture in each well of the rack was easily kept in wax-based system. The cooled mixtures were calcined in air at 500 °C for 6 h with a ramping rate of 420 °C/h to remove the contained organic components, followed by grinding in an agate mortar. This process was repeated one more time to improve the mixing. The powdered materials were manually pressed in a cylindrical steel die (8 mm in diameter) at 80 MPa to thin pellets. The pellets were sintered at 1300 °C with a ramp rate of 300 °C/h for 70 h in alumina crucibles, and finally quenched in water.

2.4. *Characterizations*

X-ray powder diffraction (XRD) measurements were carried out using Cu Kα radiation ($\lambda = 1.54178$ Å) in a Siemens D-500 diffractometer equipped with a graphite monochromator in the range from 15 to 65° in 2θ and a counting time of 4 s/step. Scanning electron microscopy (SEM, JEOL JSM 6400F) and optical microscope (Olympus Optical Co. Ltd.) were used to observe the morphology of the sintered samples. Atomic ratio of iron, titanium, and aluminium of the prepared samples were analyzed by using atomic emission spectroscopy (ICP-AES, Horiba Jobin Yvon GmbH).

3. Results and discussion

In a three-layer unit of the Fe_2O_3–TiO_2–Al_2O_3 ternary system, each composition in this library depends on its geometrical position in the honeycomb and the content of metal oxide in each layer. The total thickness at any cell along the honeycomb net is equal to the sum of the individual thicknesses, which vary proportionally from cell to cell. The composition in molar fraction in each cell of the honeycomb was calculated with the solid loading in the corresponding feedstock, the molecular weight of the components, and the individual thickness ratio of the central point in the respective cell within the honeycomb net and is visualised in Fig. 3. As the amount of contained metal oxide in each layer depends on the solid loading in the corresponding feedstock and the respective molecular weight, the distribution of compositions in the library is not in equal increments. Experimental compositional verification for the sintered samples using ICP-AES measurements was done to demonstrate the consistence between the calculated and the measured composition values. The relative errors are below 10%. This error might be explained by the slight shifting of three layers during the honeycomb cutting, which might be further minimized by careful adjustment of cutting speed. On the whole, the tendency of the compositional spreading in the whole library analyzed by ICP-AES was consistent with the expected calculated composition values.

To compare our method with conventional solid-state reaction method, the similar sintering conditions as that of Pownceby et al.[14] were chosen. The phase relations of the samples in the Fe_2O_3–TiO_2–Al_2O_3 ternary system sintered at 1300 °C are presented in Fig. 3. Seven phase regions, marked by different symbols, could be identified. These regions can be attributed to hematite solid solution (empty triangle) at Fe_2O_3-rich composition, a continuous pseudobrookite-structure solid solution (empty circle) between Fe_2TiO_5 and Al_2TiO_5, a three-phase region (the assemblage of hematite, pseudobrookite and corundum), and four two-phase regions. In the XRD patterns of the two samples near Al_2TiO_5 in pseudobrookite-structure

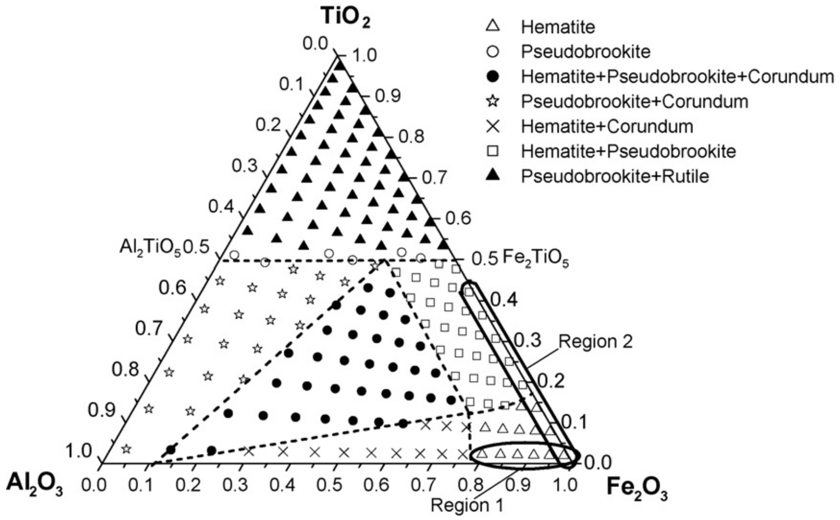

Fig. 3. Compositions (molar fraction) and phase relationship for combinatorial library prepared by the injection moulding technique in the system Fe_2O_3–TiO_2–Al_2O_3 in air at 1300 °C. The dashed lines are phase boundaries reported by Pownceby et al.[14]

solid solution between Fe_2TiO_5 and Al_2TiO_5, both rutile and corundum in very small amounts were also observed besides pseudobrookite-structure. It is possible that due to the sluggish reaction the equilibria were still not achieved. Above the decomposition temperature at 1281 ± 1 °C, which was determined by Kato et al.,[15] the further reaction to Al_2TiO_5 is possible in an oxidizing atmosphere.[16] Furthermore, Fe_2O_3 can serve as stabilizer in this reaction.[17] Therefore, longer treatment might be needed for further reaction to get complete conversion. The phase relationship reported by Pownceby et al.[14] were also shown in Fig. 3. The phase boundaries with the same phase distribution regions were demonstrated by dashed lines. Our results closely follow the previously reported phase relations constructed by a series of discrete data points obtained by conventional method.[14] The consistency with the previous report proved the reliability of the phase relationship analysis developed by the new combinatorial technique.

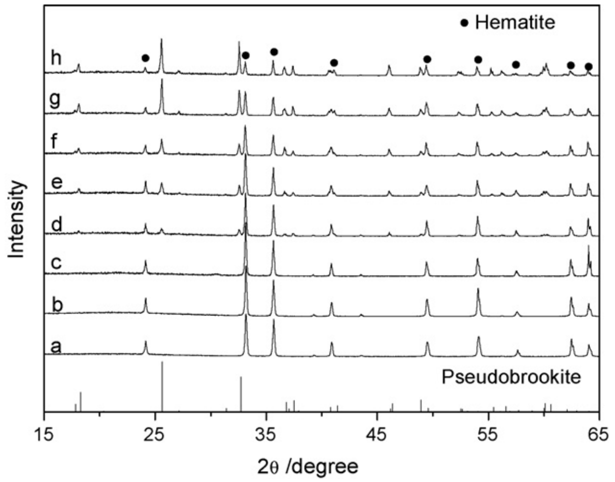

Fig. 5. XRD patterns of samples in Region 2 of Fig. 3 with composition (molar fraction) of Fe_2O_3:TiO_2:Al_2O_3 in starting mixtures of (a) 97.1:1.9:1.0, (b) 91.3:7.7:1.0, (c) 85.5:13.5:1.0, (d) 79.7:19.3:1.0, (e) 74.0:25.0:1.0, (f) 68.3:30.7:1.0, (g) 62.6:36.4:1.0 and (h) 56.9:42.1:1.0.

The representative XRD patterns for details of structural changes and progression are demonstrated in Figs. 4 and 5. Fig. 4 shows the six selected XRD patterns of samples which are indicated along the Fe_2O_3–Al_2O_3 edge in hematite solid solution in Fig. 3 (Region 1). These patterns exhibited the same rhombohedral structure. No alumina or titania phases were detected. With the replacement of ferric oxide by alumina, a shift of the diffraction peaks towards higher 2θ values was observed. The variation of the lattice parameter of these samples as a function of aluminium atomic content is obtained by Rietveld analysis and shown as inserted figures in Fig. 4. The lattice parameters exhibit a linear decrease with increasing aluminium content. This is probably attributed to the relatively smaller ionic size of Al^{3+} (0.054 nm) replacing the larger ionic size of Fe^{3+} (0.065 nm) which results in a shrinkage of the lattice edges.[18] The XRD patterns of the samples, which are indicated along the Fe_2O_3–TiO_2 edge from hematite solid solution to the two-phase region of (hematite + pseudobrookite) in Fig. 3 (Region 2), are presented in Fig. 5. When the three components formed solid solutions as seen from pattern (a) to (c), the rhombohedral structure was the only phase. When the concentration of TiO_2 was above the solubility limit as seen from pattern (d) to (h), across phase boundary the intensity of hematite decreases while that of the pseudobrookite increased with the increasing concentration of TiO_2.

By controlling sintering conditions such as temperature and time, it is possible to obtain very different microstructures. Such

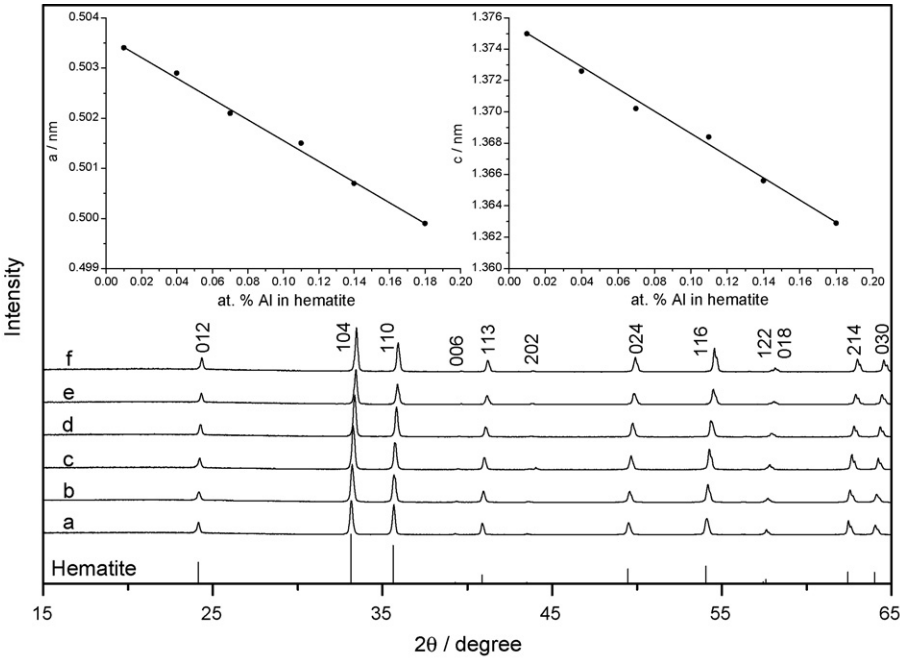

Fig. 4. XRD patterns of samples in Region 1 of Fig. 3 with composition (molar fraction) of Fe_2O_3:TiO_2:Al_2O_3 in starting mixtures of (a) 97.0:2.0:1.0, (b) 94.0:2.0:4.1, (c) 90.7:2.0:7.3, (d) 87.2:2.1:10.7, (e) 83.5:2.1:14.3 and (f) 79.6:2.2:18.2. The top left and right insets show the lattice constants a, c as a function of Al atomic content in hematite.

control is very interesting in the design of materials for special applications. Three different particle size ranges were used in this system. Nanoscaled TiO_2 and Al_2O_3 and submicron scaled Fe_2O_3 were chosen as raw materials, based on two reasons, one is to show the broader selection for raw materials could be applied in this new technique, the other is that the smaller particles could be inserted into the gap among bigger particles to get a more tightly packed structure. The morphological difference in the high alumina, titania or ferric oxide content compositions of the prepared sintered library is illustrated in Fig. 6. Interestingly, a considerable influence arising from the bulk composition was observed. Composition at high Al_2O_3 content produced fine-grained assemblages and dense structures. In contrast, Fe_2O_3-rich composition produced grain sizes averaging at 10–20 μm. Even coarser grain sizes were observed in the high-TiO_2 bulk composition. This differs with the investigation of Pownceby et al.,[14] who reported near to or along the Al_2O_3–TiO_2 binary join, fine-grained assemblages, generally ≤2–3 μm in diameter, whereas Fe_2O_3-rich compositions have grain sizes averaging 20–30 μm in diameter. Grain growth depends on several factors such as heat treatment, grain size distribution, grain morphology and the presence of second phases, etc.[19] The preliminary results obtained in this study suggest that a systematic study for the effect of heat treatment and sintering conditions on microstructure of the samples is required. Further investigation of this relationship is underway.

Compared with many combinatorial materials based on thin films,[3–5] in which phase diagram mapping investigation could be complicated by the interaction between the substrate and thin films and the difficulty of crystal structure identification due to strong textures often forming in the deposited films, the products achieved with our technique suffer less from substrate influence and they are bulk-form ceramic materials. Therefore, the final libraries are applicable for determination of bulk properties.

It is worth to mention the advantages to use paraffin wax as a medium to produce the library. The mixing of library members was realized by a paint mixer above the melting point of the organic vehicle based on paraffin wax. The final mixing status was kept in the cooled solid organic vehicle. The sedimentation, which probably happens in nano-powder suspensions during aspirating-dispensing by the robot,[8] seems not to be a problem because the particles were totally “fixed” in the solid organic vehicle. One problem existing in the present method is that, demixing might occur during the thermal treatment of the mixtures. Therefore, the fast thermal treatment for the purpose of quick removing the organic components after mixing was chosen here in order to reduce the possibility of demixing. Meanwhile, the splashing during the quick burning of organic components might also prevent the possible demixing.

We showed that injection moulding techniques can be used to produce highly precise geometry to realize the three-dimensional composition spreading library. In a further step, the honeycomb cutting produces the library members and the mixing in the wax-based system. In this flow, some factors may be modified, such as the original powder property, the choice of surfactant, the viscosity of the blends, the cutting speed, and the firing procedure, etc. All those factors can influ-

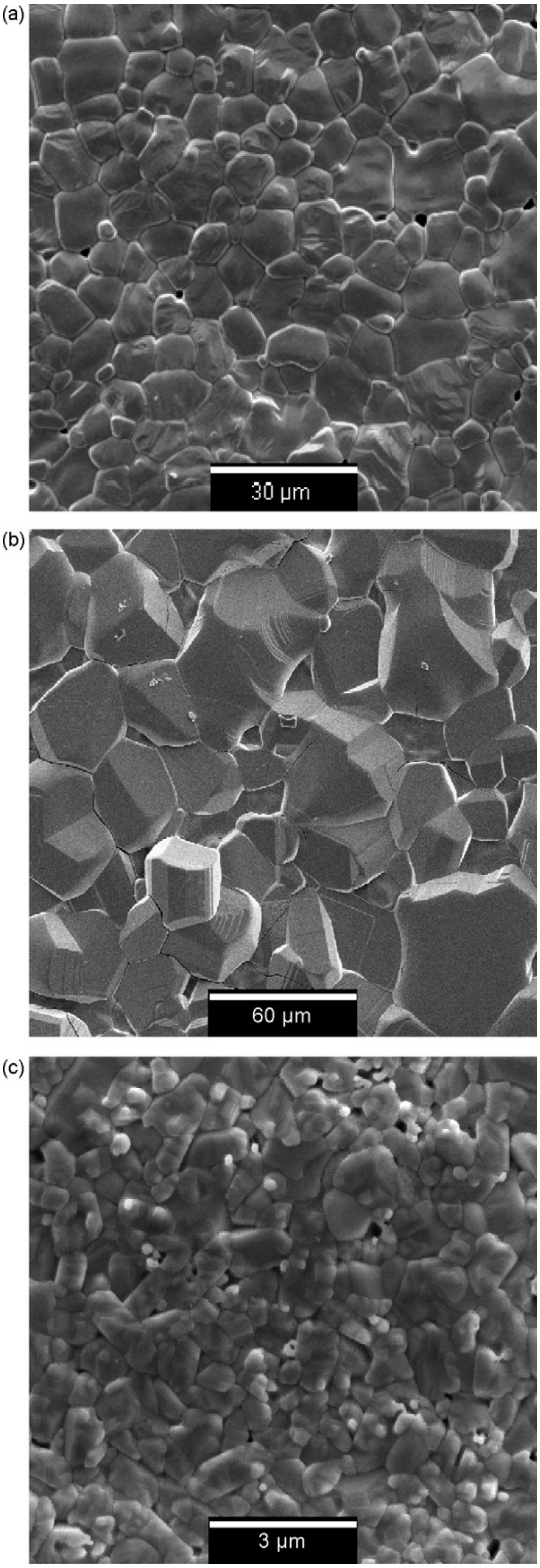

Fig. 6. SEM micrographs for sintered samples in air at 1300 °C. The composition (molar fraction) of Fe_2O_3:TiO_2:Al_2O_3 in starting mixtures is (a) 88.0:4.6:7.4, (b) 3.5:95.3:1.2 and (c) 5.3:2.7:92.0.

ence the homogeneity of mixing and the maintenance of the mixing status during firing and finally influence the quality of the final mixtures. We still have to study these impacts in detail.

The advantage of the presented procedure is that the same method can be used for a multitude of ternary component systems. Much more compositionally varying samples may be synthesized in a single experiment during honeycomb cutting by use of a honeycomb with smaller cell size. Furthermore, this approach can easily be extended to more complex combinations. A quaternary system for example can be realized by adding one additional layer in shape of prism on top of the ternary system as the fourth component. The concentration of the fourth component can be adjusted by the height of the fourth layer. This method, in contrast to other combinatorial methods, such as thin-film synthesis techniques, etc., offers a new and efficient technique to reveal the complex relation of composition–structure–property of unknown materials systems.

4. Conclusion

A new parallel synthesis method by injection moulding technique to produce the compositionally spreading materials library followed by the honeycomb-dividing and mixing process has been developed in the present study. The ternary system Fe_2O_3–TiO_2–Al_2O_3 was chosen as an example to show the applicability of this new technique. The tendency of the compositional spreading in the whole library analyzed by ICP-AES was consistent with the expected calculated composition values. The similar phase relationship with previous reports, the regular tendencies and the linear lattice parameter variation in hematite solid solution prove the reliability of the new parallel synthesis technique. In the present study, paraffin wax-based organic media played a specific role in mixing due to their low melting point. Above the melting point, this medium provided free fluidity for mixing of the different ceramic powders. Below the melting point, the medium was used to fix the mixed ceramic powders separated in space. The factors which may modify the property of final products need to be studied further in the future.

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