Deflocculation and stabilization of Ti$_3$SiC$_2$ ceramic powder in gelcasting process

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This paper presents results on the deflocculation and stabilization of Ti$_3$SiC$_2$ that are crucial for determining the quality of the ceramics after sintering in colloidal processing. Five different dispersants diammonium hydrogen citrate, citric acid, polyethyleneimine, polycarboxylic acid and ammonium polyacrylate were examined by measuring the zeta potential and performing stabilization tests and rheological measurements. The dispersant, found to exhibit the most desirable properties, was then used in the gelcasting process as a novel and attractive means of obtaining high-quality Ti$_3$SiC$_2$ materials with a complex-shape without the addition of pressure. Furthermore, the utility of a glycerol derivative as a low-toxicity, water-soluble monomer in the fabrication of Ti$_3$SiC$_2$ by gelcasting was examined. Our measurements showed that polyelectrolytes such as polyethyleneimine, polycarboxylic acid and ammonium polyacrylate have a positive effect on the deflocculation and stabilization of Ti$_3$SiC$_2$ ceramic suspensions. Nevertheless, only ammonium polyacrylate effectively stabilizes the Ti$_3$SiC$_2$ slurry in the gelcasting process. Using ammonium polyacrylate, it was possible to obtain both high solid loading of approximately 60 vol% and a low-viscosity suspension. Using a suitable monomer and dispersant, the green bodies with a high density (62% of the theoretical density) were obtained, which resulted in ceramic part with high mechanical strength. The tensile strength of the green bodies was approximately 1.5 MPa.

Key-words : Ti$_3$SiC$_2$, MAX phase, Deflocculation, Stabilization, Dispersant, Gelcasting

1. Introduction

Ti$_3$SiC$_2$ belongs to the group of materials with the MAX phase, which are layered materials with the general formula M$_{n+1}$AX$_n$, where M is an early transition metal, A is normally from the IIIA and IVA groups, X is carbon and/or nitrogen and $n = 1, 2$ or 3. Figure 1 shows the layer structure of Ti$_3$SiC$_2$.1)

Although, the term “MAX phase” has been used since the late 1990s, Barsoum and El-Raghy’s2) report in 1996 on the synthesis of pure-phase bulk Ti$_3$SiC$_2$ samples with unusual combinations of metal and ceramic properties catalyzed the new approach to this material. Ti$_3$SiC$_2$ has a relatively low thermal expansion coefficient, is elastically stiff, has good thermal and electrical conductivities superior to those of titanium metal and high resistance to chemical attack. Moreover, it shows metal-like properties. Ti$_3$SiC$_2$ is also relatively soft and readily machinable, and exhibits thermal shock resistance and damage tolerance.3)-5)

These excellent properties in addition to high-temperature stability and exceptional oxidation resistance make Ti$_3$SiC$_2$ attractive for high-temperature applications. Moreover, the unusual ceramic-metal properties of this material also make it suitable for both mechanical and electrical applications, such as sputtering targets for electrical contact deposition or electrodes for electrochemical chlorine production.6)

In the literature few methods for the fabrication and colloidal processing of MAX-phase materials can be found. Hu et al. obtained textured Ti$_3$SiC$_2$ with enhanced thermal, electrical and mechanical properties by slip casting followed by spark plasma sintering.7)-10) On the other hand, Mishra et al. fabricated Ti$_3$SiC$_2$ by electrophoretic deposition.11) Although both methods allow the fabrication of dense samples with high mechanical strength, they have the disadvantage of requiring a high temperature and/or pressure.12),13) Moreover, only samples with simple shapes can be obtained. An attractive, alternative method to slip casting and electrophoretic deposition that will enable the formation of high-quality, complex-shaped ceramic elements may be gelcasting. Gelcasting is a forming method, in which in situ polymerization is used to fabricate ceramic parts. In this process a green body can be obtained by mixing a ceramic powder, organic monomer,
dispersant and water. Then an activator and an initiator of polymerization are added and the as-prepared slurry is poured into a mold of the desired shape, in which polymerization begins. After consolidation the gel-like material is removed from the mold and dried. Then the polymer and other organics are burned out and the obtained sample is sintered. The organic monomer plays a crucial role in the process and should be selected to realize a gel-like material with high mechanical strength. The main advantage of gelcasting over slip casting and electrophoretic deposition is that a uniform structure can be obtained.\(^{15-16}\) In addition, samples with high density and mechanical strength can be obtain after sintering without applying pressure techniques.\(^{17-20}\) In gelcasting as in other forming methods based on colloidal processing the high quality of the sintered material mainly depend on the good deflocculation and stabilization of the ceramic suspension. Although, a few methods for the fabrication of Ti\(_3\)SiC\(_2\) have been reported no previous studies have focused on the selection of a suitable dispersant, particularly for the gelcasting process.

The aim of the work was to investigate the deflocculation and stabilization of Ti\(_3\)SiC\(_2\) ceramic powder as a crucial stage in obtaining ceramics with a uniform structure by the gelcasting method. The zeta potential, and the results of stabilization tests and rheological measurements of five dispersing agents were examined. The most promising dispersant was then used in the gelcasting process of Ti\(_3\)SiC\(_2\).

2. Experimental procedure

Ti\(_3\)SiC\(_2\) powder was prepared by mixing Ti, Si and C with a molar ratio of 3Ti/1.2Si/2C in a polypropylene bottle for 12 h. The prepared mixture was then calcined at 1500°C with a heating rate of 20°C/min in Ar atmosphere. To obtain a good dispersion of ceramic particles, the powder was then ball-milled in ethanol solvent for 24 h using a planetary mill machine (Planetary Mono Mill Pulverisette 6, Fritsch GmbH, Germany) with a speed 180 rpm. After drying in air, the powder was sieved with a 100-mesh screen. The average particle size of the as-synthesized powder was >5 μm. Ball milling for 24 h decreased the average particle size to 0.5 μm, making the powder more suitable for colloidal processing. The phase purity was 97% (~3% TiC). The density of the powder was 4.53 g/cm\(^3\) as measured on an AccuPyc II 1340 pycnometer (Micromeritics, USA). The phase analysis, microstructural characterization and particle size distribution are described elsewhere.\(^{21}\)

To investigate the effect of the dispersant on the deflocculation and stabilization of Ti\(_3\)SiC\(_2\) ceramic powder, five different dispersants were examined. The choice of dispersants was dictated by the deflocculation and stabilization of ceramic powders such as Ti\(_3\)SiC\(_2\) and SiC reported in the literature and dispersants commonly used in the gelcasting process.\(^{22-26}\) Table 1 gives the characteristics of these materials.

| dispersant | Appearance | Structural formula | Producer |
|------------|------------|--------------------|----------|
| Diammonium hydrogen citrate (DAC) | Solid | ![DAC formula](image) | Sigma-Aldrich |
| Citric acid (CA) | Solid | ![CA formula](image) | Sigma-Aldrich |
| Polyethyleneimine (PEI) | 50% water solution | ![PEI formula](image) | Wako Pure Chemical Industries Ltd. |
| Ammonium polyacrylate (A-6114) | 40% water solution | ![A-6114 formula](image) | TOAGOSEI |
| Polycarboxilic acid (D-735) | 30% water solution | ![D-735 formula](image) | CHUKYO YUSHI CO., LTD. |

Diammonium hydrogen citrate (DAC) and citric acid (CA) belong to the group of dispersants, that stabilize a suspension by the creation of a sufficiently large charge on the surface of colloidal particles, which provides a sufficient force to induce a repulsive electrostatic interaction (electrostatic stabilization). Therefore, the interpenetration of electric double layers leads to their mutual repulsions, as a region with a higher concentration of ions with the same sign is generated.

The remaining dispersants belong to the group of polyelectrolytes containing functional groups that are likely to ionize in an aqueous solution. In this case, the dispersion and stabilization of the suspension can result from the chemical and/or physical adsorption on the surface of ceramic particles comprising macromolecules (polymers) situated in the colloidal suspension. A steric surface is created, which prevents particle agglomeration (electrosteric stabilization). The adsorption and conformation of polyelectrolytes can be controlled via the pH of the suspension. At a low pH (ionization degree $\alpha \rightarrow 0$), anionic polyelectrolytes are adsorbed on particles creating a dense polymeric layer with low thickness. The increase in the ionization degree (ionization degree $\alpha \rightarrow 1$) of the polyelectrolyte with increasing pH results in the mutual repulsion of the ionized groups and the polymer develops the conformation of an open coil.

After the selection of a suitable dispersant Ti\(_3\)SiC\(_2\) green bodies were fabricated by the gelcasting method. Water was used as the solvent for the ceramic powder and the dispersant and monomer were mixed together using magnetic stirrer for 6 h. Then, a vacuum pump was used for 10 min to remove air from the slurry. Next, the activator and the initiator of polymerization were added. The as-prepared suspension was then placed in PVC molds of diameter 20 mm, in which it in situ polymerization began. The polymer obtained by the in situ polymerization of the monomer...
A major advantage of glycerol monoacrylate over to commercial monomers such as acrylamide and 2-hydroxyethyl acrylate is its low toxicity. Moreover, owing to the presence of two hydroxyl groups and its ability to form of physically cross-linked structures, high-quality ceramics can be obtained without the addition of an external cross-linking agent to the ceramic slurry.\(^\text{20,28,29}\) Ammonium persulfate (98\%, Sigma-Aldrich) and tetramethyl-ethylenediamine (TEMED, 98\%, Fluka) were used as the initiator and activator of the polymerization, respectively.

The deflocculation and stabilization of Ti\(_3\)SiC\(_2\) were examined by zeta potential measurements, pH measurements, sedimentation tests and rheological measurements.

The zeta potential measurements were performed on a Zetasizer Nano ZS (UK). To prepare samples for zeta potential measurements, the ceramic powder, water and suitable amount of the dispersant were mixed together in the casting mold. After gelation, the green body was removed from the mold and dried. In this study, the glycerol monoacrylate was used as an organic monomer, which was synthesized by the authors in one-step reaction from acrylic acid and glycidol. This monomer exists as two isomers, 1,3-dihydroxypropyl acrylate and 2,3-dihydroxypropyl acrylate, with a weight ratio of 70:30. The synthesis reaction is presented in Fig. 2. Details of the synthesis are given elsewhere.\(^\text{27}\)

Figure 3 shows the zeta potential as a function of pH for the Ti\(_3\)SiC\(_2\) ceramic powder. The isoelectric point of Ti\(_3\)SiC\(_2\) was observed at a pH of 7.12. Good dispersion and consequently, stabilization of the suspension can be achieved when the absolute value of the zeta potential is exceed 20 mV.\(^\text{30}\) From our data it can be seen that the Ti\(_3\)SiC\(_2\) ceramic powder exhibits a wide range of pH (pH < 5 and pH > 8) in which the suspension is characterized as having a good dispersion of the powder.

Next, the effect of the five dispersants on the dispersion and stabilization of suspensions, based on Ti\(_3\)SiC\(_2\) was investigated. First, the effect of the DAC and CA was examined (Fig. 4). It was found that the application of DAC to the ceramic powder shifted the isoelectric point from 7.12 to 3.7. The addition of DAC also affected the range of pH, in which the slurry exhibited good dispersion and stabilization. It was shown that the addition of DAC to the powder significantly increased the zeta potential at a higher pH, which had a positive effect on the dispersion and stabilization of the suspension. The addition of CA to the Ti\(_3\)SiC\(_2\) solution did not significantly change the isoelectric point and the IEP was observed at pH 6.5. The measurements also showed that CA had a negative effect on the double layer of ceramic particles at a lower pH indicating a decreased zeta potential. However, at some pH values the absolute value of the zeta potential exceeded 20 mV; the Ti\(_3\)SiC\(_2\) slurries with CA exhibited low dispersion at a lower pH indicating a decreased zeta potential. However, at some pH values the absolute value of the zeta potential exceeded 20 mV; the Ti\(_3\)SiC\(_2\) slurries with CA exhibited low dispersion and stabilization at 4 < pH < 7.5.

Next, the effect of the polyelectrolytes polyethyleneimine (PEI), ammonium polyacrylate (A-6114) and polycarboxylic acid was investigated (Fig. 5). Figure 5(a) shows the zeta potential of Ti\(_3\)SiC\(_2\) with different amounts of PEI from 0.5 to 2.0 wt\%. It was shown that the addition of even a small amount of PEI significantly shifted the IEP of the slurry from 7.12 to 10.7 for 0.5 wt\% PEI. The slurry exhibited a wide range of pH (pH < 9), in which the zeta potential exceeded 20 mV. The highest zeta potential of 40 mV was observed at a pH of less than 5.5. Each 0.5 wt\% of PEI added to the suspension increased the maximum value of the zeta potential. The addition of 1.0 and 1.5 wt\% PEI increased the zeta potential of Ti\(_3\)SiC\(_2\) as a function of pH.
potential to 50 mV. In this case, the IEP was observed at pH 10. The addition of 2.0 wt% PEI shifted the IEP to a pH of approximately 13. Although the maximum value of the zeta potential did not change, the range of pH, in which the suspension exhibited good dispersion and stabilization widened. Figure 5(b) shows the effect of polycarboxylic acid (D-735) on the zeta potential of the Ti₃SiC₂ ceramic suspension. The application of 0.5 wt% polycarboxylic acid did not significantly change the isoelectric point of the suspension (IEP = 6.9). However, the pH range, in which the suspension was stable became wider. In this case, to stabilize the suspension, a pH lower than 6.7 or higher than 7.5 had to be applied. The addition of a greater amount of D-735 resulted in the IEP shifting to a lower pH. The isoelectric points for the addition of 1.0, 1.5 and 2.0 wt% polycarboxylic acid were 6.0, 5.2 and 4.5, respectively. Although, the addition of 1.0 wt% D-735 result in a narrow range of pH, in which the zeta potential exceeded 20 mV (4.5 < pH and pH > 8.0), the addition of 1.5 and 2.0 wt% D-735 had a positive effect on the stabilization of the suspension. By adding 1.5 and 2.0 wt% D-735 a zeta potential of ~45 mV, at pH = 8 can be achieved. The results for the addition of A-6114 are shown in Fig. 5(c). The application of A-6114 shifted the isoelectric point to considerably lower pH. The isoelectric points for the addition of 1.0, 1.5 and 2.0 wt% of the dispersant exhibited excellent
dispersion and stabilization, when the slurry had a pH of higher than 6 and the absolute value of the zeta potential exceeded 30 mV. The best results were observed when 1.5 and 2.0 wt% of A-6114 were applied, which gave the absolute values of the zeta potential of approximately 50 mV at a pH higher than 6.

3.1.2 Sedimentation tests of DAC and CA

In accordance with the result of the zeta potential measurements, sedimentation tests were performed on the slurries containing DAC and CA to optimize the composition of the slurries with these dispersants. The DAC and CA contents was varied from 0 to 0.5 wt% with respect to the ceramic powder. First, the effect of DAC was examined. The measurements showed that the application of DAC made it possible to increase the pH of the suspension from 7.8 to 9.0; however, the sedimentation of the ceramic particles in the slurry could still be observed. This result was not in agreement with the zeta potential measurements, which implied that slurries with a pH higher than 5 exhibit good stabilization of the suspension. This can possibly be explained by the low concentration of the powder, which results in an increase in the distance between particles, affecting the interaction between them. Nevertheless, the addition of DAC decreased the viscosity of the slurry. Next, the effect of CA on the sedimentation and pH of the suspension was investigated. The application of 0.5 wt% CA had a positive effect on the stability of the dispersion, although a suspension with low sedimentation was still observed. The pH of the slurry was 3.0. The addition of CA also affected the viscosity of the slurry; the viscosity increased with increasing dispersant content.

In an attempt to stabilize the suspension the DAC and CA contents were varied from 0 to 0.5 wt% with respect to the ceramic powder. It was found that regardless of the amount of DAC or CA, the sedimentation of the suspension was observed. The coupling of Ti$_3$SiC$_2$ particles with CA and/or DAC did not affect the stabilization of the suspension as expected. Thus, DAC and CA were not used in the subsequent investigation.

3.1.3 Optimization of the dispersant content

In the fabrication of dense ceramics with a complex shape, not only high solid loading, stability and good dispersion but also low viscosity of the suspension is required. Therefore, the viscosity was investigated as a function of the speed of the suspension with different amounts of PEI, D-735 and A-6114 (Fig. 6).

All three dispersants had a positive effect on the rheological properties of the Ti$_3$SiC$_2$ suspensions and considerably decreases their viscosity. The lowest viscosity was obtain using D-735. Figure 6(a) shows the results, using of PEI as a dispersant, for which a favorable viscosity was achieved when 1.5 wt% PEI was applied. The viscosity at a speed of the 400 rpm for a suspension with 1.5 wt% PEI was 56 mPa·s. The suspensions with 1.0 and 2.0 wt% of the dispersant had higher viscosities of 80 and 175 mPa·s, respectively. Figure 6(b) shows the effect of A-6114 on the rheological properties of suspensions based on Ti$_3$SiC$_2$. The lowest viscosity occurred for the slurry containing 1.0 wt% A-6114. The viscosity of the suspension with 1.0 wt% A-6114 at a speed of 400 rpm was 48 mPa·s, more than 17 times lower than that for the suspension without the dispersant. The application of 0.5, 1.5 or 2.0 wt% A-6114 gave almost the same results, although the viscosities were slightly higher [Fig. 6(c)]. Slurries with D-735 exhibited the lowest viscosities, although the ob-

![Fig. 6. Viscosity of Ti$_3$SiC$_2$ containing a) PEI, b) A-6114, c) D-735 as a function of speed. Solid loading: 10 vol%.]
obtained results were comparable to those for the with addition of A-61114. The lowest viscosity was observed when 0.5 and 1.5 wt% D-735 were applied, for which the viscosity at a speed of 400 rpm was approximately 37 mPa·s.

From the zeta potential, rheological measurements and the stabilization test, it can be concluded that to prepare high-quality Ti$_3$SiC$_2$ ceramics 1.5 wt% PEI, D-735 or A-6114 should be used. All the resulting suspensions were characterized by a low viscosity and good stabilization of the suspension. In contrast, DAC and CA did not stabilize the Ti$_3$SiC$_2$ suspension.

3.2 Gelcasting process

3.2.1 Zeta potential

Figure 7 shows the zeta potential of Ti$_3$SiC$_2$ with the glycerol monoacrylate monomer and with the TEMED activator. The application of glycerol monoacrylate shifted the isoelectric point of the slurry from pH 7.12 to 5.8. The addition of TEMED also affected the zeta potential by shifting the isoelectric point to pH 7.8, and also had a positive effect on the stability of the suspension.

Figure 8 shows the zeta potential of the slurries with both the monomer and the activator containing 1.5 wt% polyethyleneimine, 1.5 wt% polycarboxylic acid or 1.5 wt% ammonium polyacrylate. It was found that the zeta potential curves of the slurries with both the monomer and activator containing 1.5 wt% polyethyleneimine and 1.5 wt% polycarboxylic acid were significantly different from those of Ti$_3$SiC$_2$ with 1.5 wt% of the corresponding dispersants. The measurements showed that the addition of both polyethyleneimine and polycarboxylic acid resulted in suspensions with low stability. Therefore, to fabricate Ti$_3$SiC$_2$ samples with high homogeneity it is better to use ammonium polyacrylate, which exhibited excellent stability over a wide range of pH. In the case of the slurry with A-6114, the addition of the monomer and activator only increased the ranges of the zeta potential and pH, in which the suspension exhibited stability. From the results of these rheological and zeta potential measurements the composition presented in Table 2 was chosen to further investigation.

3.2.2 Effect of solid loading

Figure 9 shows the influence of the volume percentage of powder on the rheological properties of the suspensions based on Ti$_3$SiC$_2$. It was shown that by applying 1.5 wt% of dispersant, it was possible to achieve as much as 60 vol% solid loading. The measurements showed that with increasing volume percentage of powder the viscosity of the suspensions increased. However, all of the slurries had sufficiently low viscosity to fill the complex mold properly. The viscosities of the suspensions with 55, 57 and 60 vol% solid loading at a speed of 350 rpm were 5.4, 87.5 and 178.9 mPa·s, respectively.

3.2.3 Characterization of the green bodies

Figure 10 shows a SEM image of a Ti$_3$SiC$_2$ green body containing 60 vol% of powder, 5 wt% of monomer and 1.5 wt% of dispersant. The image shows a uniform distribution of the polymeric binder around the ceramic particles, which indicates good wettability of the glycerol monoacrylate and the adhesion of the polymeric binder to the ceramic powder. Polymeric bridges between individual powder particles were also observed. The polymeric bridges were obtained owing to the formation of hydrogen bonds between the numerous –OH groups in the polymeric structure. This indicates that a three-dimensional network

Table 2. Composition of slurry used in gelcasting (wrp- with respect to powder, wrm- with respect to monomer)

| Component       | wt%   |
|-----------------|-------|
| Powder Ti$_3$SiC$_2$ | 84.7–87.2 (55–60% vol) |
| Monomer         | Glycerol monoacrylate | 5.0 (wrp) |
| Dispersant      | A-6114             | 1.5 (wrp) |
| Activator       | TEMED              | 2.0 (wrm)  |
| Initiator       | (NH$_4$)$_2$S$_2$O$_8$ | 1.0 (wrm)  |

Fig. 7. Zeta potential of Ti$_3$SiC$_2$, with the glycerol monoacrylate monomer and with the TEMED activator as a function of pH.

Fig. 8. Zeta potential of slurry with both the monomer and activator and 1.5 wt% polyethyleneimine (PEI), 1.5 wt% polycarboxylic acid (D-735), or 1.5 wt% ammonium polycarboxylate (A-6114).

Fig. 9. Effect of solid loading on rheological properties of Ti$_3$SiC$_2$ suspensions.
between the particles can be obtained without the use of an external cross-linking agent. This increases the mechanical strength of the green body. This is important in that it allows the amount of organic components in the ceramic slurry to be decreased. Table 3 shows the density and tensile strength of the green bodies with 55, 57 and 60 vol% of powder. It was observed that the application high solid loading resulted in green bodies with high density and tensile strength. The density of the samples increased with increasing volume percentage of ceramic powder. All the samples had a density of 58–62% of the theoretical density. High solid loading also affected the tensile strength of the green bodies; the tensile strength of the samples increased with increasing solid loading of the powder. The tensile strengths of the samples containing 55, 57 and 60 vol% of powder were 1.1, 1.3 and 1.5 MPa, respectively. The measurements showed that the obtained mechanical strength was sufficient to produce samples without any exfoliation. Moreover, samples with a complex shape could be obtained (Fig. 11). Investigation of the mechanical strength of the samples is very important owing to the fact that only specimens with high strength can be subjected to polishing and transportation.

4. Conclusions

In this work, the deflocculation and stabilization of Ti3SiC2 ceramic powder were investigated by performing rheological, zeta potential and pH measurements. Five different dispersants di ammonium hydrogen citrate, citric acid, polyethyleneimine, polyacrylic acid and ammonium polyacrylate were examined. The application of poly electrolytes such as polyethyleneimine, polyacrylic acid and ammonium polyacrylate stabilized the Ti3SiC2 suspension. Moreover, low viscosity and high solid loading (60 vol%) could be obtained. Ammonium polyacrylate (A-6114) was found to be the best dispersant for obtaining high-quality Ti3SiC2 ceramics prepared by gelcasting. Optimization of the composition of the Ti3SiC2 ceramic suspension allowed durable specimens with a complex shape to be obtained without using a pressure-driven technique. The monomer used in this process had an important role. It was shown that glycerol monoacrylate produced green bodies with high mechanical strength (1.5 ± 0.1 MPa) without the use of a cross-linking agent and allowed the amount of organic components in the ceramic slurry to be decreased.

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References

1) M. Barsoum and T. El-Raghy, *Am. Sci.*, 89, 334–343 (2001).
2) M. W. Barsoum and T. El-Raghy, *J. Am. Ceram. Soc.*, 79, 1953–1956 (1996).
3) Z. M. Sun, *Int. Mater. Rev.*, 56, 143–166 (2011).
4) P. Eklund, M. Beckers, U. Jansson, H. Högborg and L. Hultman, *Thin Solid Films*, 518, 1851–1878 (2010).
5) Z. Sun and Y. Zhou, *Phys. Rev. B*, 60, 1441–1443 (1999).
6) V. D. Jovic and M. W. Barsoum, U.S. Pat. No. 7,001,494.
7) C. Hu, Y. Sakka, S. Grasso, T. Nishimura, S. Guo and H. Tanaka, *Scr. Mater.*, 64, 765–768 (2011).
8) C. Hu, Y. Sakka, S. Grasso, T. Suzuki and H. Tanaka, *J. Am. Ceram. Soc.*, 94, 742–748 (2011).
9) C. Hu, Y. Sakka, T. Nishimura, S. Guo, S. Grasso and H. Tanaka, *Sci. Technol. Adv. Mater.*, 12, 044603 (2011).
10) C. Hu, Y. Sakka, H. Tanaka, T. Nishimura and S. Grasso, *J. Am. Ceram. Soc.*, 94, 410–415 (2011).
11) M. Mishra, Y. Sakka, C. Hu, T. Suzuki, T. Uchikoshi and L. Besra, *J. Am. Ceram. Soc.*, 95, 2857–2862 (2012).
12) K. Sato, M. Mishra, H. Hirano, C. Hu and Y. Sakka, *J. Am. Ceram. Soc.*, 97, 1407–1412 (2014).
13) K. Sato, M. Mishra, H. Hirano, T. S. Suzuki and Y. Sakka, *J. Ceram. Soc. Japan*, 122, 817–821 (2014).
14) A. Szudarska, T. Mizerski, Y. Sakka, T. S. Suzuki and M. Szafran, *J. Eur. Ceram. Soc.*, 34, 3841–3848 (2014).
15) P. Falkowski, P. Bednarek, A. Danelaks, T. Mizerski and M. Szafran, *J. Eur. Ceram. Soc.*, 30, 2805–2811 (2010).
16) P. Wieczinska, T. Mizerski and M. Szafran, *Carbohydr. Polym.*, 111, 610–618 (2014).
17) P. Wieczinska, Y. Sakka, T. S. Suzuki, T. Uchikoshi, T. Mizerski and M. Szafran, *J. Eur. Ceram. Soc.*, 30, 1975–1981 (2010).
19) A. Szudarska, M. Szafran and T. Mizerski, *Arch. Metall. Mater.*, 56, 1211–1215 (2011).
20) A. Idzkowska, P. Wiecinska and M. Szafran, *Ceram. Int.*, 40, 13289–13298 (2014).
21) M. Mishra, Y. Sakka, T. Uchikoshi and L. Besra, *J. Ceram. Soc. Japan*, 121, 348–354 (2013).
22) M. Mishra, Y. Sakka, A. Szudarska, M. Szafran, T. S. Suzuki and T. Uchikoshi, *J. Ceram. Soc. Japan*, 120, 544–547 (2012).
23) X. H. Wang and Y. Hirata, *Ceram. Int.*, 1, 677–681 (2005).
24) B. P. Singh, J. Jena, L. Besra and S. Bhattacharjee, *J. Nanopart. Res.*, 9, 797–806 (2007).
25) M. Szafran, P. Wiecinska, A. Szudarska and T. Mizerski, *J. Aust. Ceram. Soc.*, 49, 1–6 (2013).
26) A. Szudarska, D. Guryniuk, T. Mizerski and M. Szafran, *Arch. Metall. Mater.*, 58, 1299–1303 (2013).
27) C. Tallón, R. Moreno, M. I. Nieto, D. Jach, G. Rokicki and M. Szafran, *J. Am. Ceram. Soc.*, 90, 1386–1393 (2007).
28) C. Tallon, D. Jach, R. Moreno, M. I. Nieto, G. Rokicki and M. Szafran, *J. Eur. Ceram. Soc.*, 29, 875–880 (2009).
29) M. Szafran, A. Szudarska and P. Bednarek, *Adv. in Sci. & Tech.*, 62, 163–168 (2010).
30) S. Vallar, D. Houivet, J. El Fallah, D. Kervadec and J. M. Haussonne, *J. Eur. Ceram. Soc.*, 19, 1017–1021 (1999).