Rapid solidification of frits

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Abstract

By using the technology of rapid solidification, frits were obtained in their powder form directly from the molten state. To determine the properties of these materials, a comparison was made to the normally produced powder forms of frits, manufactured by grinding. Differential scanning calorimetry (DSC), hot stage microscope (HSM), dilatometry, scanning electron microscopy (SEM) and particle size analysis were employed to establish the differences between the two, differently acquired, materials. The results showed that the rapidly solidified powders, compared to the normal ones, had higher glass transition temperatures (T_g) and matching coefficients of the linear thermal expansion (α). Nevertheless, their particle size and morphology was found to be different which was expected due to the different procedure employed; rapid solidification with water atomization. In the end it was established that the new technology for frit production could be utilized in the enamel industry to directly produce frits in their powder forms, hence the production electrostatic powders is attainable in a very simple way. Significant reduction of the energy, time and labor is thus achievable.

Introduction

An ongoing trend in the enamel industry has been the usage of "pre–worked" enamels like RTU and RTM [1]. One of the main stages in the production of such enamels is the phase of grinding, as the material has to be prepared to the specific requirements of the customer [2]. As milling is a high energy and labor process and our company Emo Frite being a large producer of powder enamels, we have been researching for the method to produce powders of frits directly from the molten state. Therefore, in this work we are presenting the possibility of usage the rapid solidification technology called water atomization for the production of powder frits [3-5].

Methods/Discussion

Figure 1 represents the water atomization set-up. The process transforms the melt into fine droplets that solidify and form the micron-sized powder. The breakup of the melt stream is accomplished using water at high-pressure where high kinetic energy of the water impacts the melt stream and instantaneously disintegrates it into fine particles.

Two compositional different frits (A and B) were atomized in this study (Table 1). For each experiment the raw materials in their powder forms were carefully weighted, mixed together and then smelted. When the melting was done the melt was poured into the "tundish" (a preheated crucible with an opening in the bottom, Figure 1) from where it flowed in a steady and evenly stream to the atomization chamber. Melt was then atomized and powder was formed. Atomized powders were furthermore compared to the non–atomized ones and their properties evaluated. Additionally, the non-atomized frits were prepared using the established procedure of melting in a rotary type smelter and then milled using ball mills.

The particle size of the powders was determined with sieving and their morphologies were evaluated using a scanning electron microscope (SEM) Sirion 400 NC. Sieve sizes from 1000 to 45 µm were used. Thermal properties of the powders were determined with differential scanning calorimetry (DSC Mettler Toledo type 1), hot stage microscopy (Leitzch HSM) and dilatometry (Nietzsch dilatometer type 402 EP). The heating rate was in all cases 10 °C/min.

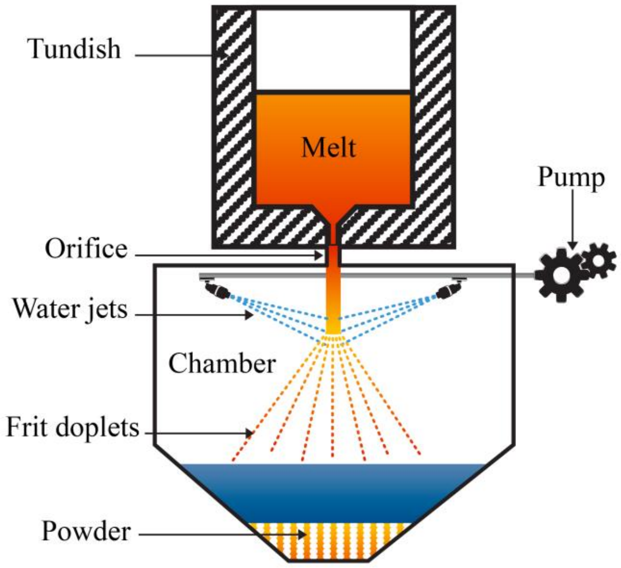

Figure 1: Water atomization system.

Table 1: Compositions of studied frits (wt. %).

Frit	A	B
SiO_2	37.63	23.53
B_2O_3	21.19	52.50
Na_2O	16.41	23.97
CaO	8.46	
Al_2O_3	5.18	
K_2O	3.14	
BaO	2.31	
Fe_2O_3	1.69	
MnO	1.13	
CoO	0.93	
P_2O_5	0.93	
Sb_2O_3	0.51	
CuO	0.51	

Results

Figure 2 shows the particle sizes of the produced powders. It can be seen that the particle sizes between the atomized (A1 and B1) and the non–atomized (A2 and B2) frits are very much different. Both frits that were atomized had larger particles compared to the non–atomized ones. However, when we compare the samples between each other we have to take into the account that the frits that were atomized were directly transformed into powder, whereas the non–atomized frits were grinded for, t = (3–5) h in order to achieve their final prescribed distributions seen in Figure 2. This is not just easier and quicker but also more energy and labor effective, as the need for the grinding phase could be completely avoided. Furthermore, as frits A and B are compositional very different (Table 1) the viscosity of the melt for frit B was due to a higher amount of fluxes lower than for frit A. This had a direct effect on the particle size of the atomized powders since a more viscous melt was not disintegrated by high-pressure water stream into a wide range of particles very easily.

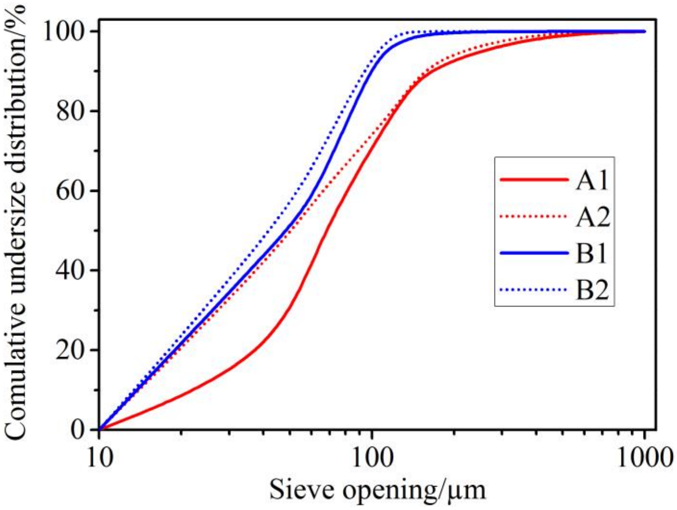

Figure 2: Particle sizes of the powders.

The SEM pictures confirm the above statement, consequently a diverse shape particles was observed for a more viscous frit (frit A), whereas frit B displayed a uniform morphology through the sample. (Figure 3). The milled powders A2 and B2 showed a typical morphology that is known for the milled samples. Flat surfaces and sharp corners are clearly visible as the effect of the grinding procedure. However, atomized frits show a quite different formulation of the particles with predominantly spherical shape. This is much better as spherical powders have better flow properties than non-spherical ones [6, 7]. Due to the high viscous nature of frit A1, irregular particles were detected between the spheres, as a result of the obstructed disintegration of the melt. Because viscosity acts as the primary resistance to the atomization non-spherical shapes of the particles were formed when it was too high. In order to reduce this effect optimization of the process parameters e.g. temperature of the melt, pressure of the cooling media, orifice diameter etc. is proposed.

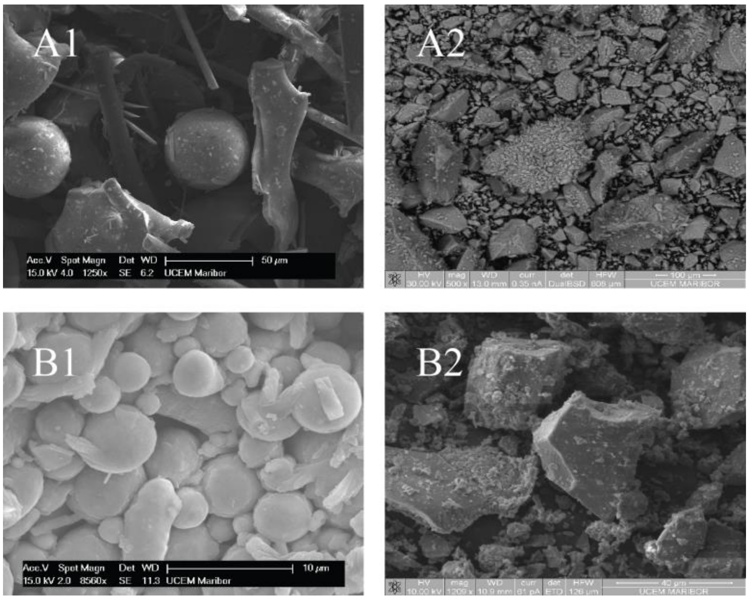

Figure 3: SEM pictures of frits A and B (1 = atomized frit, 2 = non–atomized frit)

The thermal properties of the tested frits are summarized in Table 2. From the DSC curves presented in Figure 3 it is clearly seen that both atomized frits have higher glass transition temperatures compared to the non–atomized ones. An increase in the glass transition temperature is the direct cause of the higher cooling rate achieved in atomization process. Normal cooling, without the usage of high pressure, produces a cooling rate of approximately 10^2 K/s, whereas with atomization much higher cooling rates are achievable ($v_c = (10^3–10^4)$ K/s) [8, 9]. The higher the rate of cooling the greater the glass transition temperature and vice versa [10]. Moreover, all the presented temperatures were higher for the atomized frit A (Table 2, Figures 4 and 5), opposed to the non–atomized one, while for the atomized frit B a small deviation vas found in the values determined by the HSM. This was contributed to the porosity of the two powders. From the SEM pictures of frits B1 and B2 (Figure 3), we can see that frit B1 is much more compact than frit B2. When the tablet for the HSM reading was formed the porosity was reduced the same in both cases. Therefore, the particles in frit B1 were more tightly packed together as for frit B2, hence under increasing temperature, the transformations occurred earlier for the atomized frit B1.

Table 2: Evaluated temperatures of the studied frits.

Frit	HSM				Dilatometry		DSC
	S/°C	*M*/°C	*HB*/°C	*F*/°C	T_g/°C	T_d/°C	T_g/°C
A1	550	665	715	745	482	551	667
A2	540	620	660	700	478	542	498
B1	545	610	685	740	494	543	634
B2	540	620	695	760	472	506	500

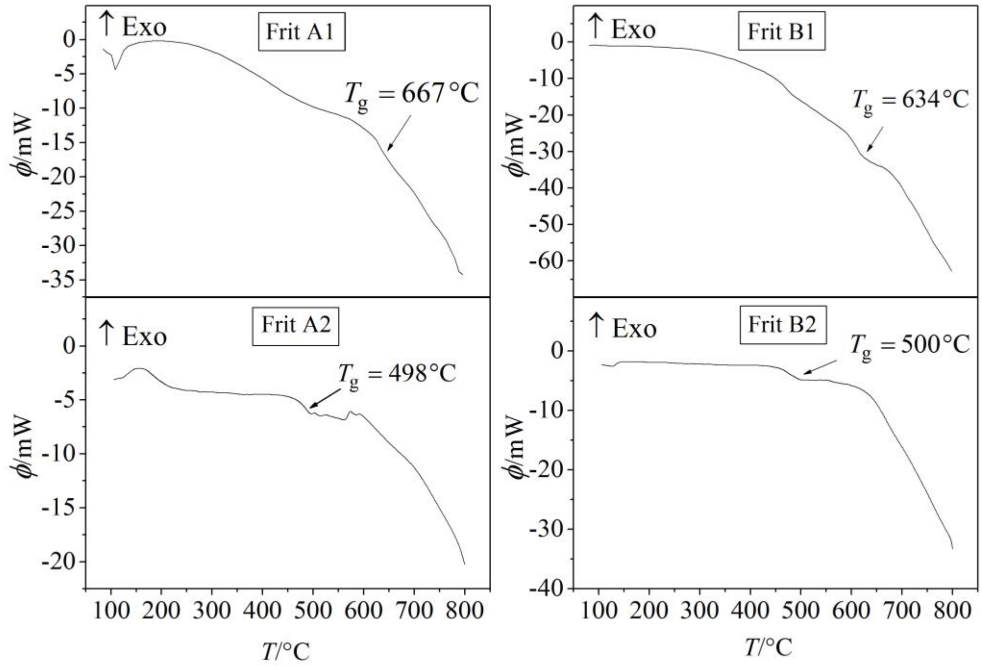

Figure 4: DSC plots of the atomized and non-atomized frits.

The dilatometric curves of the both frits show that the atomized and the non–atomized frits have identical thermal expansion coefficients in the temperature range from 20 to 400 °C. Slight deviations are observed for frit B above, T = 400 °C, but nevertheless the results are comparable between each other, thereby concluding that frits have analogous elongations under increased temperatures.

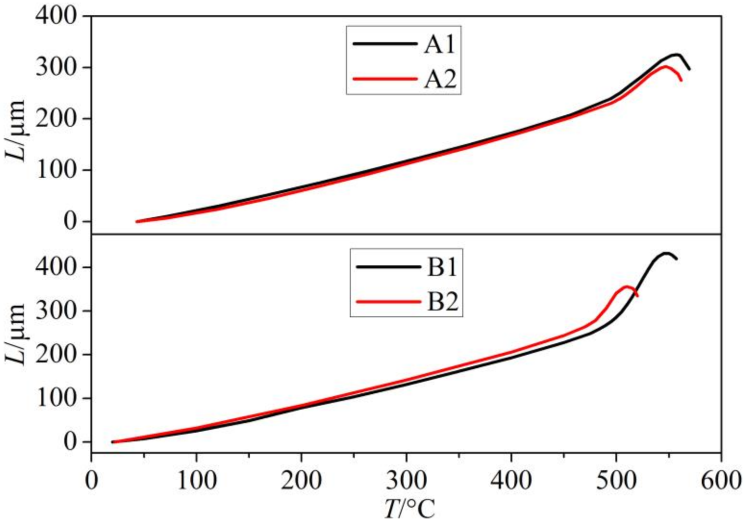

Figure 5: Dilatometric curves of the tested frits.

Lastly, to determine the possible end differences between the two differently produced powders enameled and glazed plates were formed. Frit A was enameled onto a steel surface and surface defects were evaluated (Figure 6 and 7). It was established that both frits, A1 and A2, produced the same surface, thus concluding that the newly produced frits do not alter the surface of the enameled plates. Additionally, no difference was observed between the two frits concerning the adherence, which furthermore confirms the end equality.

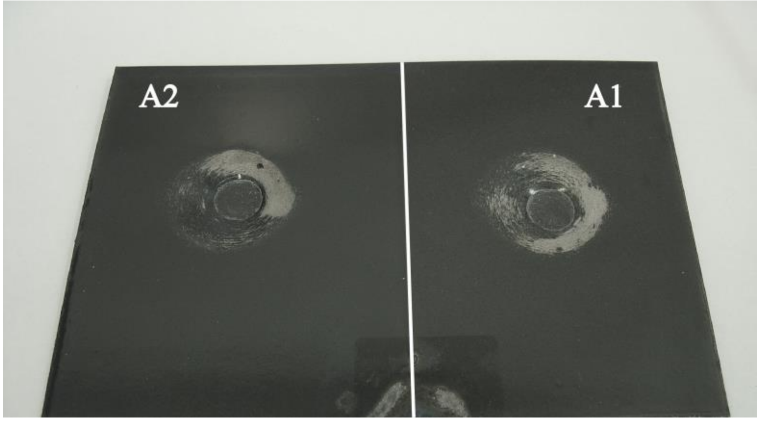

Figure 6: Frits A1 and A2 enameled onto a steel surface (wet slip application).

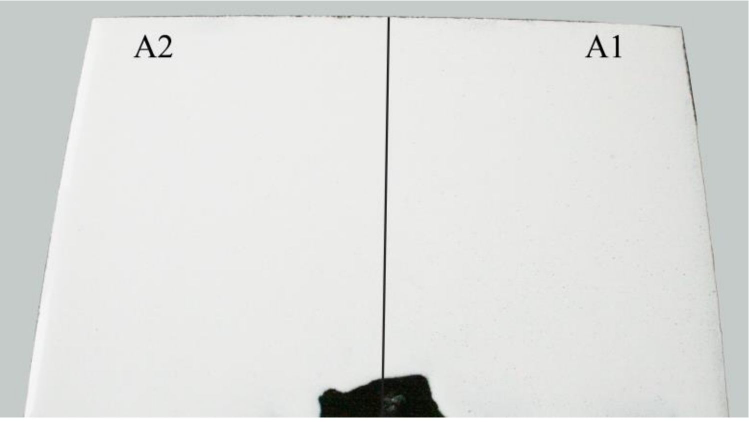

Figure 6: Frits A1 and A2 enameled onto a steel surface with the addition of the cover coat (wet slip application).

Last of all, Frit B showed the same results as frit A, hence no significant difference was detected between the two tested frits (Figure 7).

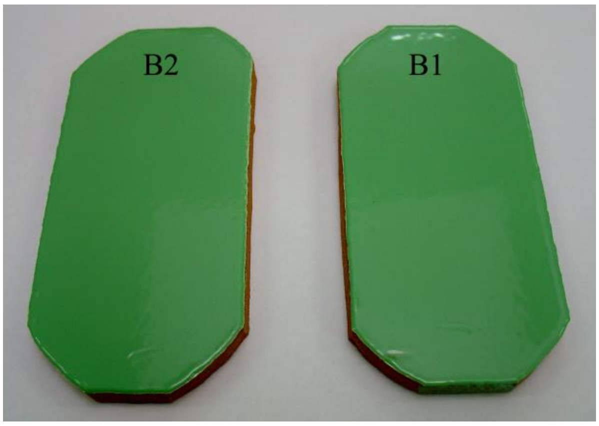

Figure 7: Test plates of frits B1 and B2.

Conclusions

Using the technology of water atomization powder frits were prepared directly from the molten state. The atomized frits were compared to the non–atomized (grinded) frits as are normally produced in the frit production process. It was found out that the atomized frits were very similar to the grinded ones with the addition of some useful differences in the morphology and thermal properties. Mostly spherical shape of the particles was observed from the SEM pictures of the atomized frits. This is clearly beneficial since spherical powders have better flow properties. Furthermore, their glass transition temperatures and temperatures of the transformations were higher, thereby increasing the stability of such products. Particle size was found to be slightly bigger compared to the grinded frits, however we have to take into the account that the atomized powders were produced directly, whereas the non–atomized frits had to be grinded for a specific amount of time to lower their particle size. Lastly, no differences were observed between the enameled or glazed plates for the atomized frits in comparison to the non–atomized (well-known) frits.

Acknowledgements and References

[1] F.A. Kuchinski, (1993), Corrosion resistant thick films by enamelling, in: J.B. Wachtman, R.A. Haber (Eds.) Ceramic Films and Coatings, Noyes Publications, pp. 77-131.

[2] A.I. Andrews, S. Pagliuca, W.D. Faust, (2010), Frit Making, in: Porcelain (vitreous) Enamels and Industrial Enamelling Processes: The Preparation, Application and Properties of Enamels, Tipografia commerciale, pp. 360-389.

[3] N. Ashgriz, (2011), Handbook of Atomization and Sprays: Theory and Applications, in, Springer, pp. 837-848.

[4] B. Zheng, E.J. Lavernia, (2011), Melt Atomization, in: N. Ashgriz (Ed.) Handbook of Atomization and Sprays: Theory and Applications, Springer, pp. 837-848.

[5] J. Hamill, C. Schade, N. Myers, (2001), Water Atomized Fine Powder Technology, Gas,80, 90.

[6] I. Tanaka, N. Suzuki, Y. Ono, M. Koishi, (1998), Fluidity of Spherical Cement and Mechanism for Creating High Fluidity, Cem. Concr. Res.,28 (1), 63-74.

[7] T. Yokoyama, (1991), Fluidity of powder, Powder technology Handbook, 127-138.

[8] B.H. Kear, (1984), Rapid Solidification Technology, in: NAE (Ed.) Cutting Edge Technologies, National Academies Press, pp. 86-108.

[9] A. Ünal, (1987), Effect of processing variables on particle size in gas atomization of rapidly solidified aluminium powders, Mater. Sci. Technol.,3 (12), 1029-1039.

[10] S.R. Elliott, (1990), The glass transition, in: Physics of amorphous materials, Longman Scientific & Technical, pp. 24-26.