

# THE USE OF WATER ATOMISATION FOR THE PRODUCTION OF FRITS

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The production of powder materials from melts is usually done by atomisation. In our research two different frits were successfully produced using water atomisation technique. An overall assessment of the powders showed that the sizes of particles and their morphologies are determined mainly by the chemical compositions of the frits and atomisation parameters. The sizes of the particles depend on the viscosities of the frits, which is governed by the melt superheating during the experimental trials, orifice diameter and interactions between droplets and particles during additional stages after primary atomisation, which were controlled by water pressure. The morphologies of the particles depend on the relationships between the times of solidification and spheroidisation and on the interactions between the particles.

*Key words:* water atomisation, microstructure, spheroidisation, frits

## INTRODUCTION

Water atomisation is known to be a very useful technique for producing the powders of various metals and alloys with uniform particle size distributions and low costs [1, 2]. The low viscosities and high surface tensions of metals enable intensive disintegration of those melts that mostly result in small, uniform and spherical particles [3]. The mechanism of disintegration is well-known and can be divided into primary and secondary atomisation. The latter is accompanied by large interactions between the formed melt drops as well as between the already solidified particles. Lowering the surface tension acts as an obstacle against spheroidisation and the drops that are formed tend to solidify into irregular particles [4]. However, the atomisation technique is much lesser used for the production of non-metallic materials such as glass and ceramics [5]. Nowadays, in practice, the atomisation of glass is mostly applied for the production of glass wool and fibres. In the case of frits that are primarily used for enamelling, where fluidity is very important, those micron-sized powders with spherical shapes of particles are the more interesting end-products [6]. Therefore, from the theoretical as well as the practical point of view the problem of usability is still open regarding high-pressure water atomisation for obtaining the spherical particles of frits.

This paper describes research work, where the possibility of applying water atomisation was checked for achieving the powders of frits. The purpose of our study

was to examine the morphologies and size distributions of particles depending on the processing parameters.

## MATERIALS AND METHODS

The experiments regarding atomisation were performed using a David Mckee atomiser type D5/2. Two different frits (A and B) with compositions as shown in Table 1 were used in the experiments.

Both frits were atomised under different pressures of cooling media and different orifice openings (Table 2).

Raw materials in powder forms were thoroughly mixed together and then smelted. Afterwards, the formed melt was poured into the atomiser's tundish. Flowing of the melt through an opening (orifice) at the bottom of the tundish [7] formed a stream that was atomised using water under high pressure.

The lengths of flow of the frits were established by the flow-test method [80] at different temperatures, and their viscosities were calculated using the equation described by Sogawa and Ozaki [9]:

$$F = 310 \cdot \eta^{-0.386} \cdot t^{0.453} \quad (1)$$

where  $F$  is the flow length of the fired frit / mm,  $t$  the time of flow length test / min and  $\eta$  the viscosity of the frit / P. Particle sizes of the powders were determined by sieving; sieve sizes from 1 000 to 45  $\mu\text{m}$  were used. A Sirion 400 NC scanning electron microscope (SEM) was employed to evaluate the morphologies of the produced powders.

## RESULTS AND DISCUSSION

The large interaction mechanism in water atomisation is the main reason why the particles consist of

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Table 1 XRF analysis of frits / mas. %

Frit	SiO <sub>2</sub>	B <sub>2</sub> O <sub>3</sub> <sup>1</sup>	Na <sub>2</sub> O	CaO	Al <sub>2</sub> O <sub>3</sub>	K <sub>2</sub> O	BaO	Fe <sub>2</sub> O <sub>3</sub>	MnO	CoO	P <sub>2</sub> O <sub>5</sub>	Sb <sub>2</sub> O <sub>3</sub>	CuO	MgO	F <sub>2</sub>
A1	33,21	24,00	20,24	7,36	4,57	2,50	1,02	1,41	0,77	0,55	0,71	0,25	0,43	0,75	1,65
A2	32,91	23,94	20,05	7,38	4,88	2,46	0,92	1,40	0,76	0,55	0,70	0,23	0,47	0,75	2,15
A3	33,40	23,66	20,68	7,07	4,96	2,45	0,88	1,41	0,74	0,53	0,76	0,22	0,49	0,70	1,59
A4	31,52	28,81	19,53	6,48	4,33	2,29	0,80	1,22	0,69	0,47	0,71	0,19	0,56	0,67	1,32
A5	30,62	27,14	20,74	7,13	4,38	2,53	0,96	1,33	0,76	0,57	0,70	0,23	0,37	0,71	1,45
B1	29,35	38,20	30,86												1,47
B2	29,84	37,90	29,54												1,68
B3	29,19	38,60	30,48												1,56

<sup>1</sup>Determined by titration

Table 2 Experimental set-up

Frit	Pressure / bar	Orifice opening / mm	Melt temperature / °C	Tundish temperature / °C
A1	215	6	1 250	1 150
A2	215	5	1 200	1 132
A3	215	4	1 276	1 126
A4	100	5	1 249	1 115
A5	50	5	1 271	1 130
B1	215	6	1 417	1 128
B2	215	5	1 324	1 117
B3	50	5	1 296	1 144

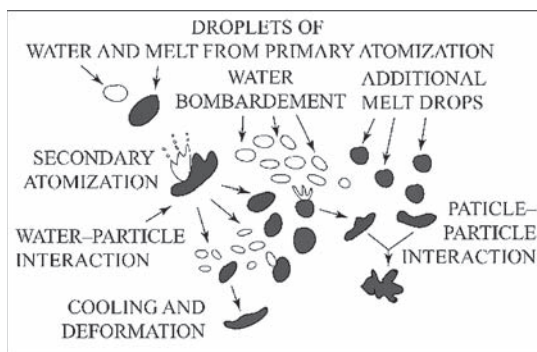


Figure 1 Stages of the atomisation process

many different forms. The process of atomisation is systematically represented in Figure 1.

During the first stage or primary atomization, the melt breaks up into droplets, which can immediately solidify and form particles. In regard to the materials with enough low viscosity, the droplets can be further transformed. They divide, change shape etc., before they achieve their end forms. Particles and droplets can undergo several impacts prior to the completion of the process, thereby altering their already-formed structures in many different ways. In the case of frits, their high viscosities already act as the main obstacle for primary atomisation. Consequently, disintegration of the melt stream is restricted. As can be seen from Table 3 and Figure 2, frit A was more viscous than frit B. This directly affected the morphologies as almost no spherical particles were observed in frit A, whilst the atomised powders of frit B contained a high degree of spheres (Figure 3).

Table 3 Results of the flow tests

Frit	Temperature / °C	Time / min	Length / mm	Viscosity / Pa·s
Frit A	800	3,00	51	38,95
	900	2,50	78	10,46
	1 000	1,33	84	4,12
	1 100	1,00	93	2,26
	1 200	1,00	107	1,57
Frit B	800	3,00	94	7,99
	900	2,50	137	2,43
	1 000	1,33	130	1,33

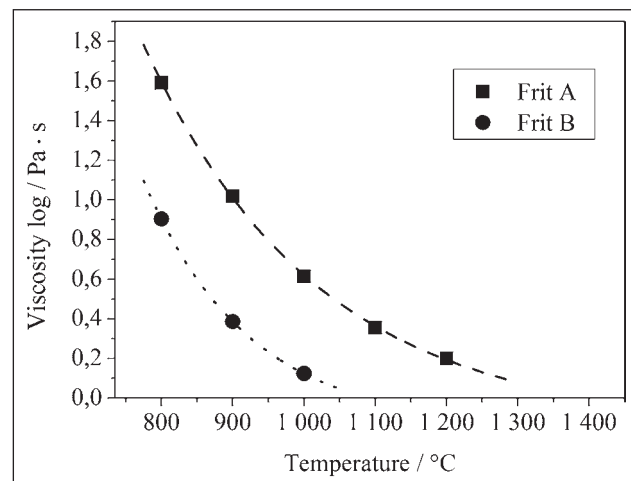


Figure 2 Viscosity curves of the two tested frits

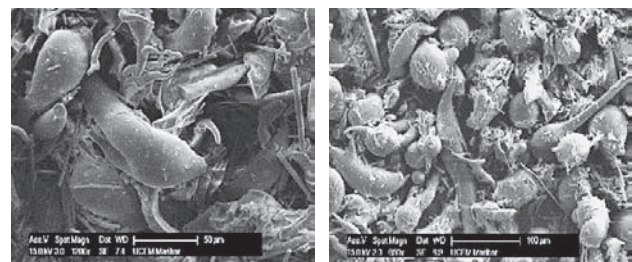


Figure 3 a) Frit A b) Frit B

The forms of the particles (spherical or irregular) are closely dependent on the times of solidification and spheroidisation. In order to elucidate which form will prevail, the theoretical times for both solidification and spheroidisation were calculated using the adequate equations. Solidification time was determined from the equation described by Nada and Nichiporenko [10]:

$$t_{\text{sol}} = \frac{d \rho_m}{6h} \left[ c_{p_m} \ln \left( \frac{T_i - T_0}{T_s - T_0} \right) + \frac{\Delta H_1}{(T_s - T_0)} \right] \quad (2)$$

where,  $d$  is the particle diameter / m,  $\rho_m$  the density of the melt / kg/m<sup>3</sup>,  $h$  heat transfer coefficient / W/m<sup>2</sup>K,  $c_{p_m}$  the specific heat of the melt / J/kgK,  $T_i$  the initial melt temperature / K,  $T_0$  the temperature of the water / K,  $T_s$  the solidus temperature / K and  $\Delta H_1$  the latent heat of fusion / J/kg. In the case of amorphous solidification, the total discharged heat during atomisation is equal to the difference of the heat content of the melt between the temperature of overheating and the glass transition temperature. Therefore, for solidification of frits, equation 2 can be transformed into:

$$t_{\text{sol}} = \frac{d \rho_m}{6h} \left[ c_{p_m} \ln \left( \frac{T_i - T_0}{T_s - T_0} \right) \right] \quad (3)$$

The equation by Nichiporenko was used for spheroidisation time [11]:

$$t_{\text{sp}} = \frac{3\pi^2 \eta_m}{4\gamma_m V} [r_1^4 - r_2^4] \quad (4)$$

where,  $\eta_m$  is the viscosity of the melt / Pa s,  $\gamma_m$  the surface tension of the melt / N/m,  $r_1$  the smallest radius of the initial non-spherical droplet / m,  $r_2$  the final radius of the sphere / m and  $V$  the volume of the droplet / m<sup>3</sup>. Figure 4 and Table 4 present the results of the calculations.

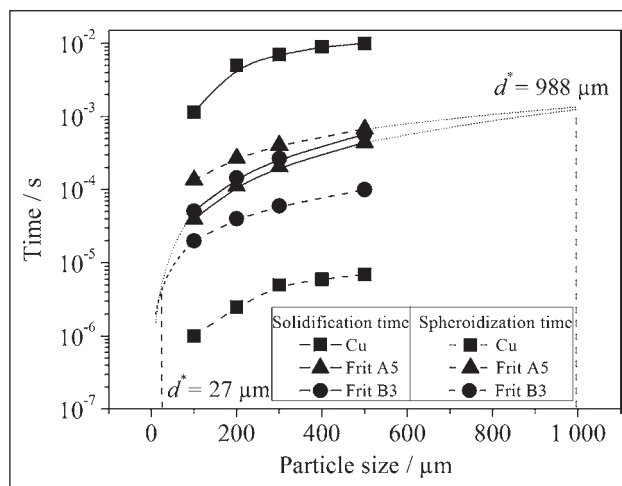


Figure 4 Solidification and spheroidisation times

The high viscosity of frit A increased the spheroidisation time so that the particles solidified before they were able to form a sphere. The ratio of  $t_{\text{sol}}/t_{\text{sp}}$  was for this case less than 1. As can be seen from Figure 4, even in test 5, where the pressure was reduced and favoured the formations of spheres, the solidification time was still too short, and irregular particles were mostly formed. For this test the critical radius had a very high value of  $d^* = 988 \mu\text{m}$ , that confirmed a tendency to irregular shapes at normally used atomisation parameters. However, for frit 2 the spheroidisation time was lower than the solidification time and spherical particles were

Table 4 Time ratios and critical radii of atomisation

Frit	$(t_{\text{sol}}/t_{\text{sp}})^1 / -$	Critical radius <sup>2</sup> / $\mu\text{m}$
A1	0,4	/
A2	0,4	/
A3	0,7	/
A4	0,5	/
A5	0,9	988
B1	5,0	28
B2	2,7	108
B3	5,1	27
Copper	1 000	/

<sup>1</sup>Calculated for size of particles up to 1 000  $\mu\text{m}$ .

<sup>2</sup>Radius at which solidification and spheroidisation times are equal.

formed (Figure 3b). In this case, the critical radius was much lower as can be seen from Table 4.

In comparison to copper, where the spheres are easily made, the values of the time ratios for frits were much smaller.

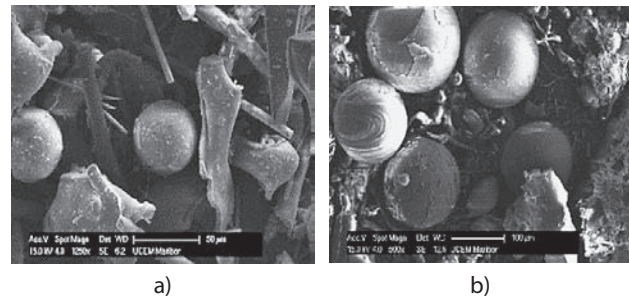


Figure 5 a) Frit A, b) Frit B

This indicated that in the case of frits we were theoretically within the zone where both times were very close. From the practical point of view, small perturbations during the atomisation process had already reversed the relationship between both times. Figure 5 confirms the above statement as the spheres were detected amongst other particles in frit A, whereas in frit B some irregular particles were still present. Lowering the pressure of the dispersed media increased the solidification time. Larger particles were formed and the degrees of interactions became greater. Because the particles were incompletely solidified at the end of primary atomisation, the secondary atomisation and interactions between them transformed and distorted the particles. Moreover, as the viscosity was reduced by increasing the melt temperature, the fluidity increased, hence the particles were very flexible before they are completely solidified.

We observed greater interactions between the particles in the case of frit B in comparison with frit A. The particles were deformed, agglomerated, broken etc., as seen in Figure 6. Thus, when the viscosities were lower the interactions were greater and vice versa. Additionally, as the frits are very brittle materials the interaction mechanism was more influential on the morphologies as in the cases of metallic materials.

Finally, the influence of viscosity on the sizes of the particles was clearly identified. The size grades for frits

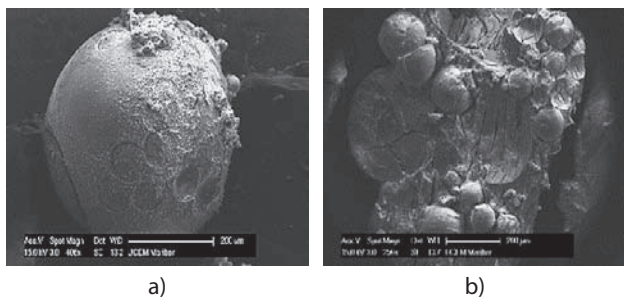


Figure 6 a) and b) Frit B

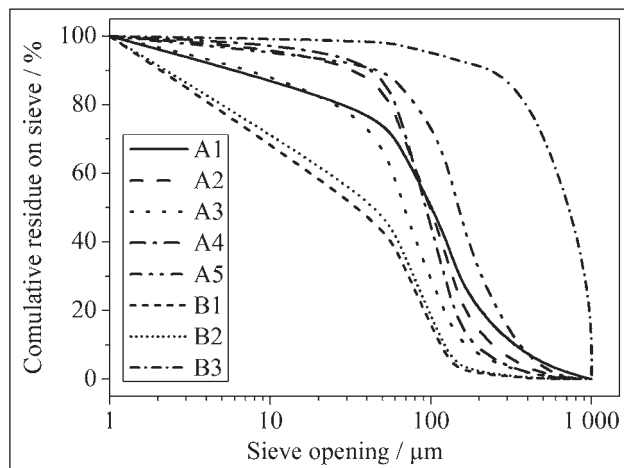


Figure 7 Particle sizes of the produced powders

B, which were atomised at much lower viscosities, were considerably lower than those for frits A (Figure 7). However, the end-sizes of the atomised particles were also influenced by the interactions of droplets and particles during additional stages after primary atomisation. Enhanced interactions and agglomeration at lower water pressure increased the sizes of the particles. This was clearly identified from tests A5 and B3, where finer particles were detected for a more viscous frit A. Additionally, the results of our research work clearly indicated that smaller orifice openings reduced the sizes of the particles.

## CONCLUSIONS

The results from this experimental work clearly confirm the opportunity for water atomisation in attaining micron-sized powders of frits. The principal conclusions of the study are:

For successful atomisation of frits, the melts need to be superheated to a greater extent than the metals and alloys because of their much higher viscosities.

The forms of the particles depend on the relationships between the times of solidification and spheroidisation as well as on the interactions between the particles after primary atomisation.

Particle sizes of powders are lower at higher water pressure and smaller orifice openings. However, when the pressure of the dispersed media is reduced, the mean particle size increases as a consequence of interactions and agglomerations.

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## REFERENCES

- [1] N. Ashgriz, Handbook of Atomization and Sprays: Theory and Applications, in (ed.), Springer, 2011, pp. 837-848.
- [2] S. Lagutkin, L. Achelis, S. Shekhaliev, V. Uhlenwinkel, V. Srivastava, Materials Science and Engineering: A, 383 (2004) 1, 1-6.
- [3] Y. Liu, S. Niu, F. Li, Y. Zhu, Y. He, Powder Technology, 213 (2011) 1-3, 36-40.
- [4] E. J. Lavernia, T. Srivatsan, Journal of Materials Science, 45 (2010) 2, 287-325.
- [5] A. J. Yule, J. J. Dunkley, Atomization of melts for powder production and spray deposition, in (ed.), Oxford University Press, 1994, pp. 241-245.
- [6] S. Rossi, E. Scrinzi, Chemical Engineering and Processing: Process Intensification, 68 (2013), 74-80.
- [7] B. Karpe, B. Kosec, T. Kolenko, M. Bizjak, Metalurgija, 50 (2011) 1, 13-16.
- [8] ISO-4534, Determination of fluidity behaviour - Fusion flow test. International Organization for Standardization, 2010.
- [9] S. Sogawa, H. Ozaki, Journal of the Ceramic Association, Japan, 75 (1967) 861, 148-153.
- [10] O. Nichiporenko, Y. I. Naida, Soviet Powder Metallurgy and Metal Ceramics, 7 (1968) 7, 509-512.
- [11] O. S. Nichiporenko, Soviet Powder Metallurgy and Metal Ceramics, 15 (1976) 9, 665-669.

**Note:** The responsible translator for English language is George Yeoman, University of Maribor, Maribor, Slovenia