

Second-Generation Aluminium Extraction Residue used as Devitrification Aid for Glass-Ceramics

M. C. Ferreira^{1,a}, W. Acchar^{2,b}, A. M. Segadães^{3,c}, S. Mello-Castanho^{1,a}

¹Institute of Energy and Nuclear Research (IPEN/SP-CCTM), 05508-000 São Paulo-SP, Brazil

²Dept. of Physics, Federal Univ. Rio Grande do Norte (UFRN), 59072-970 Natal-RN, Brazil

³Dept. of Ceramics and Glass Eng. (CICECO), University of Aveiro, 3810-193 Aveiro, Portugal

^asrmello@ipen.br, ^bacchar@dfte.ufrn.br, ^csegadaes@ua.pt

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Abstract. Brazil has one of the world's most important Bauxite deposits, the raw material for the aluminium extraction metallurgy. This work is focused on finding a suitable application for the white dross residue (WDR), a second-generation waste material produced during the metal recovery from the slag left after the primary extraction of aluminium from the ore. A commercial lime-silica based glass frit was used, to which WDR additions were made (up to 30 wt.%), aimed at studying the devitrification process of the glasses produced. Such mixtures were melted at temperatures varying from 1100 to 1500°C and the resulting fritted glasses were heat treated at 900°C. The starting materials and the mixtures thereof were characterized before and after thermal treatment by differential thermal analysis, X-ray diffraction and fluorescence, and scanning electron microscopy. The results obtained showed that the WDR is easily incorporated into the glass matrix and causes easy devitrification after short heat treatment periods at low temperature.

Introduction

Given the large Bauxite deposits in Brazil, ranking among the world's three largest ones [1], aluminium industry represents a significant share of the country's productive sector [2]. Aluminium extraction metallurgy, from the ore to metal production, generates a variety of waste materials with a heavy and worrying environmental footprint. One of these waste materials is the slag produced during the reduction process of the oxide to aluminium metal. Such slag used to be simply discarded but it has an interesting potential as alternative raw material for the production of ceramic glazes (for wall and floor tiles and electric insulators) and glass-ceramics [3-5].

Nowadays, growing environmental concerns and the emphasis placed on minimum industrial waste generation (zero residue policies) and environmentally friendly industries, justify the efforts made to recover the metal still left in the Al primary extraction slag [6]. The thermal plasma technique is one of the processes that might be used to that aim, which results in the production of a second-generation waste material, the white dross residue (WDR). The chemical composition of the WDR (> 90 mol% Al) suggests that it can be used to improve the crystallization of glasses in aluminosilicate glass-ceramics [7-8].

Glass-ceramics, found in a variety of applications [9], are polycrystalline solids with a residual glassy phase. These materials are usually produced from molten glass, which is cast to shape and subjected to heat treatment to promote crystallization. The proportion between crystalline and glassy phases determines the material's final properties and it can be controlled by the manipulation of the composition and the heat treatment.

Duan *et al.* [10], while studying the crystallization process of glasses in the alumina-lime-silica system (A-C-S) prepared from pure raw materials, showed that samples should be heat treated at temperatures close to the crystallization temperature, to develop an inner structure of fine crystals and large dendrites originating at the surface, with the growth direction pointing inwards.

Various authors [5, 11-13] successfully produced glass ceramics incorporating high contents of industrial wastes (up to 50 wt.%) with industrial application potential, and showed that, without nucleation aids, lengthy heat treatments (~10h) might be necessary to promote crystallization at comparatively low temperatures (~950°C).

Based on the above, the present work studies the effect of the presence of the white dross residue (WDR) produced in the aluminium recovery from the slag left after the primary extraction of aluminium from the ore, in the production of glass-ceramic frits used in ceramic glazes.

Experimental

The starting materials used were the white dross residue (WDR) and a typical commercial glass frit (supplied by Ferro enamel, Brazil). To ensure adequate homogeneity of the starting materials, they were dry-ground in a ball-mill for 30 minutes, sieved through 100 mesh (< 150 µm) and then kept in an oven at 110°C for 1 h.

Melting was carried out in alumina crucibles, at temperatures ranging from 1100 to 1500°C for 2 h, in a vertical electric furnace (Lindberg Blue CP 56724C), with a heating rate of 10°C/min, with mixtures of frit and 10, 20 and 30 wt.% WDR. The molten glasses were cast into stirred ambient distilled water and oven dried at 110°C for 1 h. Afterwards, they were hand ground in a porcelain mortar and sieved through 100 mesh (< 150 µm).

Both the starting materials and the glasses produced were characterised in terms of chemical composition (X-ray fluorescence, Rigaku X-Ray Rix2000). The melting and crystallization behaviour was studied by differential thermal analysis (TA Instruments SDT-2960).

Devitrification heat treatments were carried out at 900°C for 30, 60 and 120 min. After heat treatment, the presence of crystalline phases (X-ray diffraction, Rigaku Multiflex) and particle morphology and microstructure (scanning electron microscopy (Philips XL-30, at 20 kV) were investigated.

Results and discussion

Fig. 1 shows the general particle morphology of the as-received WDR, with large aggregates, seen in Fig. 1(a), of particles below 5 µm, as shown in Fig. 1(b). Table 1 presents the WDR chemical composition, as determined by XRF. Aluminium is the dominant element, followed by Mg and Ca. The presence of the latter is due to the MgCl₃ and CaF₂ used in the metal extraction process [14].

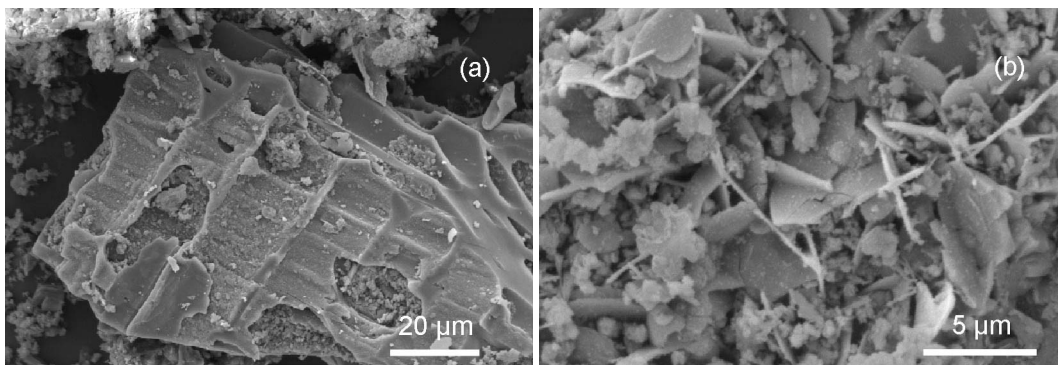


Figure 1 SEM micrographs of the as-received WDR: (a) large aggregate, and (b) small particles contained in the aggregate.

Table 1. Chemical composition (XRF, wt.%) of the as-received WDR and the commercial frit used.

	SiO ₂	CaO	MgO	Al ₂ O ₃	ZrO ₂	K ₂ O	Fe ₂ O ₃	Na ₂ O	ZnO
WDR	1.22	1.48	7.09	88.74	0.15	0.27	0.32	0.78	0.02
Glass frit	42.02	51.41	2.32	2.11	1.48	0.20	0.12	0.18	0.15

The WDR X-ray diffraction patterns are shown in Fig. 2. Characteristic peaks of aluminium oxide and nitride can be seen in the as-received WDR (Fig. 2(a)), along with spinel and traces of CaF₂. After heat treatment at 900°C for 2 h (Fig. 2(b)), the XRD pattern shows only the alumina and spinel characteristic peaks.

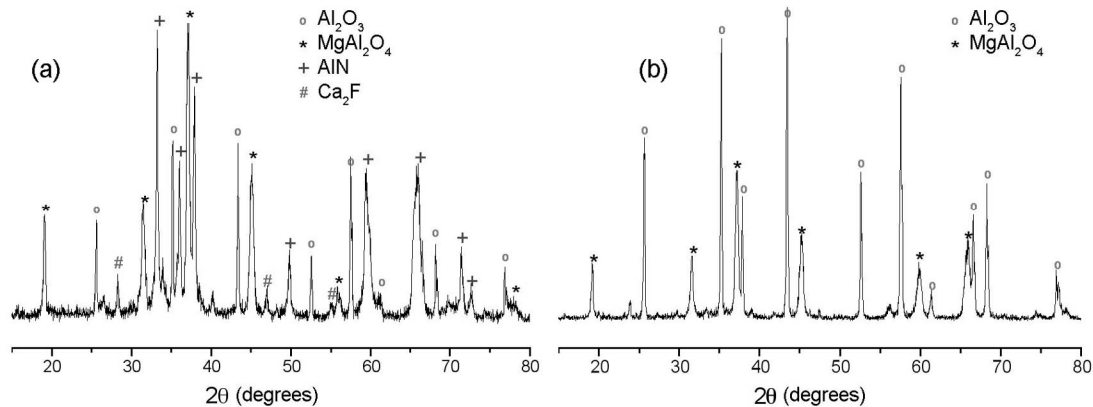


Figure 2 XRD pattern of the WDR: (a) as-received, and (b) after heat treating at 900°C for 2 h.

Table 1 also shows the chemical composition (XRF) of the commercial frit used. The major oxides present are CaO and SiO₂, nearly in the theoretical proportion of wollastonite, accompanied by lower amounts of Al₂O₃ and MgO.

Thus, the crystallization peak of wollastonite is expected to appear in the frit differential thermal analysis curve (DTA). The endothermic peak observed in the DTA curve at 680°C (Fig. 3) corresponds to the glass transition temperature, whereas the crystallization peak is observed at 830°C.

Based on the above and on the suggestions from the literature, the crystallization potential of the frit was studied at 900°C, as a function of the length of the heat treatment, as shown in Fig. 4. Annealing at 900°C for 30 min only led to the incipient crystallization of wollastonite (CaO.SiO₂). Longer exposures (60 and 120 min) resulted in stronger and well-defined wollastonite peaks.

After trial melting runs carried out with mixtures of frit and WDR in various proportions and at temperatures up to 1500 °C, the mixture containing 30 wt.% WDR and the melting temperature of 1300°C were selected for further investigation. Fig. 5 illustrates the fracture characteristics of the corresponding fritted glass as seen by SEM. The typical fracture expected from an amorphous material can be seen.

The crystallization potential of the WDR-containing fritted glass was also studied by XRD as a function of the length of the heat treatment at 900°C, as shown in Fig. 6. As expected, and given the higher alumina content of the mixture, annealing at 900°C for 30 or 60 min was not enough to promote crystallization. Annealing for 2 hours resulted in strong and well-defined peaks of gehlenite (C₂AS, 2CaO.Al₂O₃.SiO₂) and anorthite (CAS₂, CaO.Al₂O₃.2SiO₂).

Fig. 7 illustrates the corresponding devitrified microstructures, after heat treatment at 900°C for 2 hours. A network of interwoven fine crystals can be seen, showing the typical morphology expected for the primary nucleation of the high temperature aluminosilicates, such as gehlenite.

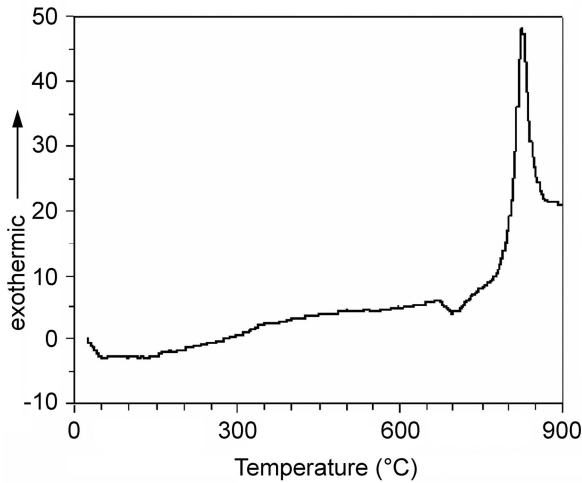


Figure 3 Differential thermal analysis curve obtained for the frit.

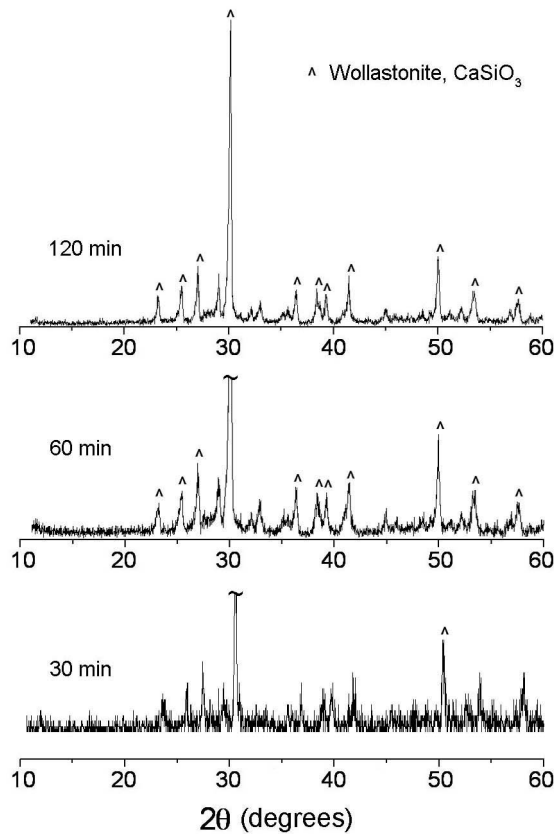


Figure 4 XRD pattern of the frit after heat treatment at 900°C, for 30, 60 and 120 min.

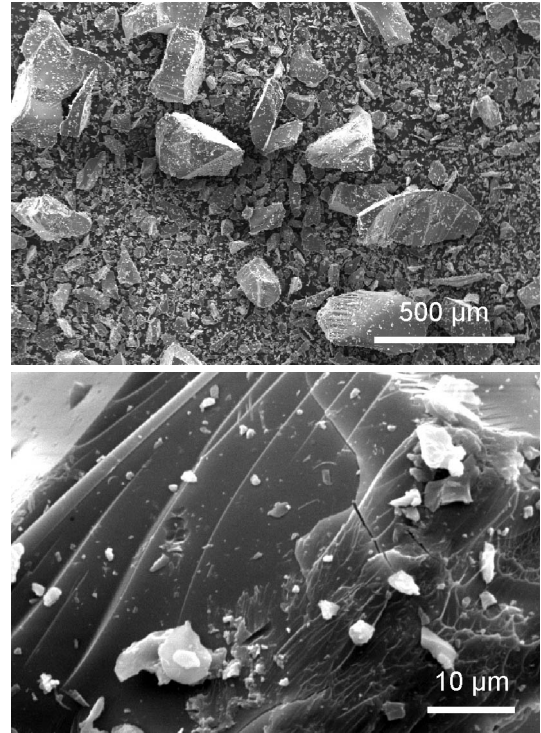


Figure 5 SEM micrographs of the fritted glass produced with 30 wt.% WDR (F30R).

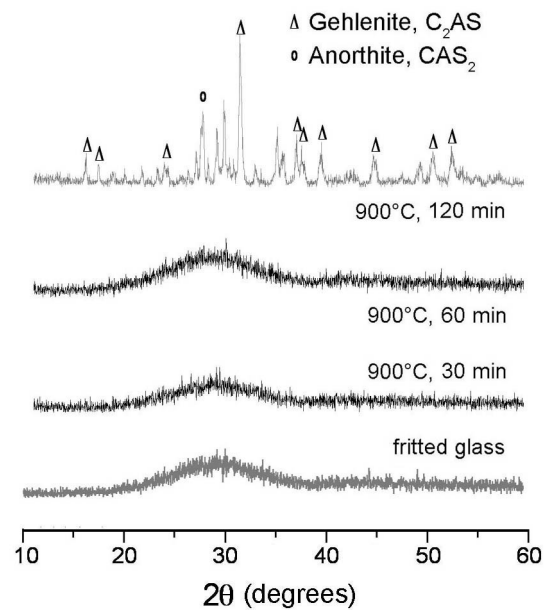


Figure 6 XRD patterns of the F30R fritted glass (melted at 1300°C, for 2 h), and after heat treatment (900°C, 30, 60 and 120 min).

Conclusions

The white dross residue (WDR) is a second-generation waste material produced in the aluminium recovery from the slag resulting from the primary extraction of aluminium from the ore. The incorporation, in glass frits, of the Al-rich WDR was shown to result in glass-ceramic materials.

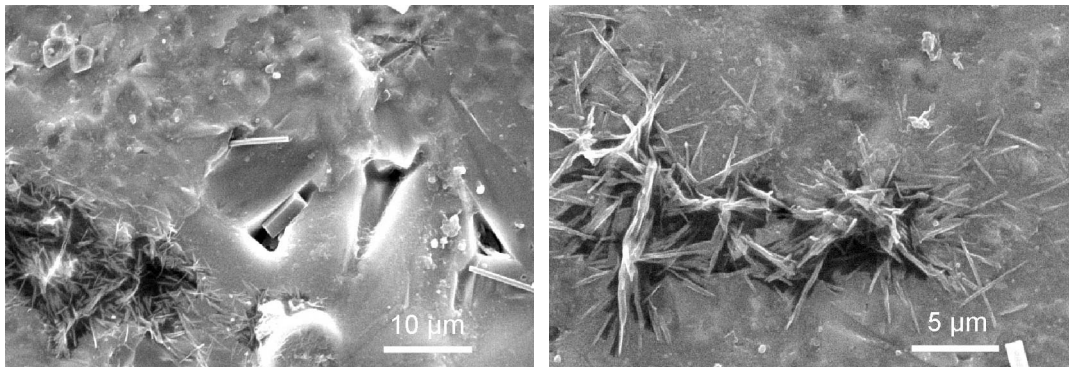


Figure 7 SEM micrographs of the fritted glass produced with 30 wt.% WDR (F30R) after heat treatment at 900°C for 120 min.

Starting with a commercial lime-silica based glass frit, up to 30 wt.% WDR could be added with no significant changes in the frit melting or casting behaviour. The presence of the WDR required melting at 1300°C and led to fritted glasses with easy devitrification at 900°C, into crystalline aluminosilicates, such as gehlenite.

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References

- [1] Information on <http://www.usgs.gov>, “United States Geological Survey”.
- [2] Information on <http://www.abal.org.br>, “Associação Brasileira do Alumínio” (Aluminium Brazilian Association).
- [3] M.R. Pérez: Bol. Soc. Esp. Cer. V. Vol. 35 (1996), p. 127.
- [4] J.M. Rincón, M. Romero, J. Marco and V. Caballer: Mater. Res. Bull. Vol. 33 (1998), p. 1159.
- [5] M. Romero, R.D. Rawlings and J.M. Rincón: J. Non-Cryst. Solids Vol. 271 (2000), p. 106.
- [6] M.C. Shinzato and R. Hypolito: Waste Management Vol. 25 (2005), p. 37.
- [7] M. Tanaka: J. Ceram. Soc. Japan Vol. 112 (2004), p. 655.
- [8] M. Roskosz, M.J. Toplis, P. Besson and P. Richet: J. Non-Cryst. Solids Vol. 351 (2005), p. 1266.
- [9] W. Pannhorst: J. Non-Cryst. Solids Vol. 219 (1997), p. 198.
- [10] R.G. Duan, K.M. Liang and S.R. Gu: Mater. Res. Bull. Vol. 33 (1998), p. 1143.
- [11] A.R. Boccaccini, W. Köpf and M. Stumpfe: Ceram. Int. Vol. 21 (1995), p. 231.
- [12] L. Barbieri and I. Lancellotti: Fuel Vol. 78 (1999), p. 271.
- [13] A. Karamanov, M. Pelino and A. Hreglish: J. Eur. Ceram. Soc. Vol. 23 (2003), p. 827.
- [14] Information on <http://www.azom.com>, AZOM, “The A to Z of Materials”.

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