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Production and characteristics of glass-ceramics derived from manganese crust tailings

Terry Lay · Maria Rockwell · Philippe Westreich

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Abstract Glass-ceramics have been produced via vitrification from manganese crust tailings with over 23% reduction in tailings volume. The crystalline behaviour of parent glass and glass-ceramics were investigated using DTA, TGA, XRD, and SEM/EDS. XRD analysis revealed that the major crystalline phase was iron manganese oxide. The Vickers microhardness (H_v) was 9.74 MPa, the indentation strength (K_c) was 1.88 Mpa m$^{1/2}$, and elastic modulus (E) was 140 MPa. The properties of the glass-ceramic compared well with known research and industrial glass-ceramic materials. Results suggest that manganese crust tailings have potential to be vitrified into useful, marketable glass-ceramic materials.

Introduction

General practice in the mining industry is to treat processed tailings by placing them behind a retaining wall called a tailings dam. The known major drawbacks to this waste processing practice are potential leachate production [1–3] with movement into water bodies and tailings dam failure [4]. In certain forecasted mining regions such as the South Pacific Islands, where marine mining of manganese-based ore deposits is eminent, it is probable that tailings dams will not be a permissible method of tailings treatment.

Vitrification has been shown to be a very promising technique for waste management since it greatly reduces waste volumes, produces a relatively inert vitreous material with acceptable chemical stability and can incorporate hazardous materials (i.e., heavy metals) into the glassy matrix [5–14].

Previous works [15–19] have shown that various types of mine tailings can be vitrified. Vitrification of manganese tailings has also been accomplished [20], although no attempt was made to control the resulting types and amount of crystalline phases. Often, waste compositions are complex and hence, various crystalline phases may be formed, unless a certain level of control is administered.

Glass-ceramics are fine-grained polycrystalline materials formed when glasses of suitable composition are heated and undergo controlled crystallization. Not all glasses can be crystallized into acceptable glass, since some are too stable and difficult to crystallize, while others crystallize too readily and form unacceptable crystal structures. Glass-ceramics are normally only 50–98% crystallized, while the composition of the crystalline phase (or phases) is normally different from the parent glass. The advantage of glass-ceramics over glasses, are their ease of fabrication and superior properties [21].

To achieve an optimal glass-ceramic, the crystalline process must be controlled to produce the desired microstructure, usually through a two-step (thermal molten process or TMP) heating process. This approach transforms the parent glass into a composite material in which the crystalline phase is bonded by the residual phase. The first step in the TMP approach at lower temperatures, involves the formation of heterogeneous nuclei (small crystallites of size range 10–100 nm [22] to promote the growth of the major crystal phase. The greater the number of nuclei formed, the finer the structure of the glass-ceramic and the

T. Lay (✉) · M. Rockwell
Department of Civil and Resource Engineering, Dalhousie University, 1360 Barrington St, Halifax, NS B3J 1Z1, Canada
e-mail: tlay@dal.ca

P. Westreich
Department of Physics and Atmospheric Science, Dalhousie University, 1360 6300 Coburg Rd, Halifax, NS B3H 3J5, Canada

more acceptable the properties of the material. Thus, the presence of an efficient nucleating agent in the correct concentration and the determination of the temperature and time of nucleation and growth, assume specific importance in glass-ceramic formation [22].

This study considers the control of potential crystalline phases in glass-ceramics derived from manganese crust tailings. The two approaches employed were (a) adjusting the chemical composition of the raw tailings with additives and (b) controlling the crystalline phases by optimizing the heat treatment schedule. The physical and chemical properties of the resulting glass-ceramics were compared to known materials as an indication of achieving suitable conditions for glass-ceramic production.

Experimental procedure

Manganese crust tailings samples came from the BHP mine and mineral processing facility at Groote Eyland in Northern Australia. The ore was mined from an island seamount. The chemical compositions of the as-received tailings and borax flux were analyzed by atomic absorption spectroscopy (AAS) and by mineralogical analysis.

Attempts were made to produce a glass from raw tailings, but failed due to insufficient glass formers being present, so experiments were conducted adding first a silica source, then silica, and a Na_2O source, then combinations of silica plus borax, and ultimately just borax, which proved to provide the best quality glass. The borax additive acted as a fluxing agent and former and produced various quality glasses. Both parent glass and borax powders were received as being 100% < 400 micron particle size. Ultimately, acceptable parent glasses were made from mixtures of 50–70 wt% manganese crust tailings with 30–50 wt% borax (sodium tetra borate decahydrate) as basic materials.

The parent glass was prepared by mixing the raw materials in a laboratory size ball mill, without the steel balls, for 15 min, then melting the starting powders in clay crucibles in an electrically heated furnace at 1160 °C for 1 h. The melts were permitted to air cool to 450 °C, held for 1 h for annealing, then cooled to room temperature in the furnace. The resulting material was crushed in a Baldor shatter box and sieved to produce glass powder of <200 μm for use in DTA/TGA (differential thermal analysis/thermo gravimetric analysis) employing a TA Instruments Q Series (SDT Q600) unit. The glass transition temperature (T_g), dilatometric softening point (T_{ds}), and crystalline melting temperature were determined from the DTA curve of the parent glass, while loss in volume was determined from the TGA curve. Leroy et al. [23] suggested that annealing of parent glasses should be conducted near the glass transition temperature and that optimal heat treatment temperatures may be found near temperatures indicated by crystallization peaks in the DTA curve from a glass particle melt.

The results of the DTA analysis were employed as a guide to produce the glass-ceramic 4-21 via the two-step vitrification procedure. The base powders were heated to 1160 °C, the melt held for 1 h, and then permitted to cool to five different nucleating temperatures (580, 630, 680, 730, and 780 °C). The melt temperature was then raised at 10 °C/min to 1005 °C for each nucleating temperature and permitted to crystallize for 1 h, then allowed to cool at 10 °C/min to room temperature in the furnace. The crystalline phases present in sample 4-21 after heat treatment were determined using an X-ray powder diffraction (XRD) Phillips PW 1720 X-ray generator unit, with <200 μm particle sizing. A Hitachi S-4700 Scanning electron microscope (SEM) was employed to observe the microstructure of sample 4-21.

The bulk density was measured by the Archimedes method [24] using water as the medium and averaging 10 trials per sample. The Vickers micro hardness (H_v) of samples was measured in (MPa) by the Vickers indentation method [25] by averaging 10 trials per sample, while fracture toughness (K_c) was determined in (MPa $m^{1/2}$) for 10 trials per sample using the equation by Evans and Charles [26]. Young's modulus (E) was determined theoretically by comparing several known equations [27–30] that calculate (E) and using hardness (K_v) and indentation toughness (K_c) values from this study according to the approach described in a con-current paper [31]. Chemical resistances of 2 g of 4-21 samples ranging in particle size from 0.3 mm to 0.5 mm were determined as the average amount of weight reduction from five trials after holding samples at 95 °C for 1 h in 60 cm^3 of respective 0.01 mol/L NaOH and 0.01 m/L HCl solutions. The samples were weighed before immersion and washed and dried then weighed after immersion [23].

The erosion behavior of glass-ceramic 4-21 was determined following a method [32] of rotating a small glass bar (5 mm × 5 mm × length 15 mm) of sample 4-21 in a slurry of 100 g of silica sand in 1000 mL water at room temperature for 9 h, then determining the weight loss from before to after rotation. Five trials were conducted to achieve an average value.

Results and discussion

The AAS results in Table 1 confirm the raw tailings to be comprised mainly of the oxides (SiO_2, Al_2O_3, MnO_2, and Fe_2O_3). Figure 1 is a SEM micrograph of a manganese crust tailings sample, showing mainly rounded powder particles ranging in size from 10 μm to 200 μm, suggesting

Table 1 Chemical compositions of manganese crust tailings and borax flux in wt%

Oxide	Slimes	Borax*
SiO_2	28.1	
Al_2O_3	20.3	
MnO_2	36.0	
Fe_2O_3	5.6	0.002
B_2O_3		36.47
Na_2O		16.47
BaO	0.60	
K_2O	0.34	
CaO	0.04	
MgO	0.14	
TiO_2	0.48	
H_2O	8.36	46.57
Others	0.04	0.49

* Merck [33]

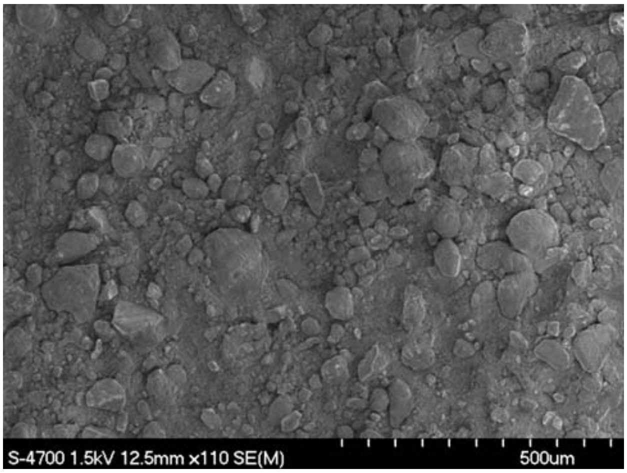


Fig. 1 SEM micrograph of the as-received manganese crust tailings

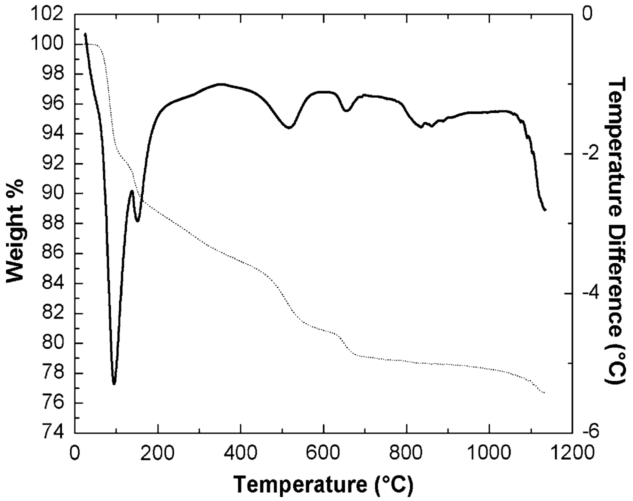


Fig. 2 DTA/TGA of glass-ceramic 4-21

that the grains could be employed in glass production without the expense of additional crushing or grinding.

Acceptable quality glass-ceramics were produced from the following sample mixtures of slimes/borax/silica (4-20 (65/30/5), 4-21 (70/30/0), 4-22 (50/40/10), 4-23 (55/40/5), 4-24 (60/40/0), and 4-25 (50/50/0). Sample 4-21 was chosen as optimal on the basis of physical appearance (colour, clarity, lack of spotting, and fractures and apparent homogeneity) and subsequently used for extensive testing to represent all samples.

Marabini et al. [16] suggested that for goethite-based mine tailings to be transformed into glass-ceramics, the melt must not be de-mixed, while it must; (a) melt within an acceptable industrial range (1000–1600 °C), (b) form a bubble-free melt, (c) pour steadily, and (d) have starting materials that are finely divided. Considering the study melt, it was observed to melt at <1160 °C, which is well within the preferred limits and to be relatively bubble-free, as large amounts of gases (>23%) were expelled during heating, as denoted by the TGA curve. The melt was observed to pour steadily during lab testing where it was poured onto a steel plate and the starting materials were finely divided and in a similar size range. Thus, given the conformity with other findings, the study mixtures had a high likelihood of producing acceptable glass-ceramic materials.

In Fig. 2, the results of the differential thermal analysis (DTA as dark line) show endothermic peaks corresponding to weight losses on the Thermo gravimetric analysis (TGA as light line) curve at 100, 145, 520, and 655 °C. The deep endothermic peak from approximately 80 °C to 120 °C, centered at 100 °C represents the release of absorbed water similar to Ford [34]. The smaller endothermic peak at 140 °C and the larger one at 520 °C may represent the dehydroxylation of aluminum hydroxides, particularly kaolinite, with water release, as found by Sglavo et al. [35]. The endotherm at 655 °C corresponding to a weight loss on the TGA curve is likely due to conversion of MnO_2–MnO_3, while the small endothermic peaks at 840 and 860 °C are probably due to conversion of MnO_3–MnO_4, similar to findings by Shah et al. [36]. The broader endothermic peak with its onset at 430 °C represents the glass transition temperature (T_g), while the base of this endothermic peak around 520 °C represents the dilatometric softening point (T_{ds}) of the low viscosity phase. Lastly, there is an endothermic peak near 1160 °C representing the formation of a liquid phase.

Generally, the nucleation temperature falls 50–100 °C above the dilatometric softening point [21, 37]. Thus, the temperature range considered for heat treatment of glass sample 4-21 was between 580 and 780 °C, which encompasses the two known crystallization peaks. Considering findings by Acosta et al. [38], the DTA graph suggests that glass 4-21 is relatively stable as it does not display any distinct exothermic curves. Shah et al. [36] suggested that a DTA graph not displaying any noticeable exothermic peaks indicates the reactants have been consumed. This suggests that a suitable heat treatment may be developed to obtain a single phase crystalline material, thus, additional efforts could be designed to optimize the relation between nucleation and crystallization temperatures, melt holding times in the furnace and rate of cooling.

Sidkova et al. [39] noted that for glasses with 10–50 wt% industrial waste, surface crystallization as a continuous thin film grew progressively denser as the temperature rose, and with further increase in waste percentage, bulk crystallization occurred in the glass. Figure 3 is a microphotograph of the surface of glass 4-21 displaying a film of crystallization, indicating that the slow cooling approach employed at 5–10 °C per minute has created surface crystallization, possible due to surface crystallization of iron oxide as reported by Karamanov and Pelino [40].

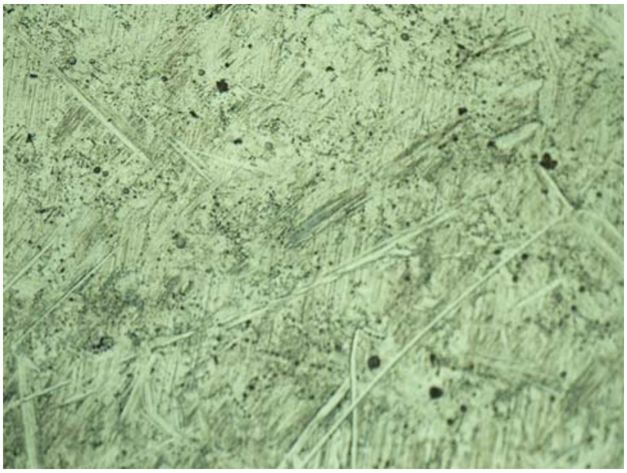
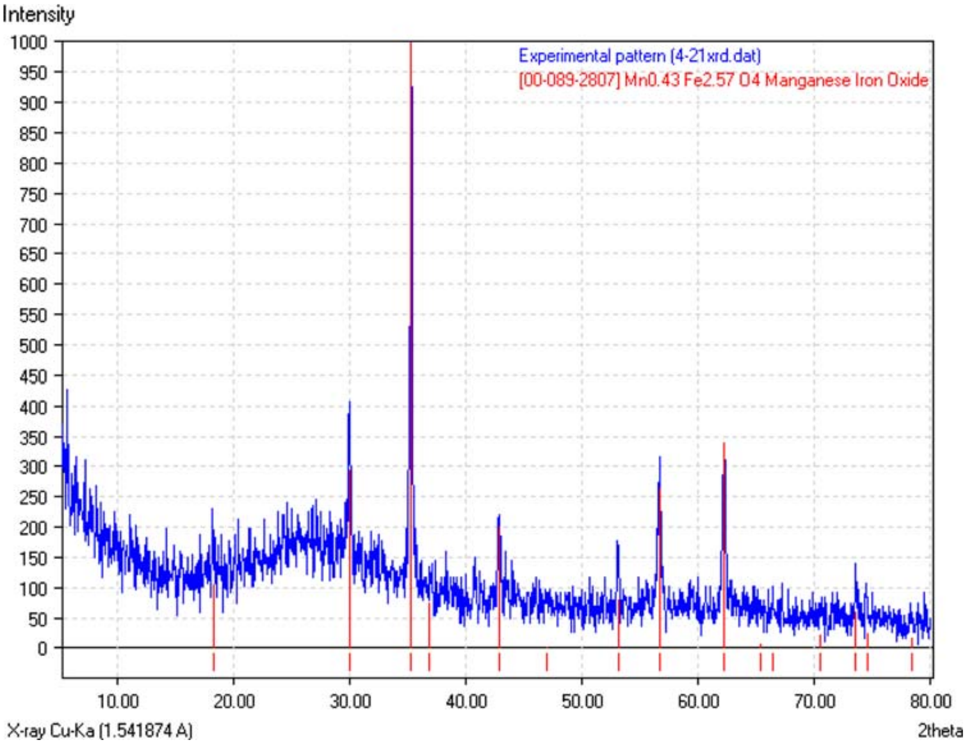


Fig. 3 Microphotograph of surface crystallization on glass-ceramic 4-21

It has been reported [41, 42] that crystallization can take place in waste materials without an intermediate stage of reheating the parent glass for crystallization, by employing controlled cooling of the melt. In addition, the cooling rate was considered the dominant factor in controlling the formation and morphology of the crystal phase, particularly in relation to iron-containing raw materials. This approach, termed the Petrurgic method [43] can provide considerable savings in melting costs for suitable melts. There was evidence of surface crystallization and partial bulk crystallization of samples in the present study. The chemistry of the study waste materials and their iron content, suggests that further research may reveal a more efficient and cost saving approach to crystallization of manganese tailings.

Figure 4 provides a XRD pattern of glass-ceramic 4-21 heated at 1160 °C for 1 h, then nucleated at 630 °C for 1 h, and crystallized at 1005 °C for 1 h to produce the crystalline phase. The 630 °C temperature revealed the most intensive crystallization peaks for sample 4-21 of the several nucleating temperatures employed. XRD results

Fig. 4 X-ray diffractogram of glass-ceramic 4-21



indicate the main crystalline phase to be manganese iron oxide ($MnO_{0.43}Fe_{2.57}O_4$).

Figure 5 shows a SEM micrograph of the manganese iron oxide glass-ceramic 4-21 with a dendritic structure, where dendrites radiate from observed nuclei. EDX analysis suggests the nuclei are composed of iron and manganese oxides. The crystals measure 20–30 μm in diameter and are intergrown in dendritic forms.

Figure 6 displays a microscope image at ×30 of a diamond-shaped indentation made by the Vickers indenter, employing a load of 1 kg, where distance from the corner of the indent to the end of the crack line was measured at each corner and the two opposing corner values were averaged and used as the values to insert into the appropriate formulas to determine H_v and K_c values of the glass-ceramic. Table 2 indicates that the physical properties of glass-ceramic 4-21 compare closely with known commercial and study glass-ceramics. These results follow from the chemistry of the study tailings waste being generally similar to several waste products previously studied and vitrified into useable glass and glass-ceramic products. Table 3 provides chemical resistance values for glass-ceramic 4-21 compared to glass-ceramics, based on weight loss measurements. It can be seen that the study glass-ceramic falls in a similar range of resistance values, which supports its envisioned use as a potential construction material. The average weight loss of the 4-21 samples after 9 h of rotation was 0.52%, which is similar to findings by previous authors [32]. The study glass-ceramic chemical resistance values correspond closely with the values reported by previous authors, which suggests the study material could be employed for similar applications such as construction materials.

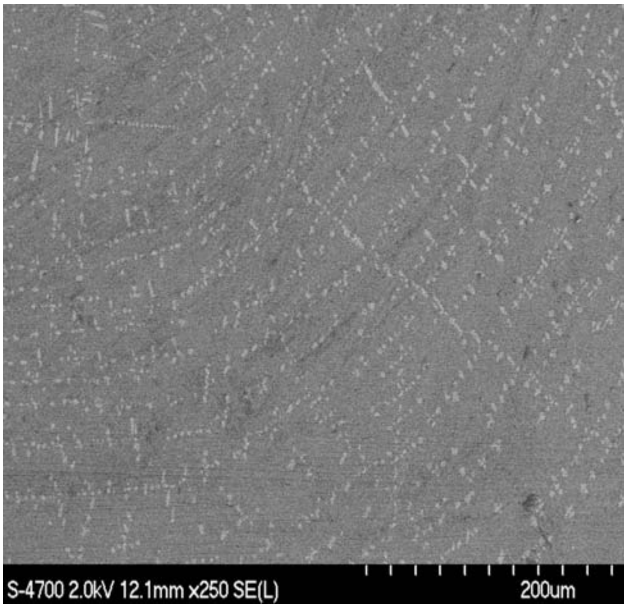


Fig. 5 SEM micrograph of manganese iron oxide glass-ceramic 4-21

Fig. 6 Representative indentation of glass-ceramic 4-21 with resultant crack lines

Table 2 Comparison of the physical properties of glass-ceramic 4-21 with those of commercial glass-ceramics

Property	4-21	Silceram	Marabini	Pelino	Kim
Density (g/cm^3)	2.93	2.9	2.66	3.65	3.3
Vickers (MPa)	9.74	7	9.5	9.5	8.3
K_c ($MPa\ m^{1/2}$)	1.88	–	1.83	1.80	1.6
Modulus (MPa)	140	122	145	1.42	140

Silceram [44], Marabini [16], Pelino [45], Kim [46]

Table 3 Comparison of the chemical resistance of glass-ceramic 4-21 and known glass-ceramics based upon weight loss measurements

Samples	NaOH (0.01 m/L)	HCl (0.01 m/L)	H_2SO_4 (0.01 m/L)
Leroy	1.08		1.06
4-21	1.22	0.64	0.91
Cheng	9.9	0.1	.05

Leroy [23], Cheng [47]

Conclusions and recommendations

The present work indicates that manganese crust tailings can be fluxed with borax to produce a manganese-based glass-ceramic by nucleating at 630 °C and crystallizing at 1005 °C. It was possible to bulk crystallize the glasses without addition of nucleating agents possibly due to the additional formers and nucleating agents in the waste material. Due to the attractive dark-brown colour and mechanical and chemical properties comparable to existing industrial materials, these materials could be considered for use as load-bearing structural materials (i.e., cladding for roofs, walls, and floors, radiant panels, aggregate and paving tiles). Additional efforts could be designed to optimize the relation between nucleation and crystallization temperatures, melt holding times in the furnace and rate of cooling.

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