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ON THE THERMAL STABILITY AND PROPERTIES OF OLIVINE-BASED MINERAL FIBRES

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ABSTRACT

Natural fibres, such as asbestos, are being substituted by man-made ones in some important composite products such as brake-linings.

The present work is concerned with some critical thermochemical properties of manufactured fibres, especially the influence of heat treatment and minor compositional variation on their crystallization. Using thermoanalytical methods combined with isothermal heat treatment, it has been shown that the glassy fibres crystallize appreciably by about 100°C below the crystallization temperature as indicated by DTA. The crystallization behaviour is discussed in the context of the variation of chemical composition and of heat treatment.

INTRODUCTION

Natural mineral fibres, notably those based on asbestos, have been and still are extensively used as a reinforcing constituent in a great number of technically important materials. One of the important applications is in brake-linings. Since the start of the discussions about the health hazards from asbestos fibres there has been quite a number of attempts to find a substitute for asbestos in brake-linings.

An extensive survey of the problem is found in ref. 1. A typical analysis of brake-lining is

Chrysotile asbestos	10–70%
Binder (mostly phenolic resin)	5–20%
Inorganic fillers	wide variation
Metal powder	wide variation

As shown, the mineral fibres may form a major constituent of this material. In developing substitutes for these fibres a number of requirements must be placed on the new product: thermal stability up to 800°C; stability of friction coefficient up to the same temperature; no adverse interaction with the surrounding materials; low thermal conductivity.

Recently, a number of new asbestos-free formulations have been made commercially available [2]. Most of them contain man-made mineral fibres (MMMF). For some of these MMMFs, such as basalt-fibre, the thermal stability can be a critical factor, in particular because of the glassy nature of these fibres.

The aim of the present work is to examine and characterize certain thermochemical properties of two olivine-based MMMF materials. The major objectives of the investigation are: to compare the crystallization behaviour for isothermal and non-isothermal heat treatment; to examine the influence of minor compositional variations; and to determine the magnitude of the thermal effects (crystallization, melting).

EXPERIMENTAL

Samples were taken from the compacted bulk materials denoted B1 and B3 containing the mineral (glassy) fibres and the resin binder. The compositions are given in Table 1. A thermobalance (Mettler TA1) capable of simultaneous TG–DTG–DTA analysis was employed. Typical instrumental and operational parameters were: Pt crucibles; sample amount, 20–400 mg; TG–DTG–DTA range, 10, 100 mg, 10 mg min^{-1}, 100 μV; heating rate, 10° min^{-1}; maximum test temperature, 1300°C; atmosphere, flowing air (6 l h^{-1}).

The enthalpy changes during the thermal processes were evaluated using the transition enthalpies of Na_2CrO_4 (2.29 kcal mole^{-1}) and ZrO_2 (1.42 kcal mole^{-1}) [3]. These substances were selected to obtain DTA calibration peaks within the temperature ranges of the observed thermal effects of the specimens.

Comparative isothermal heat treatments aimed at crystallizing these glassy fibres were made at 700–850°C for 1 h in a tubular furnace. The relative amount of the crystalline phase formed was determined with the aid of an X-ray diffractometer (Cu K_α).

TABLE 1

Compositions of B1 and B3

Sample	(wt.%)							
	MgO	CaO	Fe_2O_3	Al_2O_3	K_2O	TiO_2	MnO	SiO_2
B1	28.53	9.63	3.73	9.36	0.13	0.73	0.21	47.68
B3	28.94	8.91	3.17	9.83	0.13	0.73	0.14	48.15

RESULTS AND DISCUSSION

Figure 1 shows a thermogram obtained for the powdered B3 specimen (amount: ca 420 g). The large exothermal DTA peak initiated at 205°C is due to burning-off of the resin binder. Crystallization of the glassy matrix (exothermal DTA signal) is seen to start at 830°C. At the heating rate used (10° min^{-1}), the crystallization process can be completed before melting of the material, starting at 1090°C. The principal DTA melting peak is preceded by a small one thus suggesting two consecutive melting processes. Moreover, the large DTA peak appears to be resolvable into at least two partial steps. This stepwise melting clearly suggests that after crystallization, the material consists of more than one phase. On cooling at 10° min^{-1}, the melt is seen to start to solidify at 1160°C, 70° above the melting temperature. Again, this is an indication of the presence of a multiphase system, probably of eutectic type. The small DTA side-peak observed on melting is also seen to reappear at 970°C (120°C below the m.p.) thus indicating a significant supercooling before crystallization.

The B1 material showed a similar thermal behaviour but the DTA melting side-peak was relatively larger and more separated from the main one (melting/solidification temperature, 1075/1005°C). This seems to indicate a somewhat more extended phase separation compared to B3.

At a low-rate cycling (10° min^{-1}), the DTA side-peak reappears at well-defined melting/solidification temperatures. This shows that the same type of phase separation occurs which is observed after the first crystalliza-

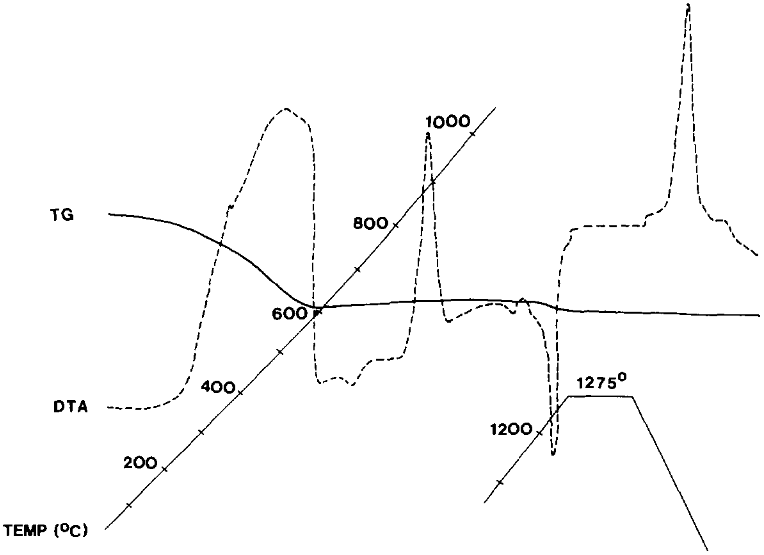

Fig. 1. A thermogram showing the TG and DTA curves obtained at 10° min^{-1} in air (sample B3).

TABLE 2

Sample	Partial process	Temp. region (°C)	ΔW (w/o)	ΔH (kcal kg^{-1})
B1	Binder burn-off	185– 595	−4.1	−84
	Crystallization	835– 950		−31
	Melting	1075–1275	−0.3	+58
B3	Binder burn-off	205– 605	−4.8	−151
	Crystallization	830– 955		−29
	Melting	1090–1270	−0.2	+41

tion. This also permits us to say, without the use of X-ray diffractometry, that the material forms crystalline phases on solidification. On increasing the rate of cooling (40° min^{-1}), the material will not crystallize completely. For the B1 specimen on reheating at 10°C min^{-1}, one can observe a glass-crystalline transition (at the same temperature, ~ 830°C) with the DTA peak area corresponding to about 65% of that obtained in a slow cycle. At a heating rate of 10°C min^{-1}, the crystallization and melting peaks are distinctly separated. The peak area for the glass–crystalline transition can thus be used as a quantitative measure of the amount of glass (crystallisable under these conditions) remaining in the material treated at different cooling conditions.

Table 2 shows the weight losses (ΔW in w/o) and enthalpy changes (ΔH in kcal kg^{-1}) obtained within the temperature regions indicated. As seen in the Table, the compositional variation in materials B1 and B3 does not markedly affect the crystallization temperature of the glassy phase. This may be expected since crystallization of this type will be more related to the formation of stable nuclei for the new crystallizing phases. The melting temperatures are affected to a greater extent and a difference of 15°C is observed. This suggests either a variation of phase composition or, that the same phases are formed which then are part of more than one eutectic system or a peritectic one. The small weight loss during the melting is, by its order of magnitude, probably due to the change of oxidation state of the iron present.

The accuracy of the enthalpy measurements by DTA as given in the Table 2 was estimated to be 10% but the reproducibility was 3%. .Thus, the difference in enthalpy of crystallization between B1 and B3 is relatively significant, the value for B1 being larger. So is the enthalpy value for melting (solid–liquid transition), by about 30%. The small compositional variation of these materials is thus seen to produce a sizeable effect. This is important to consider for devising an adequate heating schedule in order to achieve thermal balance in the commercial operation.

The enthalpy change for the glassy–crystalline phase transition appears to be of the same magnitude as that of melting, indicating a profound rearrangement of chemical bonds. Besides, it can be reproduced to 3%. After selecting a standard procedure for the preparation of glassy material of this type, the DTA peaks for the glass–crystalline transition could in general be suitable for calibration in quantitative DTA.

X-Ray diffraction analysis showed the presence of only one crystalline phase of diopside-type. Pure diopside [$CaMg(SiO_3)_2$] has a monoclinic [C2/c (15)] structure and occurs as a mineral. It is isostructural with hedenbergite [$CaFe(SiO_3)_2$] and johannsenite [$CaMn(SiO_3)_2$] where Mg can be continuously replaced by Fe and Mn present in the compositions used (see Table 1). More detailed structural analysis would be needed to determine the extent of this solubility in the present case. The oxide mass ratio $CaO:MgO:SiO_2$ in pure diopside is about 3 : 2 : 6, while it is 1 : 3 : 5 in the present composition. Calcium cannot be substituted and thus there is a Ca deficiency with respect to the diopside formation. Calculation shows that about 40% by weight of the B1 and B3 materials may form a diopside-type compound. The surplus MgO and SiO_2 might form phases of enstatite-type $(MgSiO_3)_2$, forsterite (Mg_2SiO_4) and other olivine-type silicates (together with the other metallic components). The identification of $MgSiO_3$ (enstatite, clinoenstatite), however, may be obstructed because of the coincidence of most of the reflexions for these phases and those of diopside in their X-ray spectra. The solid solubility of $MgSiO_3$ in $CaMg(SiO_3)_2$ [4] will also shift the reflexions towards those of enstatite-type phases.

The melting point for pure diopside is given [4] to be 1391.5°C. Rough extrapolation of the main DTA melting peaks yields values of about 1140°C (B3) and 1115°C (B1). This large depression of the melting point (by ca. 250°C) could be indicative of a basically eutectic system but there is no region in the pure $CaO-MgO-SiO_2$ system [4] where liquid formation occurs at such a low temperature. The low melting point and its large variation with

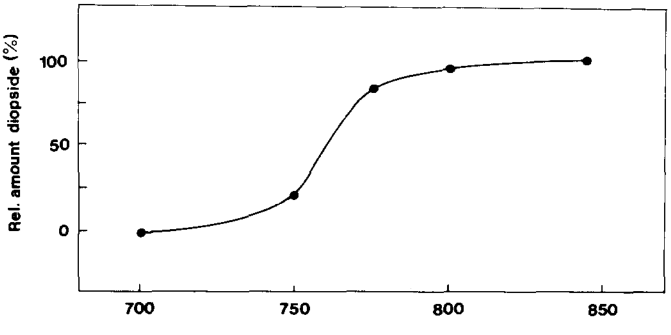

Fig. 2. The relative amount of diopside phase after heat treatments at temperatures of 700–850°C for 1 h, determined by X-ray diffractometry (relative scale, diopside amount at 850°C = 100%).

composition thus suggests that the depression effect is only due to the other metallic components present in these materials.

The process of crystallization of the glassy phase has been examined by making isothermal runs at 700, 750, 775, 800 and 850°C (holding time: 1 h) to compare it with the (non-isothermal) DTA runs. X-Ray diffraction analysis of samples heat-treated at 700°C showed only a glassy background. However, already at 750°C and higher, the pattern of the spectra due to diopside structure started to emerge. Figure 2 shows the relative increasing amount of the diopside phase formed, as determined from the intensities of the X-ray reflexions. At 850°C the crystallization is seen to be virtually complete. The X-ray spectra at 850°C did not show any glass background, suggesting that, within the limits of observation, essentially all the material has crystallized. Thus, the isothermal measurements have shown that the material can be crystallized at a temperature about 100°C lower than that indicated by DTA (830°C). Nucleation of the crystalline phase is apparently a slow process and therefore, a considerable overheating is necessary in the non-isothermal DTA runs in order to bring about the rapid crystallization observed at 830°C. For a satisfactory characterization of the crystallization behaviour of these materials a combination of isothermal and non-isothermal methods is needed. This characterization may be crucial for certain applications such as using the mineral fibres as a substitute for asbestos in brake-lining. In this case the variation of the crystallization temperature within ±100°C can be decisive for the usability of the fibres for this purpose.

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