4. S. K. RHEE, *Mater. Sci. and Eng.* **11** (1973) 311.
5. L. E. MURR, "Interfacial Phenomena in Metals and Alloys" (Addison-Wesley, Reading, Mass., 1975) pp. 91–5.
6. E. G. SHAFRIN and W. A. ZISMAN, *J. Phys. Chem.* **71** (1967) 1309.
7. H. W. FOX and O. LEVINE, The Wettability of RDX and PETN Crystal Surfaces, NRL Rept. 4714 (1956).

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Decomposition of $CaCO_3$ and formation of Ca_3SiO_5

The lowering of the decomposition temperature of $CaCO_3$ with the addition of a mineraliser (NaF) and the formation of Ca_2SiO_4 [1] and Ca_3SiO_5 [2] with the additions of mineralisers (NaF in the case of Ca_2SiO_4 and CaF_2, etc., in the case of Ca_3SiO_5) coupled with rapid heating of the raw mixes (stoichiometric proportions of silica gel and $CaCO_3$) were reported in earlier communications [1, 2]. The effect of the cations (mineraliser) appears to play a significant role as observed during continued study in this area of research.

The decomposition of $CaCO_3$ in a mix containing silica gel and $CaCO_3$ (1:3) and 2% LiF, CaF_2, SrF_2 and BaF_2 studied using differential thermal analysis (DTA), is shown in Table I and Fig. 1. In general, the drop in the decomposition temperature of $CaCO_3$ with increasing amount of mineraliser (2 to 6%) was more pronounced in the case of NaF, LiF and BaF_2 than for SrF_2 and CaF_2. Evidently, the cations have an effect on the decomposition process and it is interesting to observe the distinct grouping among the mineralisers, i.e., CaF_2, SrF_2, BaF_2 and NaF, LiF.

The mechanism of the decomposition process appears to be different, i.e., with higher atomic number, ΔT increases while the reverse is true in the cases of NaF and LiF.

The ionic radii of the cations (Li^+ – 0.78, Na^+ – 1.01, Ca^{2+} – 1.06, Sr^{2+} – 1.20 and Ba^{2+} – 1.40 Å) is an important parameter, as can be seen in Fig. 2. At higher percentage of additions (6%), the mechanism of decomposition is distinctly different. The effect of the cations (as shown by the line marked 4% with respect to Ca; this is

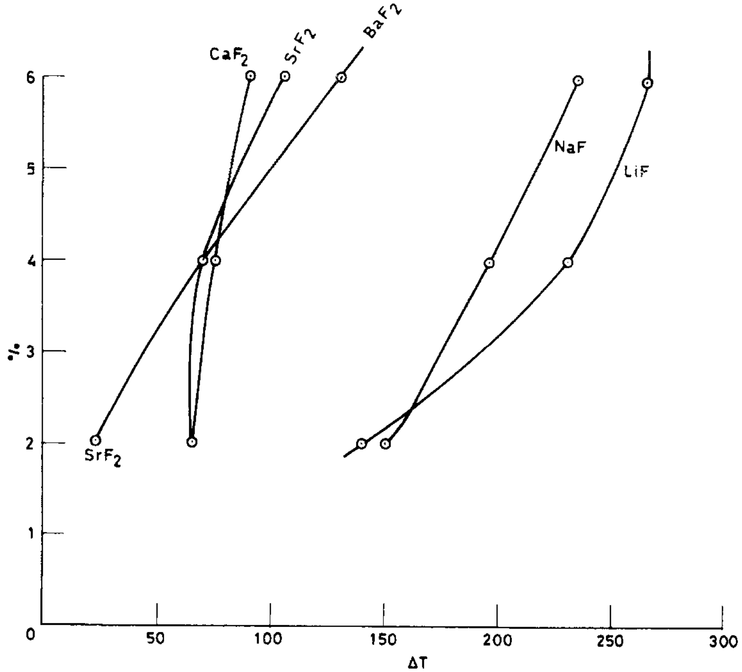

Figure 1 The variation in decomposition temperatures ($\Delta T = T\text{CaCO}_3 - T\text{CaCO}_3$ + mineraliser) of $CaCO_3$ with amount (%) of mineraliser in the mixes containing silica gel and $CaCO_3$ (1:3).

TABLE I DTA peaks (° C) of mixes containing 3:1 $CaCO_3$ and SiO_2 (gel) in the presence of mineralisers

Mineraliser	LiF	NaF	CaF_2	SrF_2	BaF_2
2%	540 (w) 620 (w) 800 (s) 850 (m)	790 (s) 825 (m) 895 (m)	875 (s) 1110 (vw)	845 (vw) 917 (s)	785 (w) 875 (s)
4%	560 (m) 710 (s) 880 (m)	560 (vw) 595 (w) 745 (s) 1020 (m)	865 (s) 890 (m) 1015 (vw)	820 (s) 870 (m)	830 (s) 880 (m) 980 (vw)
6%	530 (m) 675 (s) 830 (m)	540 (vw) 575 (w) 705 (s) 845 (m) 930 (m)	850 (s) 1010 (w)	835 (s) 870 (m) 1010 (vw)	810 (s) 870 (m) 980 (vw)

w = weak, m = medium, vw = very weak, s = strong and corresponds to large weight loss. All are endothermic peaks; high-temperature peaks, 1020, 1015° C, etc., are due to phase formation, etc. DTA peaks without mineralisers are at 560 and 940° C.

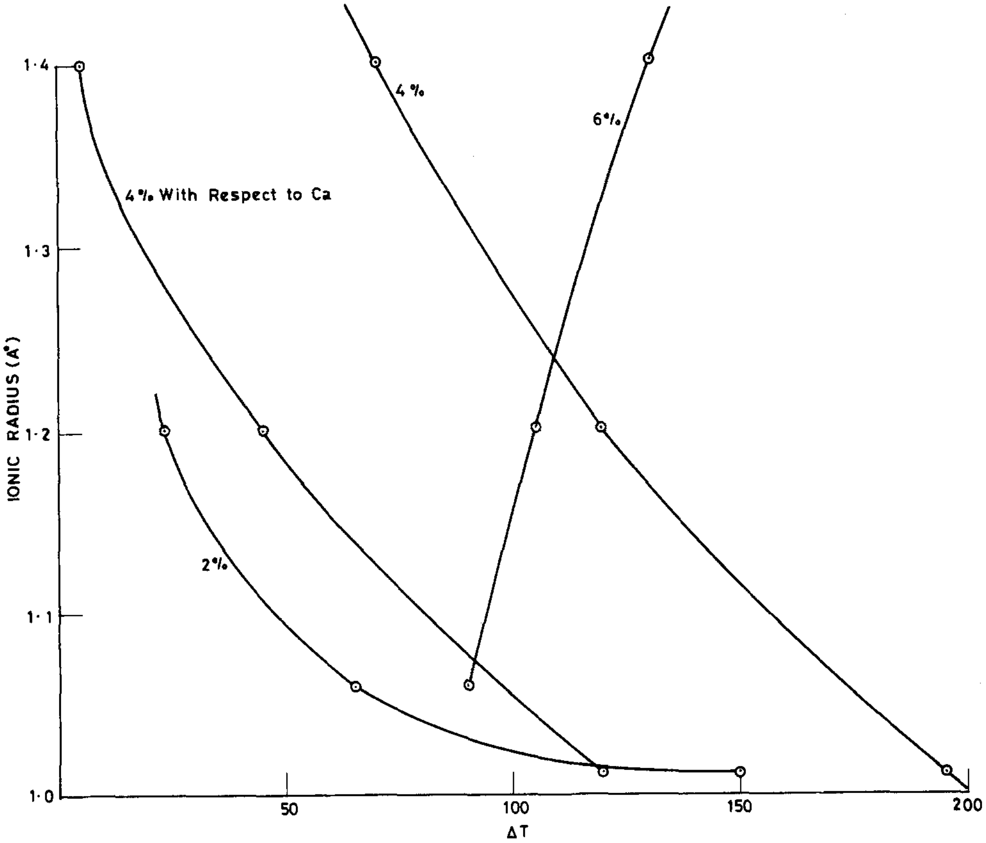

Figure 2 The dependence of ΔT on the ionic radii of the cations of the mineralisers under study.

obtained by subtracting the ΔT value of CaF_2 from those of SrF_2, BaF_2, etc.) is clearly seen.

Fig. 3 shows the effect of the addition of 2% of mineralisers on the formation of Ca_3SiO_5 (C_3S). [A] represents alite composition, i.e. 0.5% MgO and 0.25% Al_2O_3 was added to the batch together with CaF_2; [M] represents the batch containing $CaF_2 + CaHPO_4 + CaSO_4 \cdot 2H_2O + CrO_3$ (1:0.5; 0.5:0.5); and [O] represents the batch containing $CaF_2 + CaHPO_4$ (1:1). The batch containing the

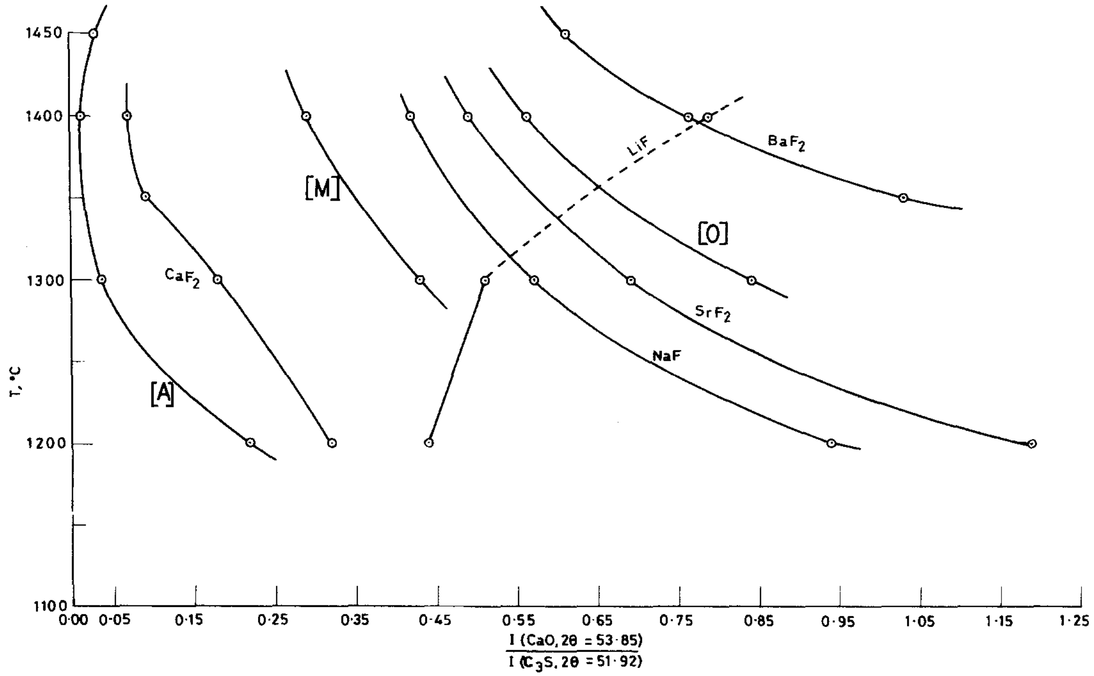

Figure 3 The formation of Ca_3SiO_5 with the addition of various mineralisers. The XRD line intensity ratio has been used.

TABLE II The time after which the first $M_{23}C_6$ carbides precipitated at grain boundaries were observed

Ageing temperature (° C)	Time (sec)	Ageing temperature (° C)	Time (sec)
500	7800	800	5–10
600	1800	900	2–5
700	30–40	1000	1–5

various mineralisers were introduced in a platinum vessel in a Quench Furnace (Stanton-Redcroft) at the sintering temperature (retention time = 1 h; air-quenched).

The kinetics of formation of C_3S are rapid when Al_2O_3 + MgO are added in addition to CaF_2. LiF appears to boil off from the batch at higher temperature.

References

1. S. N. GHOSH, A. K. PAUL and A. THAKUR, *J. Mater. Sci.* 13 (1978) 1602.
2. S. N. GHOSH, *ibid*, 13 (1978) 2739.

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On a growth mechanism for β phase silicon nitride

Boyer and Moulson have recently published [1] some very interesting results concerning the complicated reaction between silicon and nitrogen. The further clarification of the influence of many nitriding variables and impurities such as oxygen and iron is indeed welcome. It is also pleasing to see further evidence, along with other recent work [2], supporting the idea that the α- and β-phases do form by reactions which can be both kinetically