

Difference in enthalpies of decomposition of dolomite–ankerites in variable atmospheres

J.V. Dubrawski

BHP Research Newcastle Laboratories, PO Box 188, Wallsend, NSW 2287 (Australia)

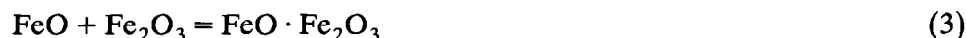
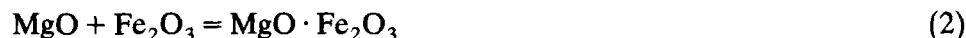
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Abstract

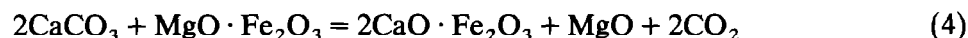
Decomposition enthalpies of minerals of the dolomite–ankerite group are influenced by atmosphere. Ferroan dolomites containing greater than about 0.2 molar ratio Fe produced lower enthalpies in flowing CO₂ compared with flowing N₂. The result is related to the extent of ferrite formation. However, the lowest enthalpy was obtained in O₂.

INTRODUCTION

The influence of atmosphere upon the thermal decomposition of dolomite–ankerites is well known [1–4]. In nitrogen for example, decomposition yields two partially resolved peaks for dolomite and generally three for ankerites. These peaks are completely resolved in carbon dioxide. For an Fe-substituted dolomite of general formulation Ca(Mg_x,Fe_{1-x})(CO₃)₂, initial decomposition produces CaCO₃, FeO, MgO and CO₂. Subsequently, the following reaction scheme occurs [5,6]



Reactions (1)–(3) account for the first, sometimes partially resolved, peak observed in DTA/DSC curves. At higher temperatures a second endotherm appears due to the reaction [5–7]



The dicalcium ferrite forms in proportion to the amount of Fe substitution in the decomposing mineral species. Finally, residual CaCO₃ breaks down to CaO producing a third strong endotherm. The enthalpies for the

Correspondence to: J.V. Dubrawski, BHP Research Newcastle Laboratories, PO Box 188, Wallsend, NSW 2287, Australia.

individual decomposition steps have been determined in CO_2 [5]. However, to date no comparison has been made regarding ΔH values obtained in these commonly used atmospheres, although values have been reported.

EXPERIMENTAL

Data described in this paper were taken from earlier reports [5,7] of DSC investigations of members of the dolomite–ankerite series in both flowing nitrogen and carbon dioxide. Their formulations are given in Table 1. Measurements were made using a Rigaku Denki 1500 thermal analyser in which samples were heated in platinum cups with loosely fitting lids.

RESULTS AND DISCUSSION

Figure 1 shows the plot of the enthalpy of decomposition ΔH for dolomite–ankerites, against their substituted Fe + Mn molar ratio. The manganese molar ratio was also included because it must also contribute to the thermal reactions of these carbonates [3].

Two lines of different slope are obtained. In nitrogen the enthalpy decreases less markedly with increasing Fe + Mn substitution than in carbon dioxide. The deviation, however, is not apparent (with the exception of the value in N_2 at 0.094Fe + Mn) up to the value of about 0.2 molar ratio substitution. Beyond this value the deviation results in ΔH being about 20 kJ mol^{-1} (about 10%) smaller in carbon dioxide atmosphere at an Fe + Mn value of 0.49, and would be expected to decrease further with increasing Fe content.

This result can be explained in terms of reactions (1)–(4), and in particular reaction (1). In N_2 , reaction (1) proceeds to the extent allowed by the partial pressure of CO_2 generated by the decomposing carbonate. As a result, only limited amounts of $\text{MgO} \cdot \text{Fe}_2\text{O}_3$ (reaction (2)), and

TABLE 1
Formulation of dolomite–ankerite minerals

Mineral sample	Molar ratio Fe + Mn	ΔH (kJ mol^{-1}) (N_2)	ΔH (kJ mol^{-1}) (CO_2)
$\text{Ca}_{1.03}\text{Mn}_{0.0016}\text{Mg}_{0.97}(\text{CO}_3)_2$	0.0016	290	289
$\text{Ca}_{0.98}\text{Fe}_{0.082}\text{Mn}_{0.012}\text{Mg}_{0.93}(\text{CO}_3)_2$	0.094	270	283
$\text{Ca}_{1.05}\text{Fe}_{0.15}\text{Mn}_{0.036}\text{Mg}_{0.77}(\text{CO}_3)_2$	0.18	267	270
$\text{Ca}_{1.02}\text{Fe}_{0.23}\text{Mn}_{0.059}\text{Mg}_{0.70}(\text{CO}_3)_2$	0.29	264	260
$\text{Ca}_{1.02}\text{Fe}_{0.42}\text{Mn}_{0.031}\text{Mg}_{0.53}(\text{CO}_3)_2$	0.45	253	233
$\text{Ca}_{1.00}\text{Fe}_{0.42}\text{Mn}_{0.032}\text{Mg}_{0.55}(\text{CO}_3)_2$	0.45	250	238
$\text{Ca}_{1.04}\text{Fe}_{0.49}\text{Mn}_{0.019}\text{Mg}_{0.45}(\text{CO}_3)_2$	0.51	247	226

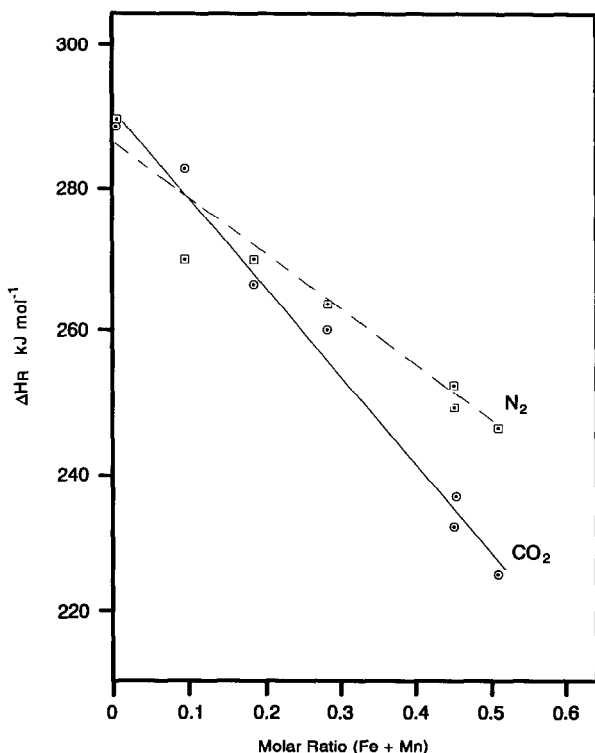


Fig. 1. Plot of decomposition enthalpy of dolomite-ankerites in N_2 and CO_2 , versus molar ratio Fe + Mn substitution.

subsequently $2CaO \cdot Fe_2O_3$ (reaction (4)) are produced. Consequently, extra $CaCO_3$ is left to decompose to CaO in a strongly endothermic reaction.

Conversely, in flowing CO_2 the FeO in reaction (1) reacts completely to form Fe_2O_3 . As a result the maximum amount of magnesioferrite and dicalcium ferrite form for a given Fe-substituted carbonate. This means that proportionally less $CaCO_3$ is left to break down to CaO , and the ΔH value is smaller.

In N_2 , the measured enthalpy is affected by gas diffusion and localised reaction effects, as well as by particle size. This may account for the poorer reproducibility of results in this atmosphere. In CO_2 , however, these factors are reduced because of the high partial pressure of the gas surrounding the sample grains throughout the entire temperature range. Naturally, at low levels of Fe + Mn substitution the differences are not observed because in any case the main portion of the enthalpy derives from the breakdown of the $MgCO_3/CaCO_3$ components. With dolomite, essentially no difference was observed.

It is also noteworthy that in O_2 the DSC curves of dolomite-ankerites are also altered [8], and the enthalpy is even more severely reduced. At an

Fe + Mn value of 0.49, the ΔH is calculated as about 170 kJ mol^{-1} . This can be explained by the fact that in O_2 , reaction (1) is overtaken by the rapid and strongly exothermic oxidation of FeO to Fe_2O_3 . Subsequently, dicalcium ferrite can still form. However, the result is that although the breakdown of the ankerites is still an endothermic process overall, ΔH is significantly offset by this exothermic step.

It is concluded that atmosphere has a significant effect on the heats of decomposition of iron-substituted carbonates, especially at the high-iron end of the series.

ACKNOWLEDGEMENT

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