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OXYSALT–METAL DOUBLE REACTIONS IN THE SOLID STATE: $Na_3Al(SO_4)_3$–Mg

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ABSTRACT

A method for obtaining the oxysalt $Na_6Mg(SO_4)_4$ by double reactions in Mg–$Na_3Al(SO_4)_3$ mixtures is proposed. When the mixtures are calcinated at temperatures in the range 600–900 °C in an argon stream or an open atmosphere, a sodium–magnesium sulphate and alumina are obtained.

A study of these double reactions has allowed us to establish that the mechanism of formation of the compound $Na_6Mg(SO_4)_4$ is an exchange reaction between MgO and $Na_3Al(SO_4)_3$.

In some cases, depending on the molar ratio Mg/Al, spinel $MgAl_2O_4$ is also formed.

INTRODUCTION

There are a number of double reactions in the solid state of the form

Reactant 1 + Reactant 2 = Product 1 + Product 2

in which Reactant 1 is a metal and Product 2 is another metal. These are known as displacement reactions. Examples of displacement reactions are

$Mg + ZnS \rightarrow MgS + Zn$ (ref. 1)

$Sn + CuO \rightarrow SnO + Cu$ (ref. 2)

$Co + Cu_2O \rightarrow CoO + 2Cu$ (ref. 3)

$3Mn + 2AlCl_3 \rightarrow 3MnCl_2 + 2Al$ (ref. 4)

A direct relation between reaction velocity and heat of reaction has been established through a comparative study of reactions of this type [5].

In these reactions, Reactant 2 is generally a sulphide, a halide or an oxide. As can be seen from examples given above, when the reaction is finished the metal Reactant 1 has formed a compound as oxide, sulphide or halide, and the metal of the compound Reactant 2 has been released: hence the term ‘displacement reactions’.

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The reactions between metals and oxysalts are less well understood. An example is the reaction between magnesium and silver sulphate. It has been found [6] that an explosion occurs when a mixture of these reactants is heated to 430 ° C, owing to structural transformation from the orthorhombic to the hexagonal crystal system. The reaction between powder wolfram and potassium dichromate is also strongly exothermic [7]. The reaction begins at 380–390 ° C and results in a dark residue, which was not identified by the authors of ref. 7.

We began the present investigation by preparing mixtures of powdered magnesium metal and anhydrous aluminium sulphate in the molar ratio $Mg/Al = 3/2$. These mixtures were heated isothermally for 1 h at several temperatures between 400 and 650 ° C in an argon stream or an open atmosphere. Analysis by X-ray powder diffraction of the residues of isothermal calcination at 400, 500 and 600 ° C indicated that reactions between the components had not taken place. However, at 650 ° C an explosion occurred which projected the sample away from the crucible.

This behaviour of the magnesium–aluminium sulphate mixture (very similar to that of the mixtures studied by Hedvall [6] and Charsley and Tolhurst [7] prevented us from carrying out a detailed study of the reaction, so we decided to use a double oxysalt as Reactant 2, expecting that the reaction of the magnesium with the aluminium sulphate would be less violent. In fact, we have studied several mixtures of magnesium and double sodium–aluminium sulphate in various molar ratios, and have identified the products obtained after the reactions.

EXPERIMENTAL

Materials

The materials used were: magnesium metal in powder form (Merck, AR grade); hydrated aluminium sulphate (Carlo Erba, AR grade) of formula $Al_2(SO_4)_3 \cdot 18.4H_2O$, deduced from the TG curve; anhydrous sodium sulphate (Merck, AR grade). Aluminium sulphate and sodium sulphate were dissolved in water in the molar ratio 1/3. The solution was evaporated and the solid residue calcinated at 500 ° C. It was found by X-ray diffraction that this residue was the double sodium–aluminium sulphate of formula $Na_3Al(SO_4)_3$. This compound is a non alum-type double sulphate, of m.p. 675 ° C [8]. Mechanical mixtures of magnesium metal and sodium–aluminium sulphate in the molar ratios 1/2, 3/2 and 5/2 were then prepared.

Apparatus

Thermogravimetry

A Chevenard thermobalance (model 93) from Adamel was used, with photographic recording and a heating rate of 5 K min^{-1}.

Differential thermal analysis

A home-made system involving a vertical furnace and a temperature regulation system, both from Adamel, was used, with a differential chromel–alumel thermopar and a heating rate of 5 K min^{-1}.

X-ray powder diffraction

A Philips PW 1130 diffractometer was used, with a Ni filter and Cu $K\alpha_1$ radiation.

Thermal study

Figure 1 shows TG and DTA curves obtained for the sodium–aluminium sulphate in an open atmosphere (curves (a) and (b), respectively). From curve (a) it can be seen that the sulphate is stable up to approximately 665 °C. At this temperature decomposition begins, occurring slowly at first and then more quickly from 865 °C. The X-ray diagram of a sample taken at 1000 °C (when decomposition has not yet finished) corresponds to a mixture of sodium sulphate (in two crystalline forms), aluminium sulphate, α-alumina and a small quantity of $Na_3Al(SO_4)_3$.

The DTA curve shows a plateau up to 640 °C. The double sulphate does not undergo any structural change before the sharp endothermic peak of fusion, with a maximum at 710 °C. Decomposition begins immediately thereafter, which confirms the data of the TG curve.

The TG curve (c) in Fig. 1 corresponds to magnesium. This curve shows a plateau up to 570 °C. Above this temperature there occurs an increase in the

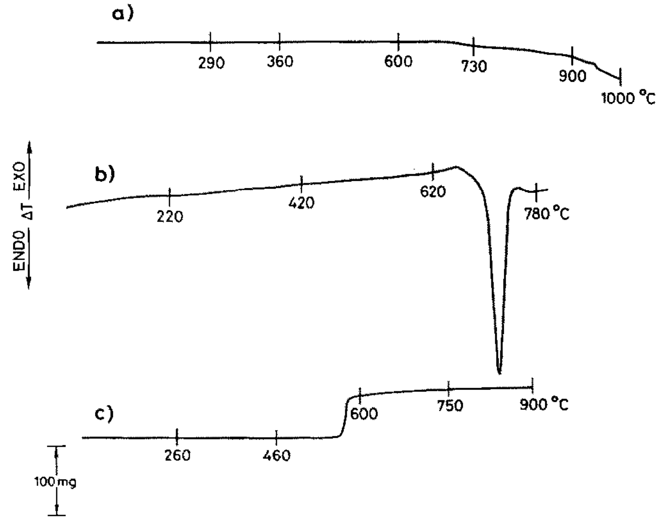

Fig. 1. TG and DTA curves in an open atmosphere: (a) TG and (b) DTA curves for sodium–aluminium sulphate (sample weight, 190.2 mg); (c) TG curve for magnesium metal (sample weight, 124.3 mg).

weight of the sample, owing to oxidation of the magnesium. TG calculations indicate transformation of the sample to MgO. The X-ray diffraction pattern of a sample of magnesium calcinated at 600 °C for 1 h in an open atmosphere also indicates that the sample has become MgO.

Solid mixtures of magnesium–double sulphate were calcinated for 1 h at 600, 700 and 900 °C. The experiments were carried out both in an open atmosphere and in an argon stream. The residues of these isothermal calcinations were then identified by X-ray diffraction.

RESULTS AND DISCUSSION

Mg/$Na_3Al(SO_4)_3$ mixture of molar ratio 1/2

Figure 2 shows the TG curve (a) in an open atmosphere. This curve is similar to that of the double sodium–aluminium sulphate (curve (a) in Fig. 1). A plateau up to approximately 660 °C indicates that no reaction has occurred. Between 660 and 900 °C the curve shows a weight loss of 16.3%. This loss is somewhat higher than that observed for the double sodium–aluminium sulphate (11.5%), owing to the presence of the Mg reactant.

The X-ray diagram for the sample taken at 900 °C indicates the presence of $Na_6Mg(SO_4)_4$, $Na_3Al(SO_4)_3$, MgO and α-Al_2O_3. Identification of the two oxides was difficult because of the overlapping of their lines with those of the double sulphates. In order to confirm the presence of MgO and α-Al_2O_3, water was added to the residue. A solution was obtained and a new solid residue, which was identified as a mixture of MgO and α-Al_2O_3. The

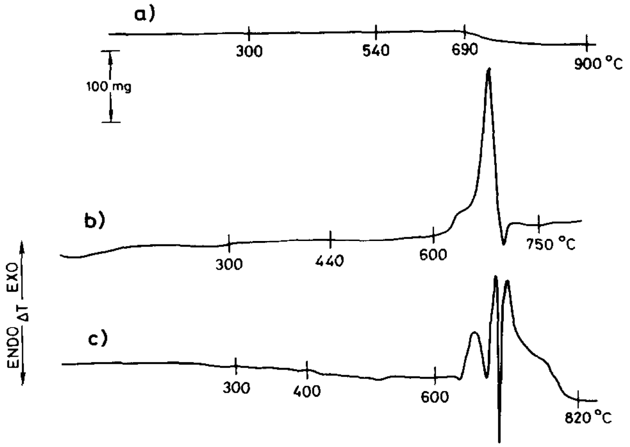

Fig. 2. Mg/$Na_3Al(SO_4)_3$ mixture of molar ratio 1/2: (a) TG and (c) DTA curves in an open atmosphere (sample weight, 193.8 mg); (b) DTA curve in an argon stream.

solution was evaporated and the residue analysed by X-ray diffraction. The X-ray diagram corresponded to a mixture of both double sulphates, with $Na_6Mg(SO_4)_4$ being the major component. As the thermal stability of the mixture is higher (~ 90 ° C) than that of the magnesium metal, it was decided to carry out an isothermal study at 600 ° C, in an open atmosphere and in an argon stream. The mixture was calcinated at a heating rate of 5 K min^{-1} up to 600 ° C, and then left for 1 h.

The X-ray diagrams for the samples at 600 ° C in the two atmospheres both correspond to a mixture of magnesium metal and double sodium–aluminium sulphate. Under these conditions, not only is the compound $Na_6Mg(SO_4)_4$ not formed, but the presence of double sodium–aluminium sulphate prevents the normal oxidation of the magnesium metal, as indicated in curve (c) of Fig. 1.

Isothermal studies were also carried out at 700 and 900 ° C, under the same conditions as for the 600 ° C experiments. The X-ray diagrams for the samples at 700 ° C in the two atmospheres both indicate that the double salt $Na_6Mg(SO_4)_4$ is being formed. The X-ray diagrams for the samples at 900 ° C in the two atmospheres show a mixture of $Na_6Mg(SO_4)_4$ and α-Al_2O_3. A secondary reaction takes place when the mixture is calcinated at 900 ° C for 1 h in the two atmospheres

$$1/3Na_3Al(SO_4)_3 + 1/6MgO \rightarrow 1/6Na_6Mg(SO_4)_4 + 1/6Al_2O_3 + 1/3SO_3 + 1/6O_2$$

and this completes the stoichiometry of the reaction between magnesium and the double sodium–aluminium sulphate.

Figure 2 also shows DTA curves for the mixtures in an open atmosphere and in an argon stream (curves (b) and (c), respectively). Both curves show a large exothermic peak (slightly displaced towards higher temperatures in the case of the argon stream) which includes several endothermic and exothermic phenomena: oxidation of the magnesium, melting and the beginning of decomposition of the double sodium–aluminium sulphate, and formation of $Na_6Mg(SO_4)_4$.

The results obtained with an open atmosphere and with an argon stream are similar, which confirms the existence of an oxidant other than air, the SO_3, which arises from decomposition of the sodium–aluminium sulphate.

In our opinion, the results described above indicate that with the oxysalt a reaction of substitution of the aluminium by the magnesium cation, as occurs in displacement reactions, does not take place; rather, Al_2O_3 formed by the decomposition of the oxysalt is displaced by the MgO previously formed.

$Mg/Na_3Al(SO_4)_3$ mixture of molar ratio 3/2

Figure 3 shows the TG curve (a) for an open atmosphere. This curve is somewhat different from curve (a) of Fig. 2, owing to the higher proportion

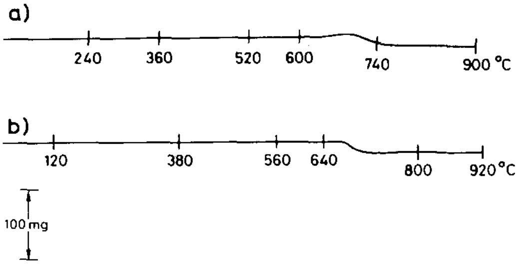

Fig. 3. TG curves in an open atmosphere: (a) Mg/$Na_3Al(SO_4)_3$ mixture of molar ratio 3/2 (sample weight, 183.8 mg); (b) Mg/$Na_3Al(SO_4)_3$ mixture of molar ratio 5/2 (sample weight, 182.4 mg).

of magnesium present. The TG curve shows a weight increase (resulting from oxidation of the magnesium) and a plateau from 850 °C which indicates that the reaction has finished.

The X-ray diagram for the residue taken at 900 °C indicates the presence of $Na_6Mg(SO_4)_4$ as the only sulphate, together with magnesium oxide and traces of $MgAl_2O_4$.

This residue was treated with water and a white insoluble solid was obtained. The X-ray diagram for this solid indicated a mixture of MgO, Al_2O_3 and $MgAl_2O_4$. Although the temperatures of formation of spinel from the two oxides are higher than 1200 °C it is possible, under different conditions, to obtain spinel at temperatures of 1000 °C or lower [9]. In our case, both oxides are recently formed, and therefore they were very reactive.

The X-ray diagrams for the residues of calcination at 700 °C in an open atmosphere and in an argon stream correspond to a mixture of $Na_6Mg(SO_4)_4$, MgO and Al_2O_3.

Isothermal calcination was also carried out at 900 °C in an open atmosphere and in an argon stream. The X-ray diagram for the residue in an open atmosphere indicates a mixture of $Na_6Mg(SO)_4$, MgO, Al_2O_3 and $MgAl_2O_4$. This last compound is obtained by reaction of Al_2O_3 with MgO. The X-ray diagram for the residue in an argon stream shows the above-mentioned mixture and Na_2SO_4.

Mg/$Na_3Al(SO)_3$ mixture of molar ratio 5/2

Figure 3 shows the TG curve (b) in an open atmosphere. This curve is very similar to that obtained for the 3Mg/2Al mixture. The reaction finished at 850 °C, and the X-ray diagram of the residue taken at 930 °C shows a mixture of $Na_6Mg(SO)_4$, MgO and $MgAl_2O_4$. The absence of Al_2O_3 can be explained because all of this compound has reacted with the magnesium oxide, which is in a higher proportion than in the 3Mg/2Al mixture.

The residues of the isothermal calcinations at 700 ° C in the two atmospheres were found to consist of $Na_6Mg(SO)_4$, Al_2O_3 and MgO.

The composition of the residue of isothermal calcination at 900 ° C depends on the atmosphere in which the calcination is carried out. Thus, in an open atmosphere the residue has the same composition as that indicated by the TG curve: $Na_6Mg(SO)_4$, MgO and $MgAl_2O_4$. In an argon stream, by contrast, the components are Na_2SO_4, MgO and $MgAl_2O_4$. In this case, the double sodium–magnesium sulphate is not formed. This is because in this mixture, with Mg/Al being in molar ratio 5/2, the magnesium disposes of the only source of oxidation, the SO_3 liberated in the dissociation of the sodium–aluminium sulphate. At this temperature, the dissociation is so advanced that the reaction

$$SO_3 + Mg \rightarrow MgO + SO_2$$

uses up all the SO_3 present in the sample, and formation of the double sodium–magnesium sulphate cannot take place.

Finally, when the proportion of metal to double sodium–aluminium sulphate is increased, the temperature of formation of the double sodium–magnesium sulphate is decreased. Thus, when this molar ratio is 3/2 or higher the reaction is complete at 700 ° C, as against 900 ° C when the molar ratio is 1/2.

On the other hand, when the mixtures are richer in magnesium, spinel is formed through a secondary reaction at 900 ° C between the alumina and the magnesium oxide which arise from previous reactions: the first by dissociation of the sodium–aluminium sulphate, and the second by oxidation of the magnesium.

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