

MAGNESIUM SALT DECOMPOSITION AND MORPHOLOGICAL DEVELOPMENT DURING EVAPORATIVE DECOMPOSITION OF SOLUTIONS *

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ABSTRACT

The effect of magnesium salt on the morphological development of MgO powders synthesized by the evaporative decomposition of solutions (EDS) technique is presented. Thermal analysis at 10 and 100 °C min⁻¹ was used to determine the effect of increased heating rate on the decomposition temperatures of Mg(C₂H₃O₂)₂·4 H₂O, MgCl₂·6 H₂O, and Mg(NO₃)₂·6 H₂O. Full decomposition to MgO powder was only achieved during EDS with magnesium acetate and magnesium nitrate. The decomposition of the chloride precursor during EDS was incomplete as a result of kinetic limitations imposed by the high heating rate (~ 300 °C s⁻¹) associated with the EDS process. Generally, the particle morphology consists of large aggregates when produced from the chloride and nitrate salts. However, fine, dispersed, sub-micrometer particles are formed from magnesium acetate under oxidizing conditions. These differences are demonstrated to be a direct result of the decomposition path of the magnesium salt.

INTRODUCTION

The thermal decomposition of metal salts is important for the synthesis of ceramic powders. Solution techniques such as coprecipitation [1], sol-gel [2], freeze drying [3], and spray drying of salt solutions [4] offer the advantages of ease of preparation, accurate compositional control, homogeneity (atomic scale mixing), and high purity. Each of these techniques involves mixing and/or reacting metal salts in solution. Following solvent removal, the salt or precipitated oxide precursors are decomposed in a separate step to form the oxide powder.

Another non-solid state powder synthesis method which incorporates both oxide precursor formation and controlled decomposition in a single process

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is the evaporative decomposition of solution (EDS) [5] or spray roasting [6,7] technique. In this process, a salt solution is atomized to form a spray of droplets which traverse through a heated furnace. Initially, the droplets dehydrate, causing the precipitation of the salt particles which subsequently decompose in the furnace to form an oxide powder.

Although a large number of water soluble salts are available as precursor material, there has been little study of their effect on powder synthesis during EDS. Thus, the objective of this study was to relate the thermal decomposition characteristics of some magnesium salts to the synthesis of MgO by EDS.

EXPERIMENTAL

American Chemical Society certified $\text{Mg}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 4 \text{H}_2\text{O}$, $\text{MgCl}_2 \cdot 6 \text{H}_2\text{O}$, (both from J.T. Baker, Co., Phillipsburg, NJ 08865) and $\text{Mg}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$ (from Baker, Co., and Fisher Scientific Co., Chemical Mfg. Division, Fairlawn, NJ 07410) were used throughout this study. The decomposition characteristics of the salts were determined by differential thermal analysis

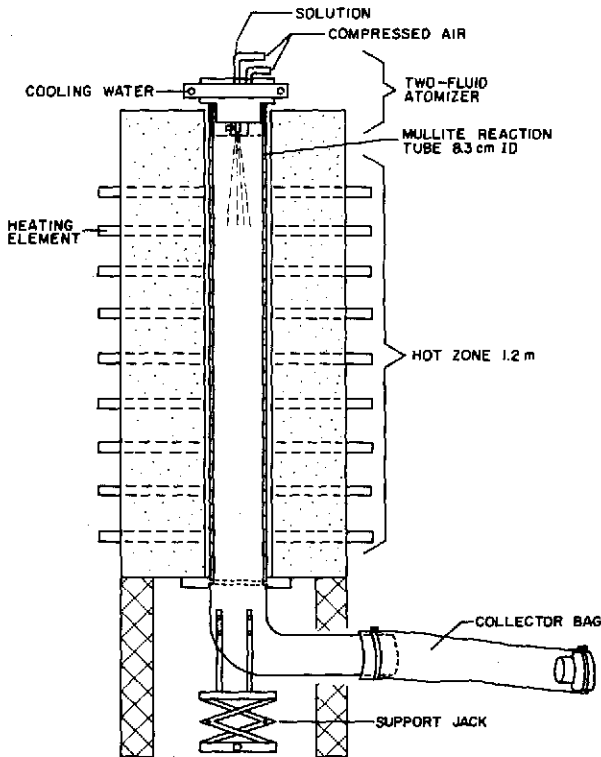


Fig. 1. Schematic diagram of the EDS apparatus.

(DTA; DuPont 1600 °C differential thermal analysis cell) and thermogravimetric analysis (TGA; DuPont Model 951, thermogravimetric analyzer). A sample heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$ was used with a purge gas of either air or N_2 at a flow rate of 250 ml min^{-1} . The samples were also tested at the maximum programmable heating rate of $100\text{ }^{\circ}\text{C min}^{-1}$ to simulate the effect of the heating conditions on salt decomposition during EDS. The DTA module was calibrated against the melting points of tin ($232\text{ }^{\circ}\text{C}$) and gold ($1063.5\text{ }^{\circ}\text{C}$) standards. The temperature correction required between these two temperatures was approximated by the microcomputer in the thermal analysis system (DuPont 1090 thermal analyzer) using linear interpolation. Salt samples of $32.5 \pm 0.5\text{ mg}$ were placed in platinum sample cups and analyzed relative to a 31.7 mg alumina standard. For TGA experiments, $32.5 \pm 0.5\text{ mg}$ salt samples were analyzed in platinum pans. Sample weight ($\pm 0.01\text{ mg}$) relative to the initial salt weight was measured as a function of sample temperature.

Each salt was dissolved in deionized water at room temperature to form a 1 M solution which was atomized into the EDS furnace (Fig. 1) with a two-fluid atomizer. For all experiments, the salt solution flow rate was 4 ml min^{-1} and the atomizer gas (air or N_2) pressure was 0.13 MPa, yielding a median droplet size of $\sim 10\text{ }\mu\text{m}$ [8]. The nominal furnace temperature ranged from 500 to $1000\text{ }^{\circ}\text{C}$, and a furnace atmosphere of air or N_2 was provided by the atomizing gas. Upon exiting the reaction chamber, the powder was collected from the exhaust gas with a cotton jet mill bag.

RESULTS AND DISCUSSION

Thermal analysis

The thermal analyses of $\text{Mg}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 4\text{ H}_2\text{O}$ heated at $10\text{ }^{\circ}\text{C min}^{-1}$ in flowing N_2 and air are shown in Fig. 2. The reactions can be divided into dehydration (A) processes for temperatures less than $200\text{ }^{\circ}\text{C}$ and decomposition (B) and other type reactions for temperatures greater than $200\text{ }^{\circ}\text{C}$. After completion of the dehydration of the salt, an exothermic reaction occurs at $235\text{ }^{\circ}\text{C}$, which is independent of reaction atmosphere. This fact and the absence of any weight loss suggests that this is the recrystallization of amorphous, anhydrous magnesium acetate as hypothesized by McAdie and Jervis [9].

Comparison of the thermal analyses at temperatures greater than $235\text{ }^{\circ}\text{C}$ clearly indicates that the decomposition of the anhydrous acetate is atmosphere dependent as evidenced by the exothermic decomposition in the presence of an oxidizing atmosphere (i.e., air), whereas decomposition in the N_2 atmosphere follows a multiple stage endothermic reaction with peak temperatures at 325 and $365\text{ }^{\circ}\text{C}$. Since no weight loss is observed at $325\text{ }^{\circ}\text{C}$,

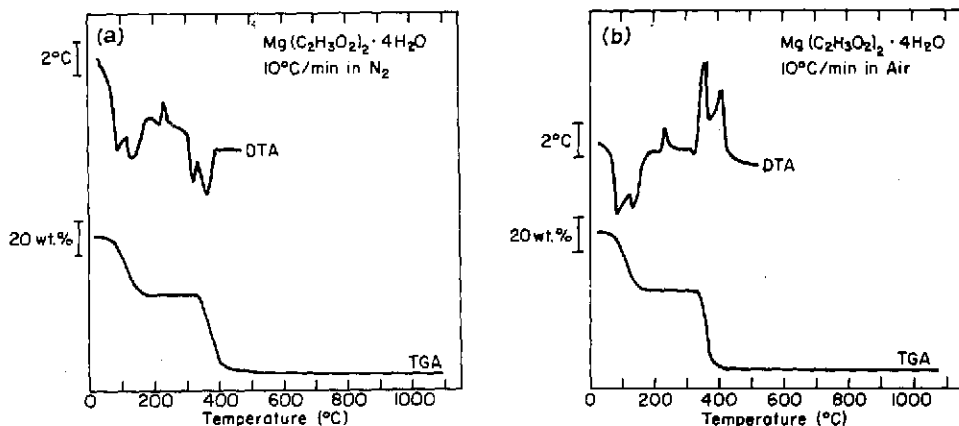
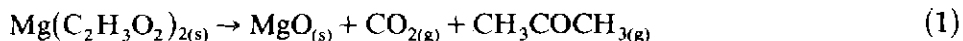


Fig. 2. Thermal analysis of $\text{Mg}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 4 \text{H}_2\text{O}$ heated at $10^\circ\text{C min}^{-1}$ (a) in N_2 and (b) in air.

it is believed that the anhydrous acetate melts which is in agreement with earlier reports [9]. The peak at 365°C results from the endothermic decomposition of the acetate radical with its decomposition at temperatures greater than 400°C characterized by a slow, gradual weight loss. This is possibly associated with the pyrolysis of a carbonaceous residue in the sample, which would have slow decomposition kinetics in an inert atmosphere. The temperature of full decomposition, as determined from the completion of the weight loss with respect to sample temperature, is 575°C . TGA did not indicate the presence of any stable intermediate phases during the decomposition of $\text{Mg}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 4 \text{H}_2\text{O}$ in a N_2 atmosphere, contrary to the findings of Yakerson et al. [10] and Bernard and Busnat [11]. It is concluded that the overall decomposition reaction



is in agreement with that suggested by McAdie and Jervis [9].

In oxidizing conditions, the initial decomposition is characterized by a small endothermic peak at $\sim 330^\circ\text{C}$. As suggested above, this is probably the melting of the anhydrous acetate salt. When the sample reaches 360 and 400°C the exothermic oxidation of the acetate radical occurs. Apparently, the exothermic processes mask any endothermic decomposition processes over this temperature range. The temperature of full decomposition under these conditions is 400°C , which is significantly less than that observed for the decomposition of the acetate salt in a N_2 atmosphere. This large difference is attributed to the additional heat provided by the exothermic nature of the oxidation reaction.

The thermal analysis results for $\text{MgCl}_2 \cdot 6 \text{H}_2\text{O}$ heated at $10^\circ\text{C min}^{-1}$ in air and N_2 atmospheres are equivalent, and therefore only the thermal analyses obtained in air are presented in Fig. 3. The processes which occur

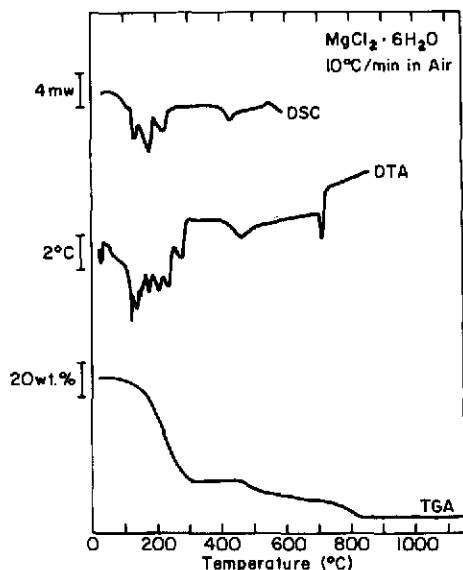


Fig. 3. Thermal analysis of $\text{MgCl}_2 \cdot 6 \text{H}_2\text{O}$ heated at $10^\circ\text{C min}^{-1}$ in air.

during the heating of $\text{MgCl}_2 \cdot 6 \text{H}_2\text{O}$ can be divided into three general types of reactions: dehydration (A) at temperatures less than 300°C , rehydrolysis or decomposition (B) at temperatures ranging from 400 to 800°C , and melting (C).

Re-hydrolysis or decomposition reactions involving anhydrous MgCl_2 are highly dependent on the partial pressure of water vapor during decomposition. DSC and DTA indicate peak temperatures of 425 and 460°C , respectively, and at 450°C TGA shows the existence of a stable intermediate phase after 62.5 percent weight loss from the initial hydrated salt. This corresponds to a salt composition of $\text{Mg}(\text{OH})\text{Cl}$ and its formation according to the following equation [12]



The sharp endothermic peak at 710°C without a corresponding weight loss is due to the melting of anhydrous MgCl_2 , which has a reported melting point at 714°C [13]. Since anhydrous MgCl_2 melts within the sample, the reaction shown in eqn. (2) is not complete at this temperature. Thus, residual MgCl_2 undergoes direct re-hydrolysis or decomposition according to the following equation [12]

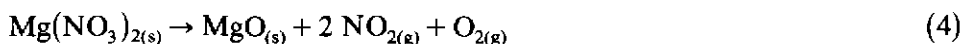


The general reaction during EDS is probably a combination of reactions (2) and (3) as proposed by Dutt et al. [12] This is supported by the identification of both $\text{Mg}(\text{OH})\text{Cl}$ and MgCl_2 in samples at various stages of decomposition. The derivative of the sample weight loss with respect to

temperature shows that the final stage of decomposition has a peak temperature of 805 °C, with the temperature of full decomposition equal to 830 °C.

The thermal analyses of $\text{Mg}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$ heated at $10^\circ\text{C min}^{-1}$ in air and N_2 atmospheres are equivalent, and therefore only the results obtained in air are presented in Fig. 4. These results can be divided into two general types of reactions: dehydration (A) at temperatures less than 350°C , and decomposition (B) at temperatures greater than 350°C .

The decomposition of $\text{Mg}(\text{NO}_3)_2$ occurs by a multiple-stage endothermic reaction. Initially, an endothermic peak, possibly associated with the melting of the anhydrous $\text{Mg}(\text{NO}_3)_2$, occurs at 425°C , without a corresponding sample weight loss. The main decomposition process has a peak temperature of 450°C and the temperature of full decomposition is 500°C . TGA did not indicate the existence of any stable intermediate phases in the decomposition process, contrary to the findings of Oza and Mirza [14], who suggested that $\text{Mg}(\text{NO}_2)_2$ formed during decomposition. The overall decomposition reaction was assumed to be in agreement with that proposed by Stern [15]



An increase in sample heating rate can be expected to increase the peak temperature and the peak intensity of reactions due to kinetic effects. Each salt precursor was thermally analyzed by DTA and TGA at a programmed heating rate of $\sim 100^\circ\text{C min}^{-1}$. For all salts, the average sample heating rate was $120^\circ\text{C min}^{-1}$ for the DTA module and $107^\circ\text{C min}^{-1}$ for the TGA module. Although the actual sample heating rates are different for the two

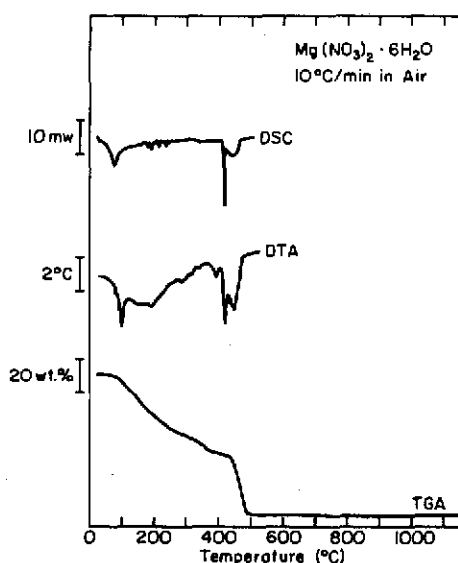


Fig. 4. Thermal analysis of $\text{Mg}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$ heated at $10^\circ\text{C min}^{-1}$ in air.

techniques, the relative shift in peak temperatures and temperatures of full decomposition should be comparable.

The effect of increased sample heating rate is shown in Fig. 5 for $\text{Mg}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 4 \text{H}_2\text{O}$ analyzed at $100^\circ\text{C min}^{-1}$ in air. In comparison with Fig. 2, the peak temperatures have shifted to higher temperatures and peak intensities have increased by at least a factor of two. DTA shows an endothermic dehydration with a peak temperature at 180°C , an endothermic decomposition with a peak temperature at 375°C , and an exothermic decomposition with a peak temperature at 445°C . From TGA, the temperature of full decomposition has increased from 400 to 500°C , a result of the increased heating rate.

When $\text{MgCl}_2 \cdot 6 \text{H}_2\text{O}$ was heated at $\sim 100^\circ\text{C min}^{-1}$ in air, the dehydration reactions overlap to form two endothermic peaks at 250 and 295°C , (Fig. 6), with the re-hydrolysis or decomposition peak temperature shifting to 530°C . The melting point of the anhydrous MgCl_2 (715°C) is unaffected by the change in heating rate. A small endothermic DTA peak associated with the final stage of decomposition to MgO is observed to have a peak temperature of 1117°C . Peak intensities have increased by at least a factor of five and the temperature of full decomposition has increased to 1080°C from the 830°C observed at $10^\circ\text{C min}^{-1}$.

When $\text{Mg}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$ is heated at $100^\circ\text{C min}^{-1}$ in air the dehydration reactions overlap to form one large endothermic peak at 235°C , and decomposition is a single stage endothermic reaction with a peak temperature at 490°C (Fig. 7). Peak intensities have increased by a factor of ten as a

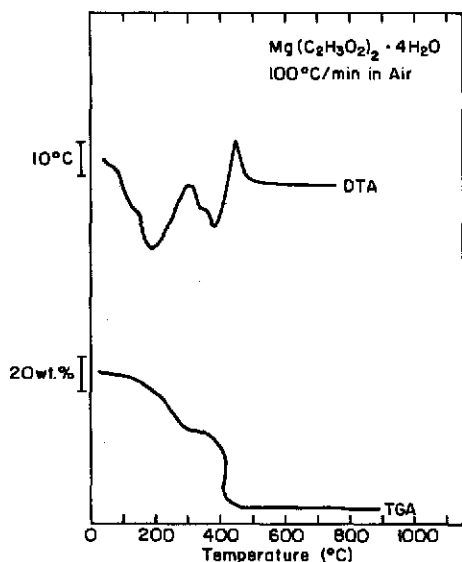


Fig. 5. Thermal analysis of $\text{Mg}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 4 \text{H}_2\text{O}$ heated at $100^\circ\text{C min}^{-1}$ in air.

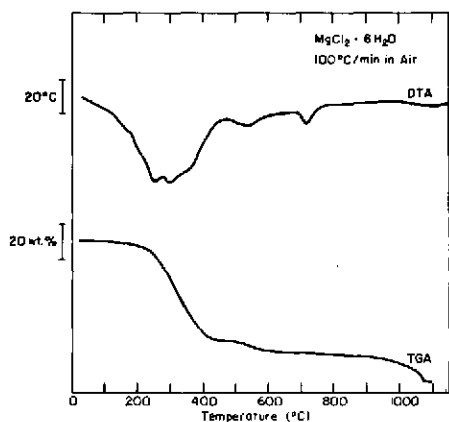


Fig. 6. Thermal analysis of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ heated at $100^\circ\text{C}/\text{min}$ in air.

result of the increased sample heating rate and the temperature of full decomposition has increased from 500 to 610°C .

In general, the temperature of full decomposition increases by 100 to 250°C as the sample heating rate is increased from 10 to $100^\circ\text{C}/\text{min}$. The magnitude of the increase in the temperature of full decomposition depends on the decomposition reaction kinetics, with a larger increase associated with those salts with slower reaction kinetics. From the thermal analyses, it can be concluded that the acetate and nitrate salts are preferable precursors for EDS powder synthesis since full decomposition can be achieved at fairly low temperatures ($\sim 650^\circ\text{C}$) with rapid heating rates ($\sim 100^\circ\text{C}/\text{min}$). Since

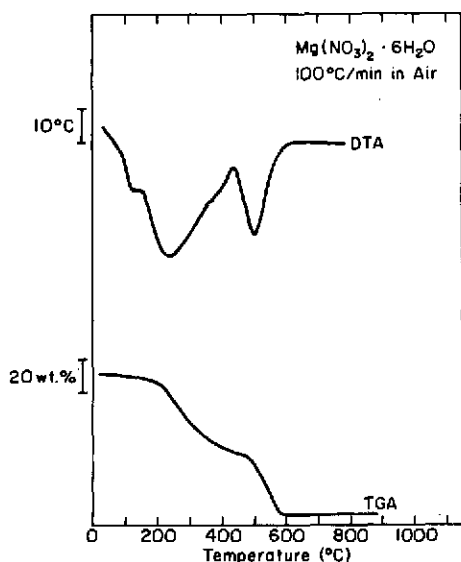


Fig. 7. Thermal analysis of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ heated at $100^\circ\text{C}/\text{min}$ in air.

the effective heating rate of a salt droplet/particle during the EDS process has been estimated at $\sim 300^\circ\text{C s}^{-1}$ [16] complete decomposition of the chloride and sulfate precursor salts would not be expected since the maximum reaction temperature of the EDS furnace is 1000°C .

EDS results

At an EDS reaction temperature of 1000°C , only partial decomposition of the chloride salt occurred. The particle morphology of the chloride-derived powder consisted of fractured, hollow spherical particles. However, two distinct particle microstructures are observed at higher magnification. In Fig. 8 a fractured spherical particle with a “crystal fur” at the surface is shown. This morphology arises from the entrapment of a saturated MgCl_2 solution within the dried crust and its escape, when the sphere fractures, to form the needle-like morphology at the particle surface [17]. The smooth texture of the solid particle suggests that the anhydrous MgCl_2 crust melts during EDS.

In contrast to the chloride-derived powders, the nitrate salt was fully decomposed to form MgO during the EDS process. A low magnification SEM photomicrograph of the nitrate-derived powder prepared at a reaction temperature of 1000°C is shown in Fig. 9a. The particles consist of hollow spherical shells and shell fragments. This type of morphology is consistent with the observations of Charlesworth and Marshall [17] for spray dried inorganic salt solution droplets. Fracture of the shells arises due to the

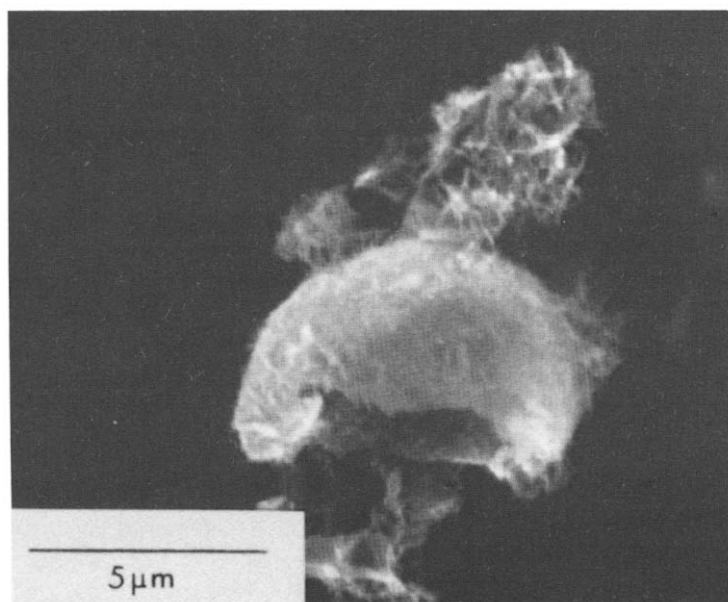


Fig. 8. SEM photomicrograph of the chloride-derived powder showing the precipitation of MgCl_2 “crystal fur” at the particle surface.

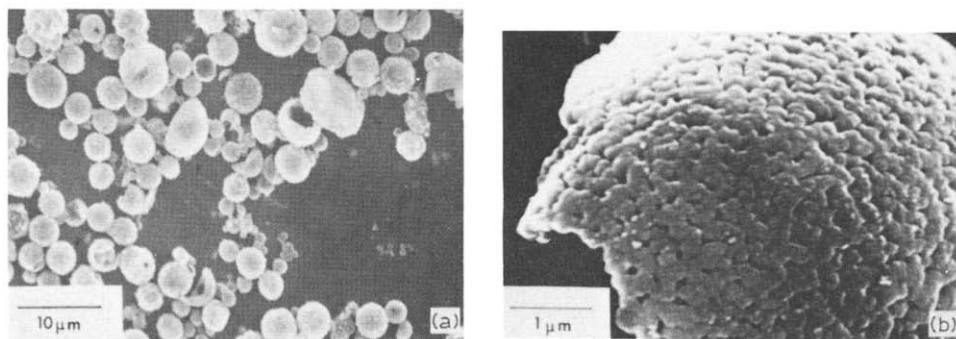


Fig. 9. SEM photomicrograph of the nitrate-derived powder prepared at 1000 °C. (a) Low magnification; (b) high magnification.

development of a positive vapor pressure from the evaporation of liquid within the precipitated salt crust. At higher magnification (Fig. 9b) each shell is seen to consist of an aggregate of small MgO particles which are less than 0.25 micrometers in size. Because of the high EDS temperature relative to the decomposition of magnesium nitrate, the MgO particles have sintered together to give a strong aggregate.

Magnesium acetate was completely decomposed during the EDS process at 875 °C in an air atmosphere. A SEM photomicrograph (Fig. 10) of the acetate-derived powder is completely different from the morphology observed for the nitrate-derived MgO. This powder consists of individual, unaggregated 0.1 to 0.3 micrometer MgO particles. To explain the difference in morphology between the acetate and nitrate-derived powders, the decomposition paths of the precursor salts must be considered. It is suggested that even though a hollow, spherical dried salt aggregate is originally generated

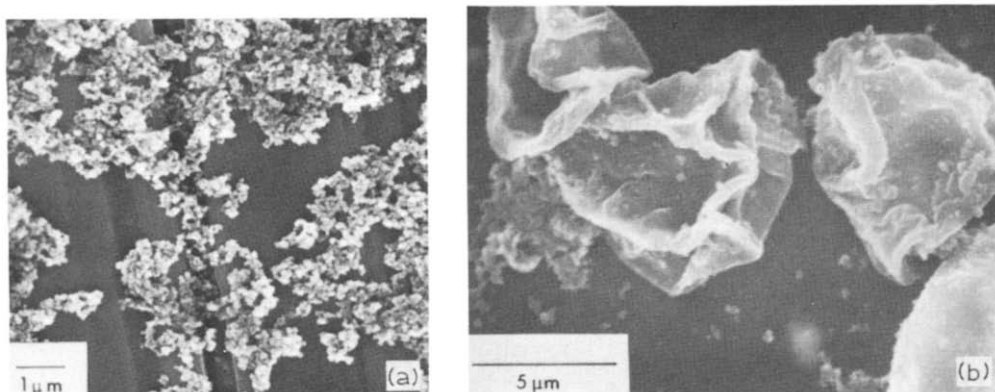


Fig. 10. SEM photomicrograph of the acetate-derived powder prepared in air at (a) 1000 °C and (b) 750 °C.

during the EDS process, the exothermic oxidation of the acetate radical and carbonaceous residue during decomposition caused fragmenting of the aggregate into individual MgO particles that are free from strong interparticle contacts. Indeed, this yields MgO powder with desirable characteristics for ceramic applications [18].

Further evidence for the above argument is presented in Fig. 10b. The spherical shell has obviously collapsed and may be attributed to the melting of the anhydrous salt. Since decomposition is not complete at 750°C, this morphology must exist just prior to the exothermic oxidation of the acetate radical. Thus, it is concluded that the exothermic oxidation reaction is critical to the attainment of the individual, unaggregated particles shown in Fig. 10a.

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