JOURNAL OF MATERIALS SCIENCE 26 (1991) 3004–3008

Secondary grain growth in ammonium nitrate crystallization

K. V. RAMANA RAO, P. L. HARIHARAN
IDL-NitroNobel Basic Research Institute, P. B. No. 397, Malleswaram, Bangalore 560003, India
D. K. CHAKRABARTY
Department of Chemistry, Indian Institute of Technology, Bombay 400076, India

Crystallization and ageing of pure ammonium nitrate crystals was studied by scanning electron microscopy. Ageing the crystals beyond 1 h led to the growth of secondary grains along the grain boundaries of primary grains (140–200 μm). After 6 h ageing secondary growth along grain boundaries was not observed; instead, distinct clusters with morphologies similar to the secondary grains were formed. The ancillary growth obeys approximately the parabolic relation $L = (Kt)^{1/n+1}$ where $n = 1$ justifies grain growth in the pure crystals, and its formation is ascribed to the dissolution of dendrites, edges and corners. The high interfacial activity and interparticle voids can affect the storage and mechanical properties of the material.

1. Introduction

Ammonium nitrate (AN) is a common high-explosive ingredient. Based on their different morphologies, we have recently classified AN prills into three categories: porous, irregular and dense, and assessed their explosive behaviour in the ammonium nitrate–fuel oil (ANFO) system [1]. The origin and kinetics of secondary grain growth observed on several dense prills is not well known. In the present work, attempts were made to understand the mechanism and kinetics of the secondary grain growth in ammonium nitrate grown from solution and to relate it to the prills.

2. Experimental procedure

2.1. Purification of AN crystals

Because impurities [2, 3] influence the crystallization of AN, high-purity material was employed in the present work. The following impurities were present in the crystals (Nice reagent): non-volatile matter 0.05% max., chloride (Cl) 0.002% max., sulphate (SO_4) 0.01% max., iron (Fe) 0.0005% max., and lead (Pb) 0.0005%.

The crystals were purified by recrystallization in conductivity water (14 MΩ) and the presence of metal ions checked by polarography. Because metal ion impurities were not detected in the crystals these were employed in the crystallization experiments.

2.2. Crystallization and ageing

AN is highly soluble in water. At 293 K, 100 ml water dissolves 185 g salt to yield a 23.5 M solution and the dissolution is endothermic. A supersaturated solution of 33 M was prepared at 343 K in several beakers and was allowed to cool slowly to room temperature to induce precipitation. The precipitated crystals were allowed to ripen in the mother liquor for different periods varying from 30 min to 6 h. The crystals were filtered under suction to drain trapped mother liquor, dried in an air oven at 373 K and stored in vacuum desiccators.

2.3. Characterization by SEM

Morphological observations on crystallized and ripened AN crystals were conducted on a scanning electron microscope (SEM), model JSM 35CF, Jeol, Japan. SEM samples were prepared by conventional methods, such as mounting the material on specimen studs using double-sided adhesive tape and coating with gold–palladium alloy, 12 nm thick, in an argon ambient of 8–10 Pa in a Polaron sputter-coating unit. Growth kinetics were studied by estimating average particle size from various micrographs recorded on different aliquots of aged crystals and the same micrographs were also used to assess the morphology.

3. Results and discussion

The general crystallization of polydisperse AN with dendritic arms and faceted tips is shown in Fig. 1. In the early stages of ripening the crystals had dendritic nature (Fig. 1a). With increasing ripening their morphologies tend to become round, plate-like and form faceted tips (Fig. 1b). Ageing beyond 4 h (Fig. 2) resulted in crystals with spherical and rectangular shapes. Agglomerates and aggregates were observed at all stages of coarsening.

Ageing the crystals for more than 1 h caused the growth of minute secondary grains along the grain

0022–2461/91 $03.00 + .12

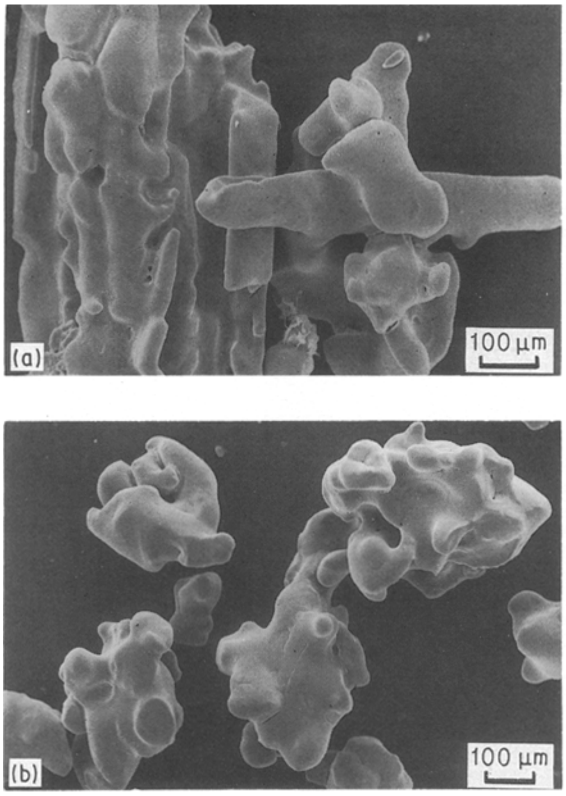

Figure 1 Crystallization patterns in aged AN crystals: (a) 0.5 h, dendrites; (b) 1 h, faceted tips.

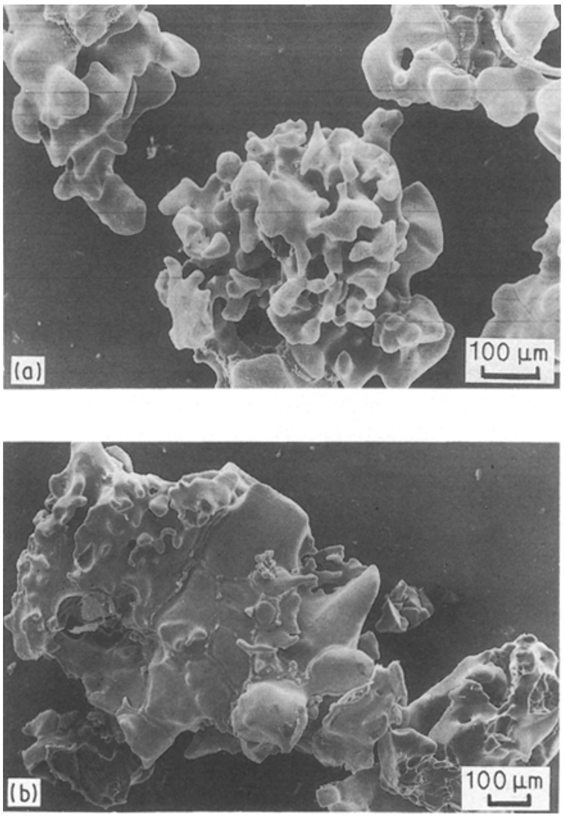

Figure 2 Crystallization patterns in AN crystals aged beyond 6 h. (a) Spherical clusters, (b) approximately plate-like morphology.

boundaries of larger primary grains which had acquired a critical size of about 140–200 μm (equivalent diameter) as shown in Fig. 3. The polydisperse precipitates with edges, corners and dendritic features are thermodynamically unstable in the mother liquor because of their large interfacial area which is a source of free energy. Hence they dissolve and grow on the stable crystals and initiate the ripening process (Ostwald). The extent of secondary grain growth increases as a function of ageing and follows the trend shown in Table I.

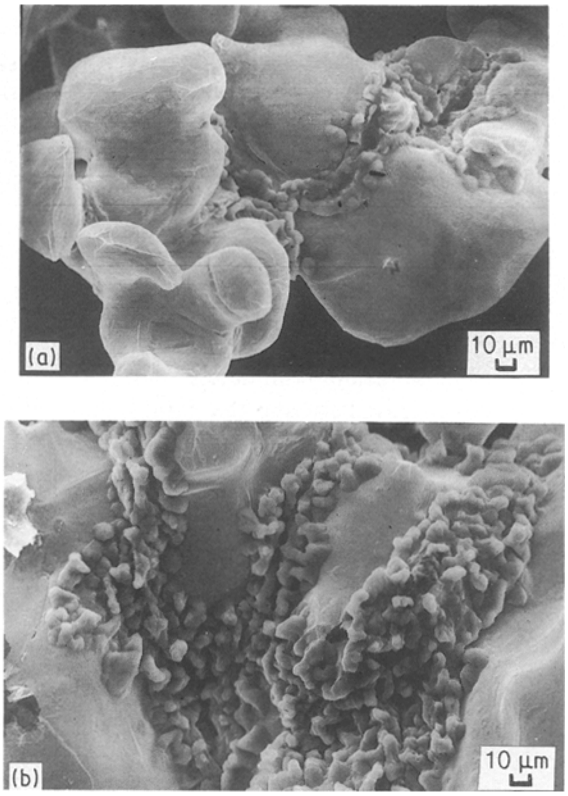

Figure 3 Ripening of secondary grains (necklace structure) along primary grains after (a) 1.5 h, (b) 4 h.

The secondary growth was not observed at the grain boundaries at 6 h ageing. However, distinct clusters (Fig. 2a) were observed with morphologies quite similar to the secondary grains. It seems likely that after formation by optimization of factors related to their growth the clusters are dislodged from the grain boundaries. The dimensions of the clusters were taken into consideration for assessing the growth and kinetics.

The dendrites in crystals of ammonium salts have high interfacial area, high free energy and generate periodic or quasi periodic growth forms [4–7]. It is well known that the mechanism of dendritic fragmentation and dissolution accelerates ancillary crystal

TABLE I Extent of secondary growth and *D*/*d* ratio as a function of ageing

Ageing (h)	Secondary growth (%)	Ratio of size of large grains to secondary grains (*D*/*d*)
0.5	–	–
1	< 5	–
1.5	30	18
2	50	37
4	70	20
6	80	24

growth in systems which involve dendrites [8]. Hence it is quite plausible that even in AN crystals, the formation, breakdown and dissolution of dendrites, gives impetus to secondary grain growth. In addition to edges and corners, dendrites, after dissolution, precipitate at grain boundaries of larger crystallites which, having acquired sizes of about 140–200 μm, are quite stable and provide sites for nucleation and crystal growth.

The profuse growth at the grain boundaries of larger crystals may be explained on the basis of interfacial strain at grain boundaries and reduction of interfacial energy between the larger and minute grains. The interfaces between the grains are regions of strain and imperfection and hence they can be regarded as potential sites for crystal growth. Thus nucleation is promoted in the vicinity of dislocations and grain boundaries because it relieves tension and facilitates processes such as diffusion, orientation and relaxation during crystal growth [9]. It is these factors which prompt crystals with high interfacial energy after dissolution, to precipitate at the grain boundaries. Because the secondary growth is not observed on all boundaries it seems that its mechanism is governed by the factors enumerated above and that growth occurs preferably on those locations where these factors are favourable.

The presence of the grain boundaries has a stabilizing role on the nucleation and grain growth. In the absence of these surfaces the minute grains would require a high energy of activation to achieve critical size and coalesce. The strained grain boundaries provide sites for the attachment of nuclei of minute sizes which subsequently ripen to minimize their interfacial energy. Without the surface it is inconceivable that the nuclei will be stable as they have to attain higher critical sizes to attain stability. On the grain boundaries the grains of AN can crystallize under conditions where (1) their tendency to dissolve is minimum and (2) they would not be able to undergo homogeneous nucleation. Based on this perspective the secondary growth can be regarded as heterogeneous nucleation.

The coarsening of the larger grains is also promoted by the reduction of interfacial energy between larger and smaller grains. Assuming approximately spherical shapes, if D is the average diameter of the larger grains and d is the average diameter of the smaller grains, σ_{S-L} is the interfacial tension between smaller and larger grains, σ_{S-S} is the interfacial tension between smaller grains, for the growth of the large grains [10, 11]

$$D > 2\frac{\sigma_{S-L}}{\sigma_{S-S}} d \qquad (1)$$

During ageing the larger grain grows by the absorption of smaller grains. The smaller grains with their higher interfacial energy grow at the boundaries of the larger grains to reduce their free energy. Over a period of 6 h the size of the secondary grains increase as a result of continuous ripening (Fig. 4). The formation of a chain of secondary grains on the boundaries of primary grains may be termed a "necklace" structure.

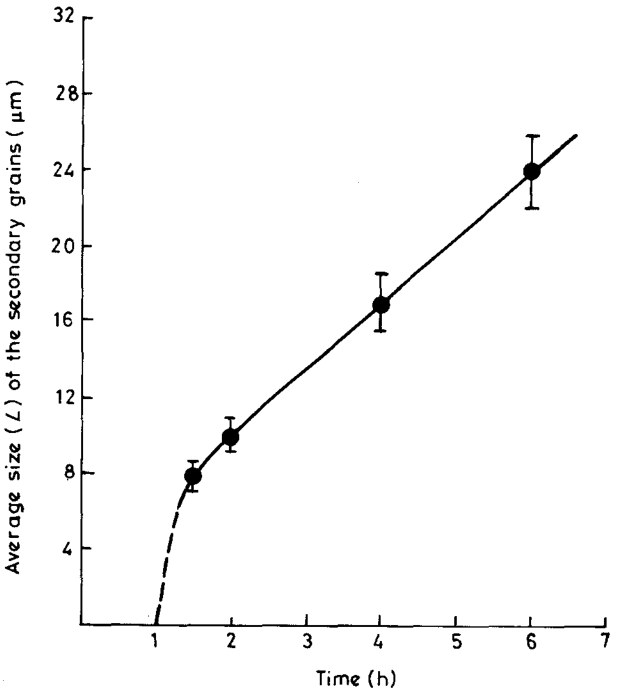

Figure 4 Secondary grain growth as a function of ageing.

The thrust for the grain growth is apparent from the ratio D/d which varies from 18–37 (Table I).

The secondary grain growth in AN crystallization follows an approximately parabolic relation as

$$L^2 = Kt \qquad (2)$$

where L is the average diameter of the secondary grains, t is the time of ripening and K is the kinetic parameter. This equation is quite similar to the relation which describes the grain growth in many pure substances [12].

The L^2–t plot as shown in Fig. 5 is a straight line, whose slope yields the kinetic constant $K = 28.125 \times 10^{-3}\ \mu m^2\, s^{-1}$. The deviation from linearity of the plot may arise due to two causes: (1) the estimation of average grain size from micrographs and (2) the paucity of crystals of high interfacial area for dissolution. It is difficult to estimate the average grain diameter accurately as the majority of them are non-spherical and the micrographs could not be recorded at higher magnification (> × 1000) because the crystals were prone to damage by electron beam. If the regeneration of dendritic arms or corners or faceted tips is not fast enough, then in some instances of ripening there may not be sufficient crystals for dissolution and secondary growth. Hence, these factors may cause non-linearity in the L^2–t plot.

Equation 2 above resembles the familiar equation [13] which relates grain growth and time

$$L = (Kt)^{1/n+1} \qquad (3)$$

In commercial substances the value of $(n + 1)$ ranges from 3–6 where the larger value is attributed to the influence of grain growth by impurities. In this study, because the value of $n = 1$, it justifies the secondary grain growth in the pure AN crystals.

The process of secondary grain growth can be visualized in three stages: (1) initial growth of corners,

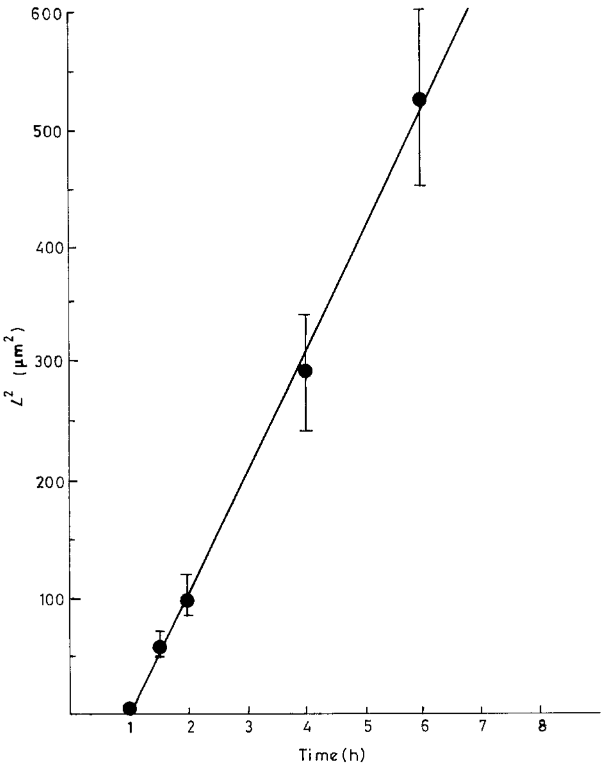

Figure 5 Kinetics of secondary growth.

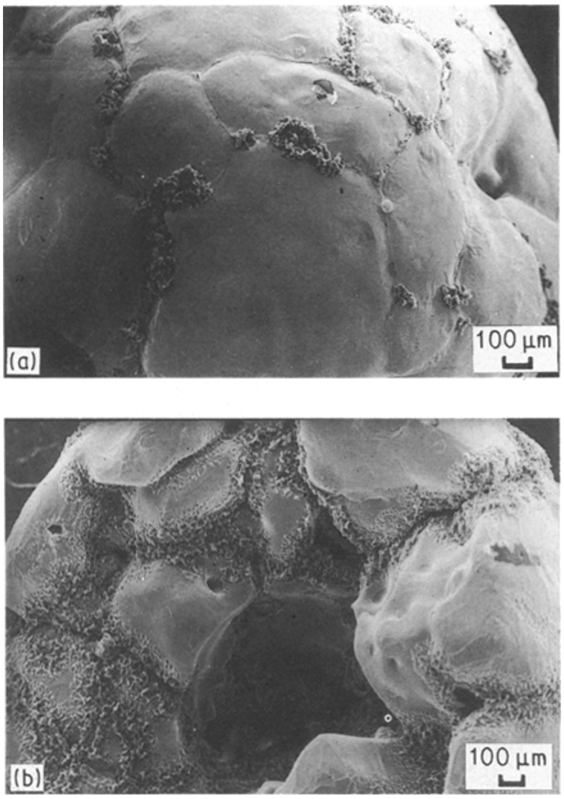

Figure 6 Secondary grain growth in dense prills: (a) external surface, (b) internal surface.

edges and dendrites which undergo dissolution, (2) nucleation followed by precipitation at grain boundaries, and (3) coarsening and morphological changes in crystals to form aggregates and agglomerates. The dashed line in Fig. 4 indicates the inception of secondary growth which was observed microscopically after 1 h ageing. Although it is quite likely that the growth is initiated below 1 h, due to experimental limitations such as interaction of the electron beam with the crystals at high resolutions, it was not possible to record the phenomenon. The non-spherical habits of the secondary grains even beyond 6 h ageing imply that the grains have appreciable surface activity which causes precipitation as a chain of agglomerates and aggregates (necklace structure).

Typical secondary grain growth is observed in dense commercial AN prills (Fig. 6) which are formed by spray-drying highly concentrated AN solution at high temperature. Rapid cooling of the concentrated solution can generate polydisperse crystals with large interfaces which, being unstable, dissolve and grow on the boundaries of primary grains. Because AN is hygroscopic the secondary growth augments its hydrophilic nature and thereby causes caking in the crystals. The higher interfacial activity of the minute grains can initiate ripening by fusing two or more prills together. Therefore, the secondary growth in the crystals may affect the storage and explosive property of prills in ANFO applications. The porous morphology of the secondary grains can localize stress and affect mechanical properties such as toughness and attrition [1].

4. Conclusions

The nature and kinetics of secondary grain growth in AN crystals were studied and attributed to the dissolution and regeneration of dendritic arms, corners and faceted tips. Ripening the crystals for more than 1 h led to secondary grain growth along the boundaries of primary grains. The growth kinetics reveal a simple parabolic relation which yields a kinetic constant $K = 28.125 \times 10^{-3}$ μm^2 s^{-1}. The secondary growth occurs to relieve strain at grain boundaries and to minimize the interfacial tension between the grains. The presence of such ancillary growth in commercial AN prills is likely to affect its storage and mechanical properties in explosive applications.

Acknowledgements

The authors thank IDL Chemicals Ltd, for permitting the publication of this work, gratefully acknowledge the suggestions of Mr R. Vedam, General Manager, INBRI.

References

1. K. V. RAMANA RAO, P. L. HARIHARAN, K. JAGANNATHAN and S. R. YOGANARASIMHAN, *Fuel* **68** (1989) 1118.
2. T. SRAMKO and E. JONA, *Thermochim. Acta* **92** (1985) 731.
3. C. N. R. RAO, B. PRAKASH and M. NATARAJAN, in "Crystal structure transformations in Inorganic nitrites, nitrates, and carbonates", NSRDS Report, US Department of Commerce, National Bureau of Standards. May 1975, pp. 24–30.

4. H. FREDRICKSON, *Mater. Lett.* **5** (1987) 414.
5. R. J. SCHAFFER, *J. Crystal Growth* **43** (1978) 17.
6. N. GOLDENFELD, *J. Power Sources* **26** (1989) 121–128.
7. ELI RAZ, S. G. LIPSON and E. POLTURAK, *Phys. Rev. A* **40** (1989) 1088.
8. H. FUREDI-MILHOFER and A. G. WALTON, in "Dispersion of powders in liquids", edited by G. D. Parfitt (Applied Sciences, London, 1981) pp. 203–72.
9. W. J. DUNNING, in "Particle growth in suspensions", edited by A. L. Smith (Academic Press, London, 1973) pp. 3–28.
10. R. A. LAUDISE, "The growth of single crystals" (Prentice Hall, NJ, 1970) pp. 121.
11. HERMANN SCHMALZRIED, "Solid state reactions" (Verlag Chemie, Weinhein, 1981) pp. 153–63.
12. I. M. LIFSHITZ and V. V. SLEZOV, *J. Phys. Chem. Solids* **19** (1961) 35.
13. L. H. VAN VLACK, "Materials Science for Engineers" (Addison-Wesley, Massachusetts, 1970) pp. 183.

Received 24 April
and accepted 4 September 1990