

Technical Note

Hydrothermal curing of lead/acid battery positive plates

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Abstract

The curing process is the longest step in the manufacture of lead/acid batteries. In this work, curing of lead/acid battery pastes is undertaken by a hydrothermal method with the aim of shortening the duration of the process. The effects of curing temperature, time and atmosphere on the composition and toughness of the positive plates are investigated. Both the latter parameters are found to be strongly influenced by these curing conditions. In particular, the strength of positive plates prepared either in the presence of water vapour or in an atmosphere containing O₂ and water vapour is lowered with increasing temperature and time. This is due to the formation and growth of large tetrabasic lead sulphate (4PbO·PbSO₄) crystals. By contrast, if the hydrothermal curing is conducted in an atmosphere containing CO₂ and water vapour, plate strength is increased as a result of the formation of small crystals of PbCO₃ and a reduction in the number of large 4PbO·PbSO₄ crystals.

Introduction

The lead/acid battery continues to be the most important electrochemical system for energy storage. Its economy has not been surpassed by any other system [1]. When using pasted positive plates, curing is the most time-consuming stage in battery manufacture. The following processes occur simultaneously during curing: (1) recrystallization of basic lead sulphates (major paste constituent is tribasic lead sulphate, 3PbO·PbSO₄·H₂O) and lead oxide to form a matrix of strongly interconnected crystals; (2) corrosion of the grid, whereby the contact between the grid and the paste is enhanced;

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(3) oxidation of free-lead particles in the paste to give PbO (an exothermic process from which the released heat maintains the plate temperature above ambient and thereby causes the processes taking place during curing to proceed at a higher rate); (4) evaporation of water from the paste resulting in drying of the plates [2].

In classic technology, curing is performed at 40 °C for 72 h, including 24 h at 100% relative humidity [3]. It is known that moisture is necessary for the exothermic oxidation of metallic lead and that heat is required to evaporate the moisture from the plate. When this oxidation process proceeds at a higher rate, a greater amount of heat is released. Naturally, this raises the plate temperature and causes water to evaporate more rapidly from the paste. Under such conditions, the extent of lead oxidation will decrease before curing is completed. On the other hand, if the temperature is increased and an appropriate humidity is maintained, the curing processes will be enhanced and will probably enable the process time to be shortened.

This paper describes investigations of the effects of hydrothermal curing conditions on the composition and toughness of positive plates.

Experimental

Positive paste was prepared by mixing leady oxide with H₂O, H₂SO₄, and certain additives. Table 1 gives the composition of the leady oxide which was produced in a ball mill. The composition of the positive paste is presented in Table 2. The apparent density of the paste was 4.2 g cm⁻³ and the water content was 12 wt.%. The paste contained mainly α -PbO and 3PbO·PbSO₄·H₂O, together with some β -PbO, 4PbO·PbSO₄, Pb₃(CO₃)₂(OH)₂ and Pb. (Note, α -PbO is also referred to as tet-PbO, and β -PbO as orthorhomb-PbO). The paste composition will depend upon the holding time. The lead content in

TABLE 1
Composition of leady oxide (wt.%)

Sample	α -PbO	β -PbO	Pb
1	69.5	0.7	29.8
2	65.6	4.9	29.5

TABLE 2
Composition of positive paste (wt.%)

Sample	α -PbO	β -PbO	3PbO·PbSO ₄ ·H ₂ O	4PbO·PbSO ₄	Pb ₃ (CO ₃) ₂ (OH) ₂	Pb
1	50.8	15.4	18.5	11.2	2.6	1.5
2	29.6	12.5	43.7	6.1	4.2	3.9
3	29.8	23.5	27.5	6.5	5.2	7.5

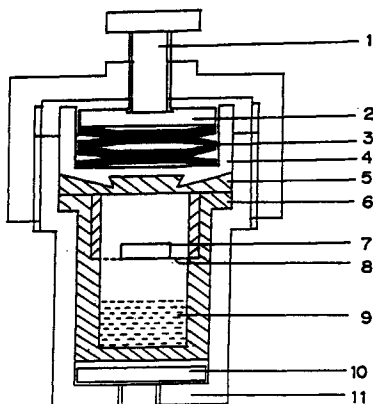


Fig. 1. Autoclave for hydrothermal curing of positive plates: (1) spring holding bolt; (2) disc for pressing spring; (3) dish-type spring; (4) well-type spring case; (5) Teflon packing; (6) Teflon liner; (7) test sample; (8) Pt mesh; (9) water or solvent solution; (10) bottom disc; (11) stainless steel body.

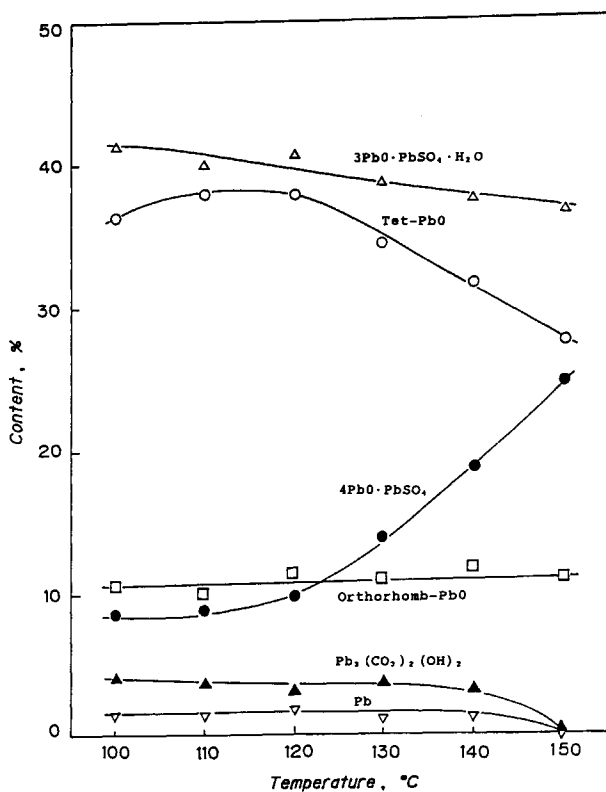


Fig. 2. Effect of curing temperature on composition of positive plates.

the paste is lower than in the starting oxide because metallic lead is oxidized during the mixing process.

Commercial grids made from Pb-0.1wt.%Ca alloy were pasted with paste no. 2. Two sizes of grid were used, namely, $28 \times 28 \times 3$ mm and $12 \times 17 \times 3$ mm. The positive plates were cured in an autoclave under hydrothermal conditions.

The autoclave is shown schematically in Fig. 1 [4]. It is made of stainless steel and has a cylindrical chamber with a Teflon liner of 30 mm i.d. A test sample of positive plate was placed on a platinum mesh inside the chamber and 10 ml water, or solvent solution, was introduced into the bottom of the vessel. The autoclave was heated to a desired temperature in a convection oven and then the curing process was carried out in the presence of water vapour. After curing, the autoclave was cooled down to room temperature

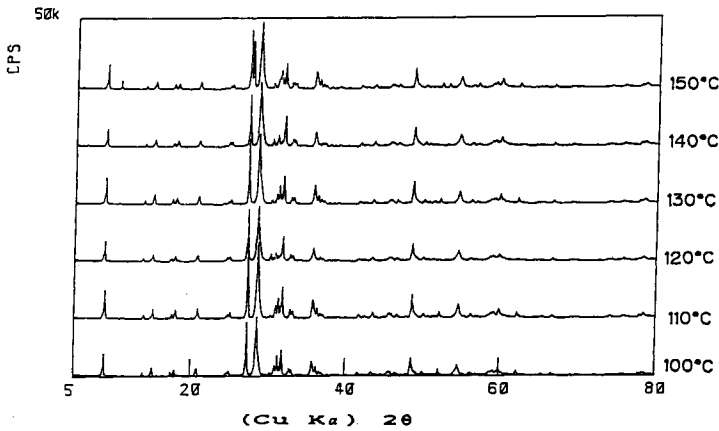


Fig. 3. X-ray diffraction patterns of cured paste at different temperatures.

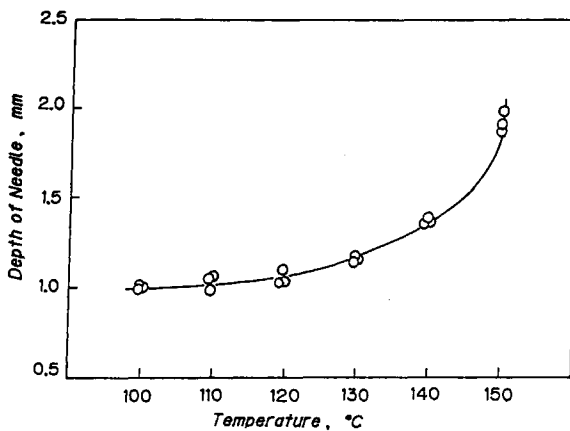
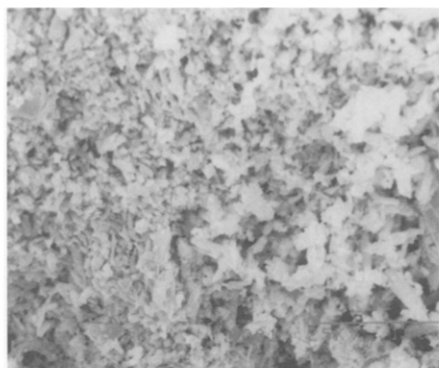
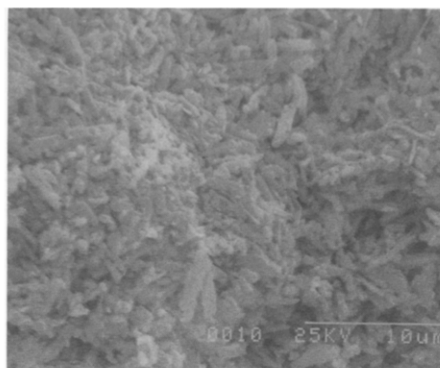


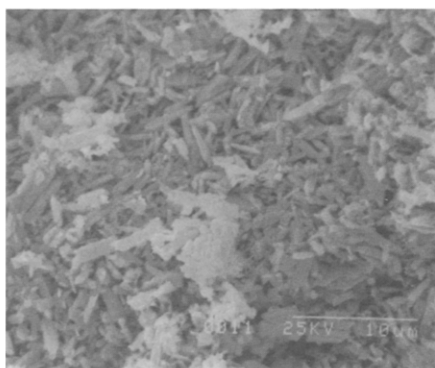
Fig. 4. Effect of curing temperature on the toughness of positive plates (conditions of needle depth test: falling weight 50 g; drop distance 36 mm).



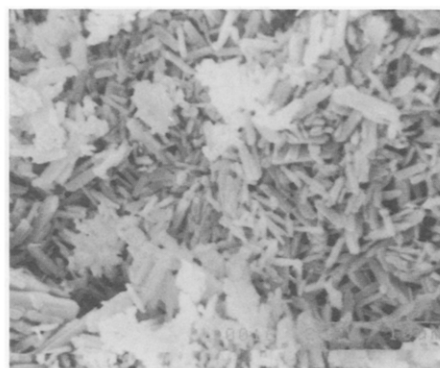
(a)



(b)



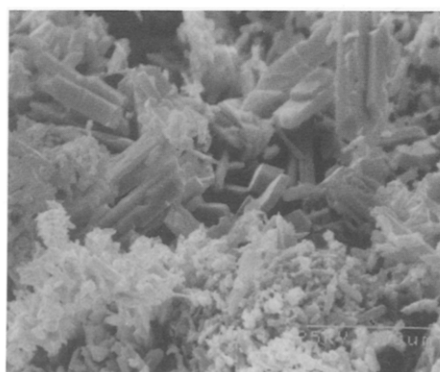
(c)



(d)



(e)



(f)

Fig. 5. Electron micrographs of paste structure and crystals after curing at the different temperatures indicated. (a) 100; (b) 110; (c) 120; (d) 130; (e) 140; (f) 150 °C.

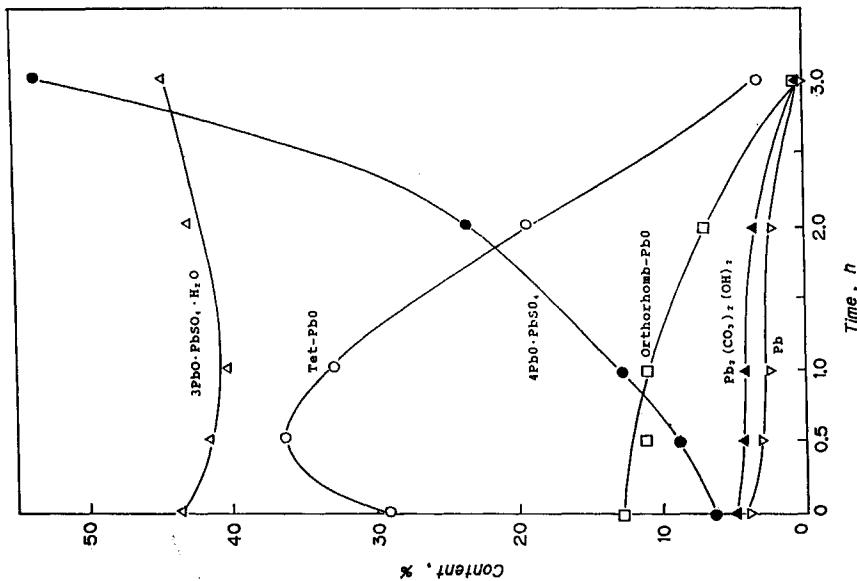


Fig. 6. Effect of curing time on the composition of positive plates under hydrothermal conditions at 100 °C.

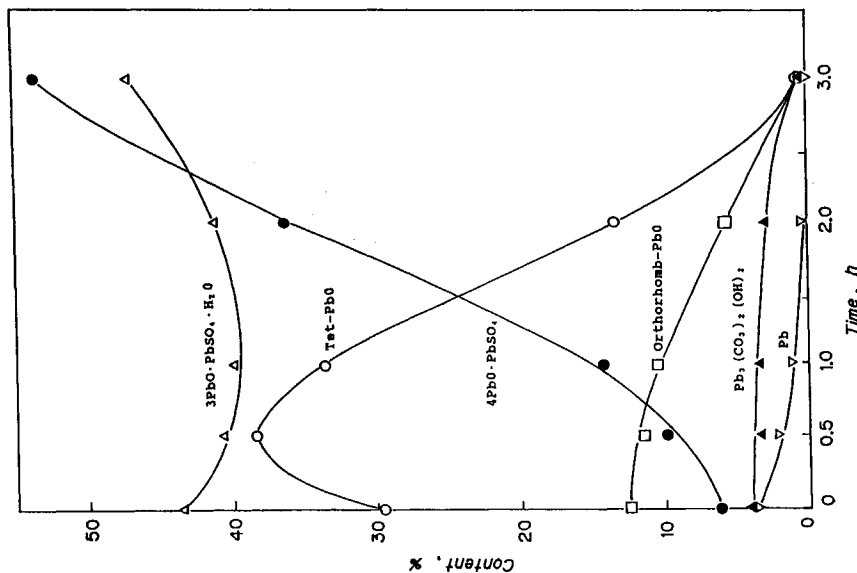


Fig. 7. Effect of curing time on the composition of positive plates under hydrothermal conditions at 120 °C.

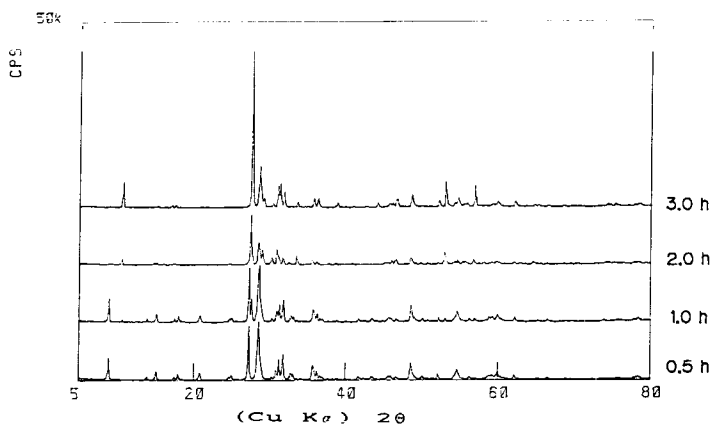


Fig. 8. X-ray diffraction patterns of cured paste at 100 °C for different curing times.

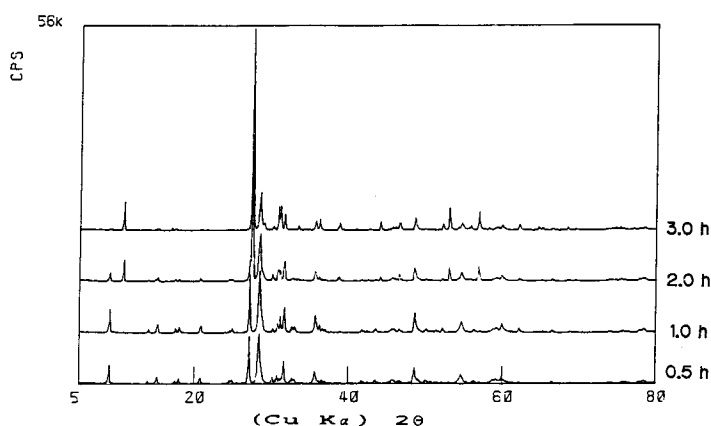


Fig. 9. X-ray diffraction patterns of cured paste at 120 °C for different curing times.

by an electric fan. The cured sample was removed and dried in air at 100 °C for 1 h.

The composition of both cured and dried samples was obtained by X-ray powder diffraction (XRD) analysis. The fractured surface of the samples was examined in a scanning electron microscope, while the toughness of the samples was determined by measuring the depth of the impression made by dropping a weighted needle on to the plates.

Results and discussion

Effect of curing temperature

Curing was performed at different temperatures within the range 100 to 150 °C for 0.5 h in the presence of water vapour. The changes in phase composition are shown in Fig. 2 and the XRD patterns are given in Fig. 3. Increasing temperature results in the growth of $4\text{PbO} \cdot \text{PbSO}_4$ and a decrease

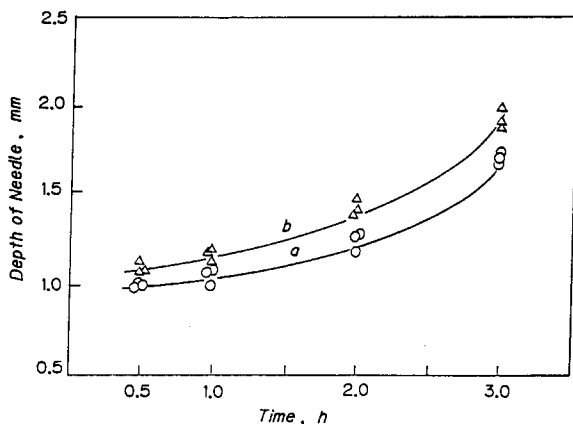


Fig. 10. Effect of curing time on the toughness of positive plates under hydrothermal conditions: (a) 100 °C; (b) 120 °C.

in the amount of $3\text{PbO} \cdot \text{PbSO}_4 \cdot \text{H}_2\text{O}$. At the same time, the amount of α -PbO decreases, the β -PbO content remains almost unchanged, and the levels of $\text{Pb}_3(\text{CO})_3)_2(\text{OH})_2$ and Pb gradually decline to zero at 150 °C.

Results obtained from the needle-depth test on positive plates cured at different temperatures are shown in Fig. 4. It can be clearly seen that above 120 °C, the toughness of the plates decreases with further increase in curing temperature.

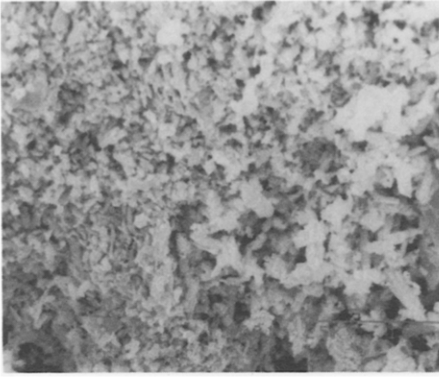
Electron micrographs of the structure and crystal morphology of positive pastes cured at different temperatures are presented in Fig. 5. The prismatic crystals of $4\text{PbO} \cdot \text{PbSO}_4$ gradually grow in size at higher curing temperatures. By contrast, the proportions of small-sized crystals of various shapes (probably α -PbO and $3\text{PbO} \cdot \text{PbSO}_4 \cdot \text{H}_2\text{O}$) are gradually decreased by conversion into $4\text{PbO} \cdot \text{PbSO}_4$. The large prismatic crystals of $4\text{PbO} \cdot \text{PbSO}_4$ have a small contact area. This weakens the interconnection between them and, thereby, lowers the mechanical strength of the plate.

Effect of curing time

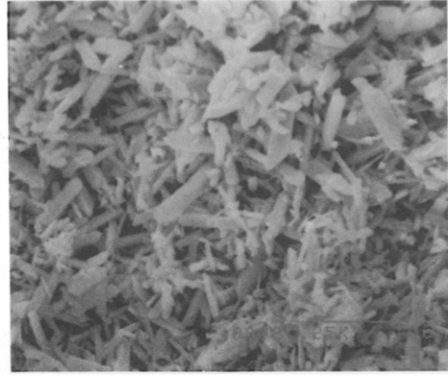
The influence of process time on the composition of positive plates was determined when curing at 100 and 120 °C. The changes in phase composition are shown in Figs. 6 and 7; the corresponding XRD patterns are given in Figs. 8 and 9. When the curing time is increased from 0.5 to 3.0 h, the amount of $4\text{PbO} \cdot \text{PbSO}_4$ formation is obviously increased.

Results from the needle-depth test on positive plates cured for different times are presented in Fig. 10. It can be seen that the toughness of positive plates decreases with increase in curing time.

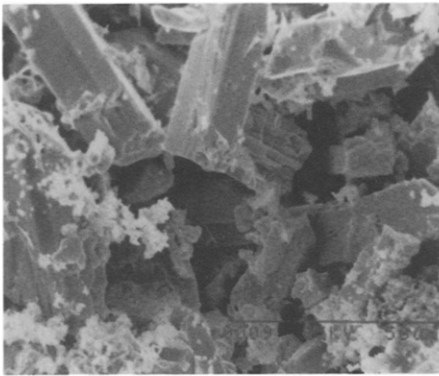
Electron micrographs of the structure and crystal morphology of positive paste cured for different times are given in Fig. 11. Large prismatic crystals of $4\text{PbO} \cdot \text{PbSO}_4$ are produced and continue to grow with curing time. It can be also seen that long curing times cause the formation of a large quantity



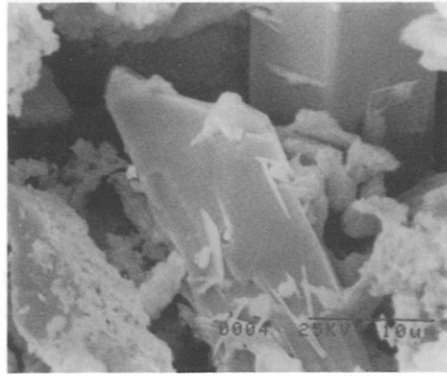
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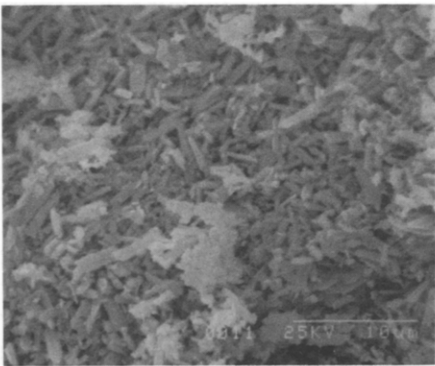
(b)



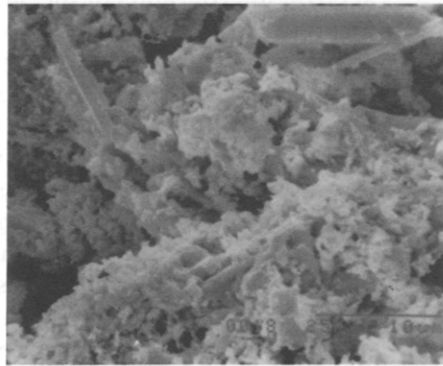
(c)



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Fig. 11.

(continued)

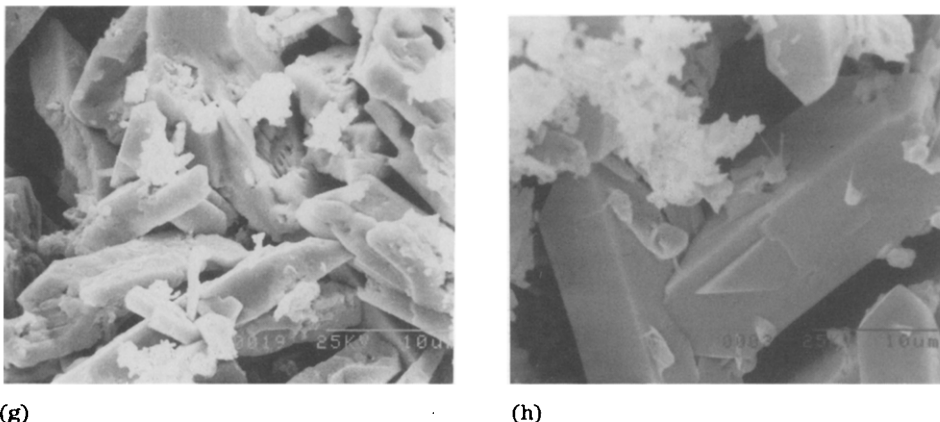


Fig. 11. Electron micrographs of cured paste structure and crystals after curing for different times. (a) 100 °C, 0.5 h; (b) 100 °C, 1.0 h; (c) 100 °C, 2.0 h; (d) 100 °C, 3.0 h; (e) 120 °C, 0.5 h; (f) 120 °C, 1.0h; (g) 120 °C, 2.0 h; (h) 120 °C, 3.0 h.

of the $4\text{PbO}\cdot\text{PbSO}_4$ phase. Under these conditions, plate toughness is decreased.

Effect of curing atmosphere

The effect of curing atmosphere was examined by varying the solvent solution in the autoclave. In the first experiment, 10 ml of 34% H_2O_2 solution was added to the autoclave to create an atmosphere containing O_2 and water vapour. The changes in phase composition of paste cured under this atmosphere at temperatures between 100 and 140 °C are shown in Fig. 12; the corresponding XRD patterns are given in Fig. 13. The formation of $4\text{PbO}\cdot\text{PbSO}_4$ obviously increases with increase in curing temperature. This results in a decrease in the mechanical strength of the plate (Fig. 14(a)).

Electron micrographs of the structure and crystal morphology of positive pastes cured at different temperatures in an atmosphere containing O_2 and water vapour are presented in Fig. 15. The $4\text{PbO}\cdot\text{PbSO}_4$ crystals grow up to 10 μm in size and have well-pronounced walls, edges and apices [5]. The formation of $4\text{PbO}\cdot\text{PbSO}_4$ is easier in an atmosphere containing O_2 and water vapour than in the presence of water vapour alone. Since the $4\text{PbO}\cdot\text{PbSO}_4$ crystals are large, there is a decrease in the strength of positive plates cured at high temperatures in an atmosphere containing O_2 and water vapour.

In a further experiment, 10 ml of 2 M $(\text{NH}_4)_2\text{CO}_3$ solution was placed in the autoclave to create an atmosphere containing CO_2 and water vapour. The changes in phase composition of paste cured at temperatures between 100 and 140 °C for 0.5 h are shown in Fig. 16. The XRD patterns are presented in Fig. 17 and peaks due to the formation of PbCO_3 are clearly discernible. The yield of PbCO_3 increases as the curing temperature is raised. By contrast, the $4\text{PbO}\cdot\text{PbSO}_4$ and $\alpha\text{-PbO}$ contents are considerably reduced.

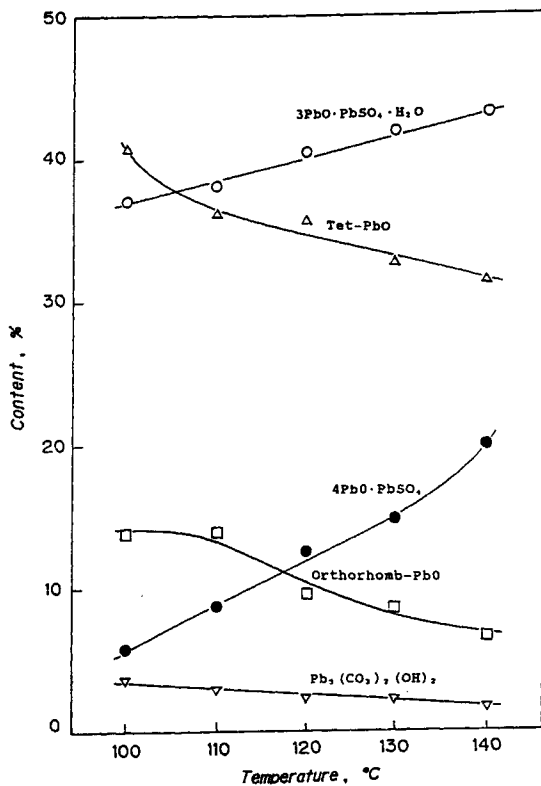


Fig. 12. Effect of curing temperature on the composition of positive plates under hydrothermal conditions of an atmosphere containing O_2 and water vapour.

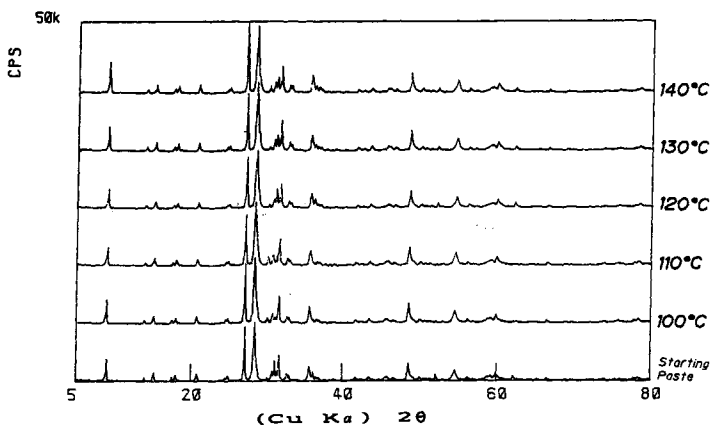


Fig. 13. X-ray diffraction patterns of paste cured at different temperatures under hydrothermal conditions of an atmosphere containing O_2 and water vapour.

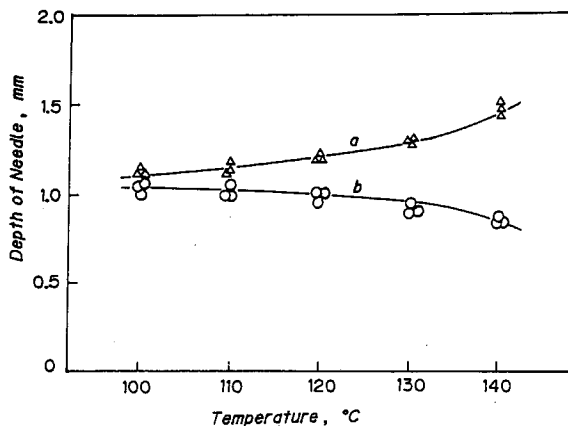


Fig. 14. Effect of curing temperature on the toughness of positive plates under hydrothermal conditions with different atmospheres: (a) O₂; (b) CO₂.

Finally, there is a slight increase in the levels of both $3\text{PbO}\cdot\text{PbSO}_4\cdot\text{H}_2\text{O}$ and $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$, but a slight decrease in the amount of $\alpha\text{-PbO}$.

Needle-depth tests of positive plates cured in a CO₂/water-vapour atmosphere indicate that plates are stronger when cured at higher temperatures (see Fig. 14(b)).

Scanning electron microscopic studies revealed that the paste cured in an atmosphere containing CO₂ and water vapour is composed of relatively equal-sized crystals of PbCO₃, $3\text{PbO}\cdot\text{PbSO}_4\cdot\text{H}_2\text{O}$ and PbO that are interconnected in a homogeneous structure (Fig. 18). The formation of carbonate roughens the surface of the $4\text{PbO}\cdot\text{PbSO}_4$ crystals [6]. This improves the contact between the crystals and, consequently, the toughness of the paste.

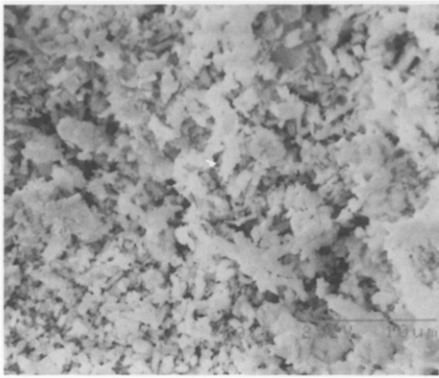
Comparison with commercial plates.

The phase composition and mechanical strength of positive plates cured both in the factory and under test conditions are compared in Table 3.

Conclusions

It has been observed that hydrothermal curing conditions in an autoclave strongly influence the composition, morphology and toughness of the positive-plate material.

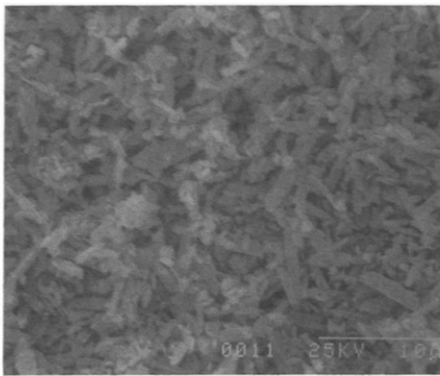
When either the temperature or the time of curing is increased in the presence of water vapour, or in an atmosphere containing O₂ and water vapour, the toughness of the cured positive plates is decreased due to the formation and growth of large $4\text{PbO}\cdot\text{PbSO}_4$ crystals. In an atmosphere containing CO₂ and water vapour, however, the strength of positive plates is increased due to the formation of small PbCO₃ crystals and a decrease in the number of large $4\text{PbO}\cdot\text{PbSO}_4$ crystals.



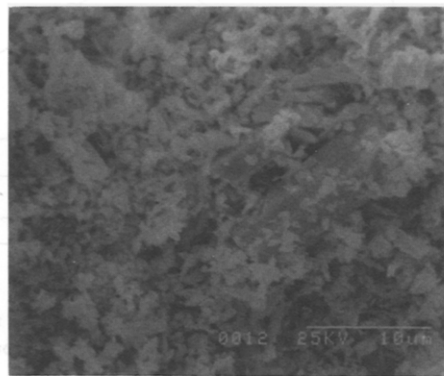
(a)



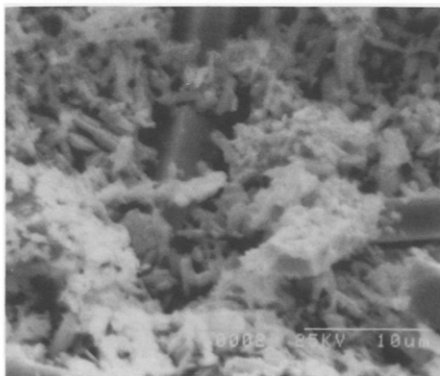
(b)



(c)



(d)



(e)

Fig. 15. Electron micrographs of paste structure and crystals after curing at different temperatures, as indicated, in an atmosphere containing O_2 and water vapour. (a) 100; (b) 110; (c) 120; (d) 130; (e) 140 °C.

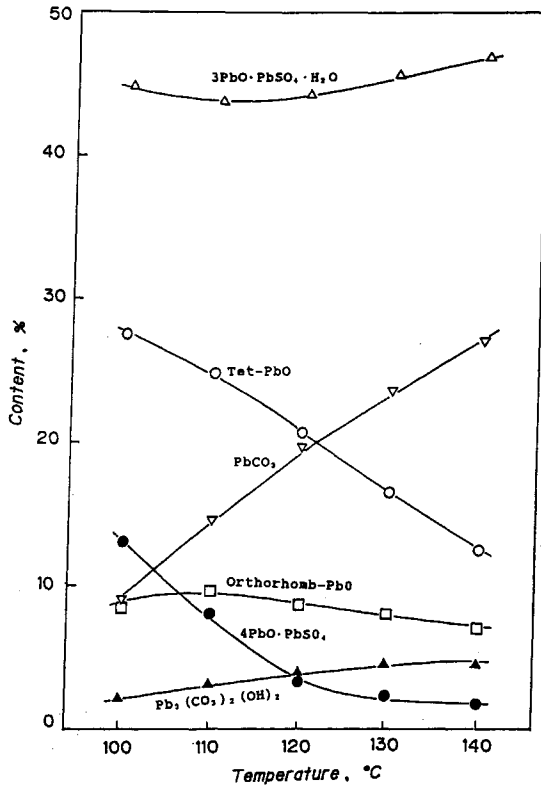


Fig. 16. Effect of curing temperature on the composition of positive plates cured in an atmosphere containing CO_2 and water vapour.

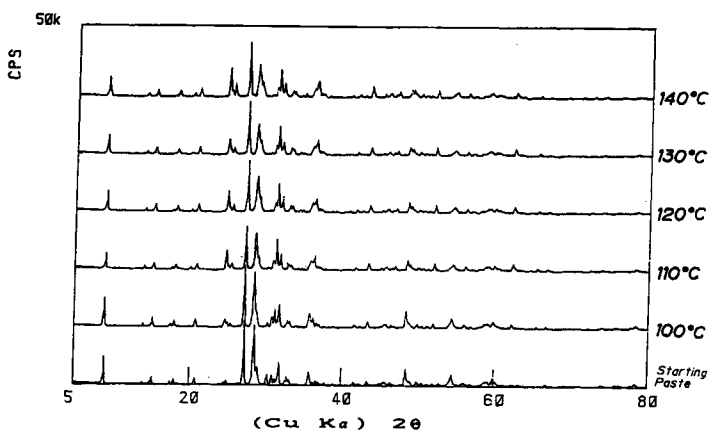
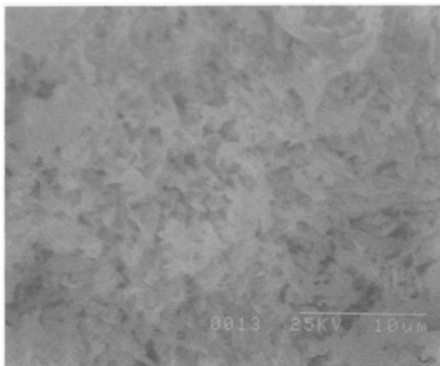
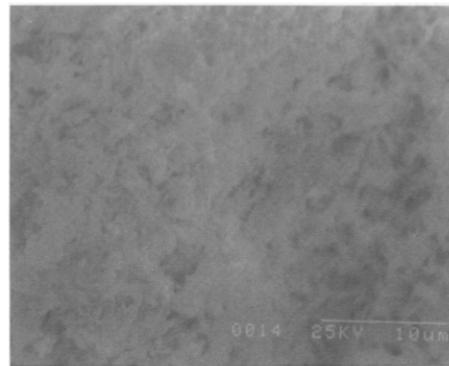


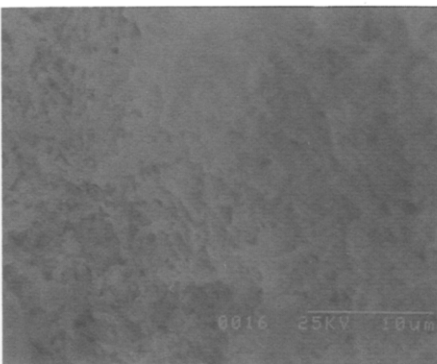
Fig. 17. X-ray diffraction patterns of paste cured at different temperatures in an atmosphere containing CO_2 and water vapour.



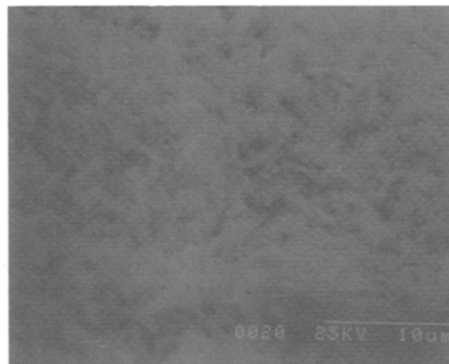
(a)



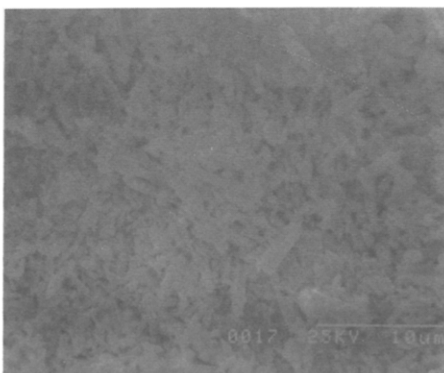
(b)



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(d)



(e)

Fig. 18. Electron micrographs of paste structure and crystals after curing at different temperatures, as indicated, in an atmosphere containing CO_2 and water vapour. (a) 100; (b) 110; (c) 120; (d) 130; (e) 140 °C.

TABLE 3

Comparison of phase composition and toughness of cured positive plates

Composition of positive plate (wt.%)	Sample ^a						
	1	2	3	4	5	6	7
α -PbO	36.4	36.7	34.3	34.7	36.3	37.2	20.4
β -PbO	2.3	14.0	10.9	19.9	9.4	10.5	8.7
3PbO·PbSO ₄ ·H ₂ O	7.0	39.0	34.2	34.3	40.1	39.2	44.4
4PbO·PbSO ₄	33.8	5.9	15.9	3.0	10.0	12.1	3.4
Pb ₃ (CO ₃) ₂ (OH) ₂	17.0	3.2	3.8	5.1	3.0	1.0	3.6
Pb	3.5	1.2	0.9	3.0	1.2	—	—
PbCO ₃	—	—	—	—	—	—	19.5
Average needle depth (mm)	1.15	0.90	0.95	0.87	1.12	1.22	0.90

^a1, first factory batch (140×240×4 mm); 2, second factory batch (118×220×3 mm); 3, second factory batch (132×240×3 mm); 4, third factory batch (28×28×3 mm); 5, test plate cured under water vapour at 120 °C for 0.5 h; 6, test plate cured under O₂ and water vapour at 120 °C for 0.5 h; 7, test plate cured under CO₂ and water vapour at 120 °C for 0.5 h.

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