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Hydrothermal solidification of β-PbO_2 and lead powder

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Using β-PbO_2 and PbO, a new type of positive plate for lead acid battery has been investigated. The paste consisting of PbO_2 and lead powder was easily solidified under hydrothermal conditions of 150 °C. The bonding material, $PbO_x\,(OH)_y\,nH_2O$, here $x = 1.5$–2, $y = 0$–0.5, was formed among PbO_2 and PbO particles during solidification under hydrothermal conditions. This new phase has a needle-like morphology. The hydrothermally formed positive plate is tough and the solidified body was contacted strongly to the grid of the lead alloy. The needle-like bonding material of basic lead oxide hydrate disappeared after the charging and discharging process. This hydrothermal process has two characteristics as follows: the curing process need not take a long time and waste batteries can be recycled.

1. Introduction

Nowadays, the spent lead acid battery is collected and reused as metal lead by the reduction process. However, a large amount of β-PbO_2 and PbO remains in a spent lead acid battery. This PbO_2 is firstly prepared by electric redox reactions in the battery fabrication process. If the mixed powder consisting of PbO_2 and PbO in waste spent batteries can be easily solidified on a lead grid, then it would be a favourite candidate for solving energy and environmental problems.

The positive plate of a lead acid battery is produced by kneading to paste PbO and Pb powder with sulphuric acid; this is called the active mass. This pasty active mass is pressed to a grid of lead alloy and then cured under warm and high humidity for three days in the traditional procedure. The resulting plate must be formed into β-PbO_2 by double charging. This traditional process has a complex, long working time and low efficiency. Some modification of this traditional process has been tried. The shortening of curing time was described in a previous report [1]. Another problem is in splitting down of the active mass from the grid. Patrick [2] and Kanai [3] have tried a new grid shape and using binder; however, the new grid shape makes the process more complex and binder gives low electric ability. The positive plate prepared by the traditional process, in which the lead powder paste is kneaded with sulphuric acid, aged for a long time and charged twice, has a low toughness. The reason for this may be that the binding among particles may be formed by only a small amount of water (hydrogen bridge) containing sulphate ions. Using the paste consisting of metal Pb and PbO_2 as the starting positive plate, it is expected that the redox reaction may easily occur at the contact positions among these two kinds of powder particles and the grid surface under hydrothermal conditions. In this study, the solidification of mixed powder containing PbO_2 and metal lead on a lead grid was examined with use of an autoclave.

2. Experimental procedure

The starting positive plate was kneaded with β-PbO_2 and lead powder with water in a mortar and pressed onto the grid. The starting lead powder prepared by grinding in a ball mill consisted of 30% metallic lead and 70% PbO. The lead grid contains 0.1% Ca. The starting powder was kneaded with 14.7% water and

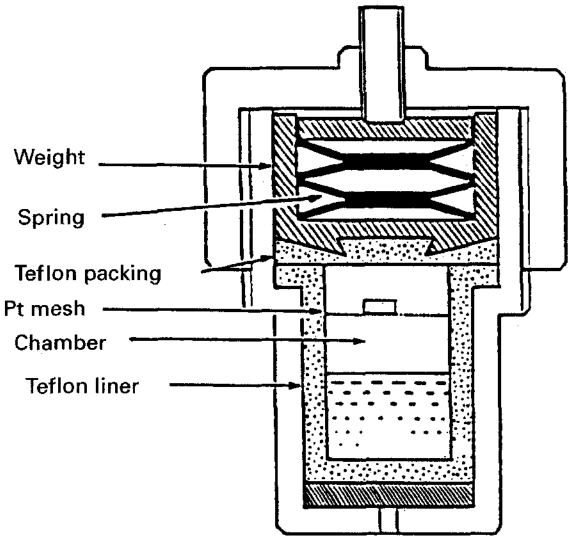

Figure 1 Autoclave for hydrothermal curing of positive plate.

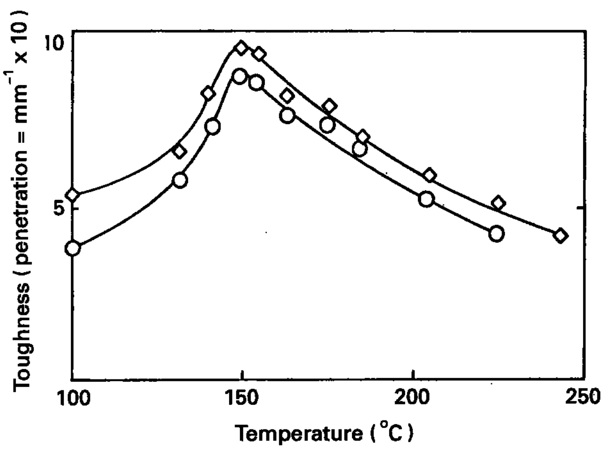

Figure 2 Toughness of curing paste with temperature. ○, PbO_2 lead powder: 1/0.11; ◇, PbO_2/lead powder: 1/0.25. Heating time 2 h.

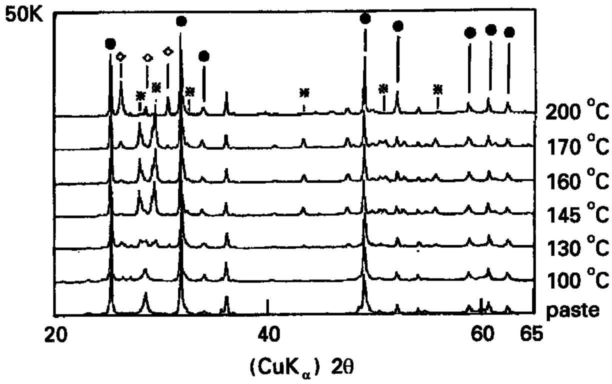

Figure 3 XRD profiles of cured pastes formed at various temperatures for 2 h. (PbO_2/lead powder: 1/0.25, ●, PbO_2; ◇, Pb_3O_4: ✻, new phase.)

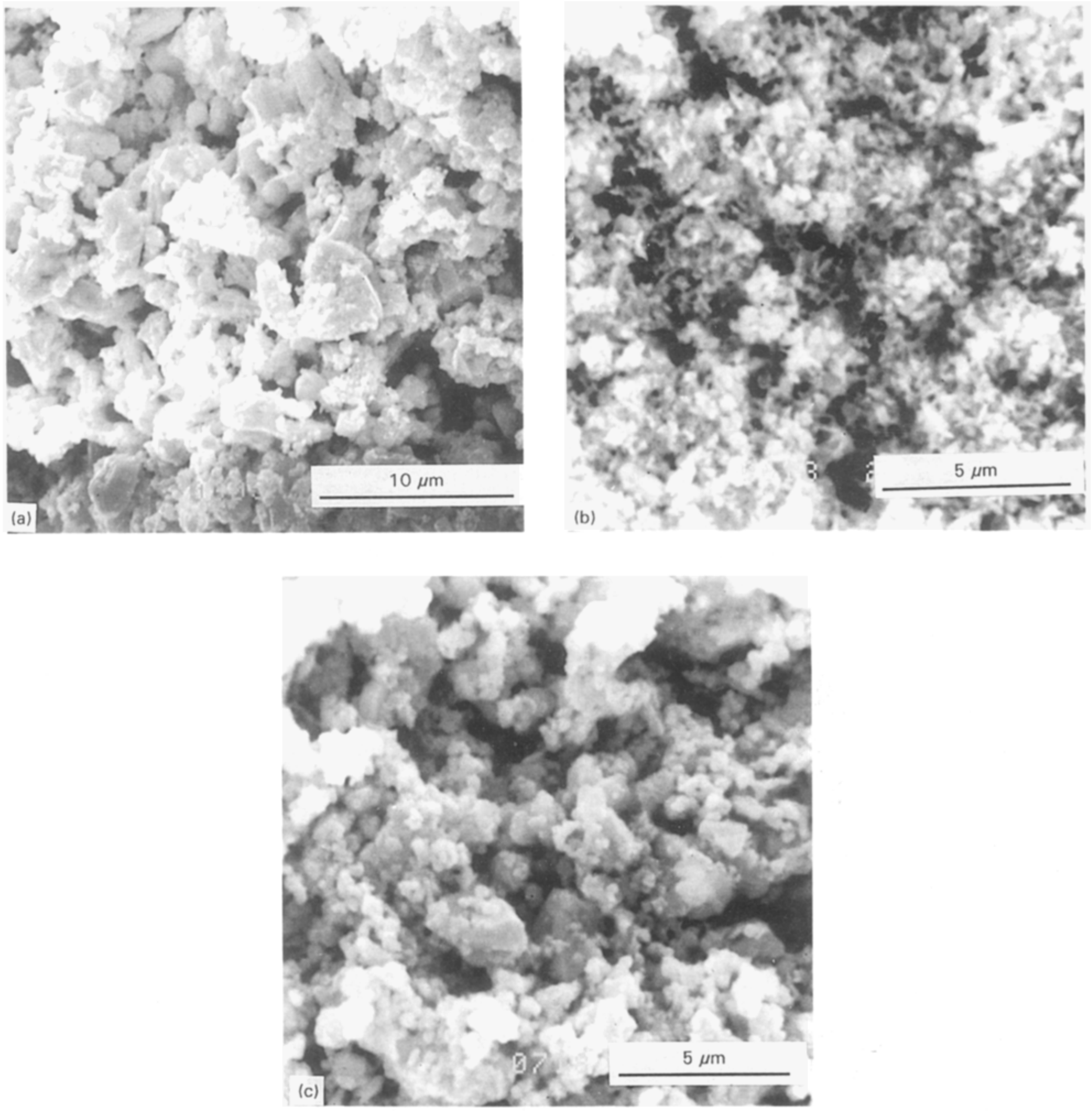

Figure 4 SEM photographs of cured pastes formed at (a) 100, (b) 145, and (c) 200 °C. (PbO_2/lead powder: 1/0.11.)

pasted onto the grid (28 x 28 x 3 mm). The mixing ratios of starting PbO_2 and lead powder were changed in a range of 0.00 to 0.40. This positive plate was aged under hydrothermally saturated vapour pressure. Fig. 1 shows the micro-autoclave made of stainless steel and lined with Teflon resin inside the chamber. The inner chamber was divided by Pt mesh. The sample was placed on the Pt mesh and water was introduced into the underpart of the chamber. The autoclave was heated for two hours. After cooling the autoclave, the sample plate was taken out and dried in air at 100 °C for 2 h. The resulting positive plate was characterized by the determination of the crystalline phase by X-ray powder diffractometry (XRD), the particle observation by scanning electron microscopy (SEM), and the relative toughness by penetration (impression depth of a charged needle of the same weight). Electrical characteristics were examined by a charging and discharging cycle test.

3. Results and discussions

Fig. 2 shows the toughness of hydrothermally cured paste with temperature. The toughness is shown as the inverse of needle depth. The toughness of paste increased with increasing temperature up to 150 °C and then decreased above 150 °C. This maximum value, 1 mm depth, is the same as that of the classical plate. These tough bodies formed up to 150 °C means that the solidification occurs at this temperature. Figs 3 and 4 shows XRD profiles and SEM photographs of solidified bodies formed at various temperatures. The new crystalline phase of needle shape was found in tough bodies. This needle-like phase disappeared and the XRD profiles in Fig. 3 show the appearance of Pb_3O_4 peaks above 200 °C. The size of the main particles consisting of solidified bodies increased with decreasing the needle-like phase and increasing the Pb_3O_4 amount. The samples from the needle-like phase exhibited a low toughness. These results support the idea that needle-shaped materials play an important role in solidification.

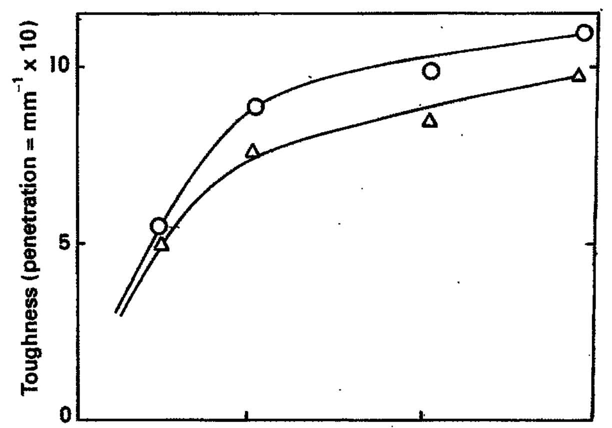

Figure 5 Toughness of cured paste with the content of lead powder. O, 145 °C, 2 h; Δ, 170 °C, 2 h.

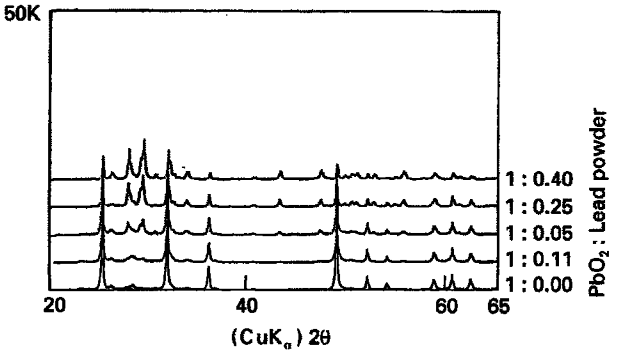

Figure 6 XRD profiles of cured paste having various lead powder contents. (Curing temperature: 145 °C, time: 2 h.)

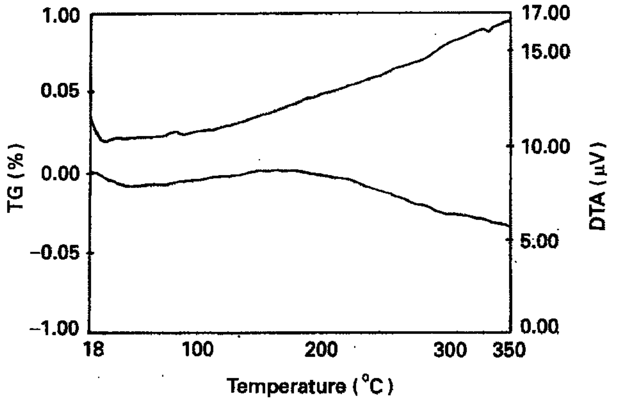

Figure 7 TG-DTA curves of cured paste formed at 145 °C for 2 h. Upper trace, DTA; lower trace, TG.

This new phase may form among β-PbO_2 and lead, and its components are PbO to Pb_3O_4 and accordingly the ratio of PbO_2 and lead may be important. Fig. 5 shows a comparison of toughness with lead powder content in a hydrothermally cured sample at 145 °C and 170 °C. Fig. 6 shows the XRD profiles of the sample formed at 145 °C. The toughness corresponds to the amount of new needle-shape phase.

This new phase of any lead oxide and related compounds is not yet shown in JCPDS data. Fig. 7 shows a thermogravimetric-differential thermal analysis (TG-DTA) profile in which a continual decrease of weight above 200 °C is shown. This new phase easily formed using pore PbO_2 and PbO or Pb under the same hydrothermal conditions, however it cannot be obtained under dry heating conditions.

The sample consisting of pure new phase could not be obtained and accordingly the accurate ratio of this needle-like phase could not be estimated. However, this material may be called basic lead oxide hydroxide hydrate as follows

$$PbO_2 + PbO(Pb) + H_2O = PbO_x(OH)_m \cdot nH_2O$$

$$(x = 1\text{–}4/3)$$

The toughness (penetration) change with reaction time is shown in Fig. 8. This figure shows a maximum value and in the case of high lead content has a tendency to high toughness at longer site. Fig. 9 shows the SEM photographs of the solidified bodies with the PbO_2/lead powder 1/0.11 cured at 145 °C for 7 h. The needle-shape phase of basic lead oxide hydroxide hydrate cannot be recognized. The XRD profiles at

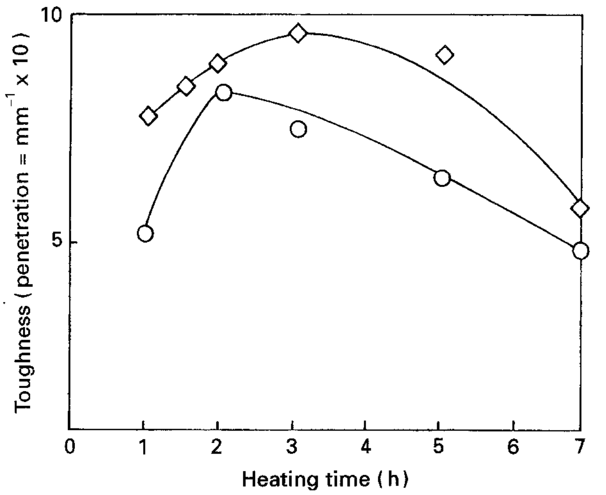

Figure 8 The toughness of cured paste with temperature change Formed at 145 °C, ○, PbO_2/lead powder: 1/0.11; ◇, PbO_2/lead powder: 1/0.25.

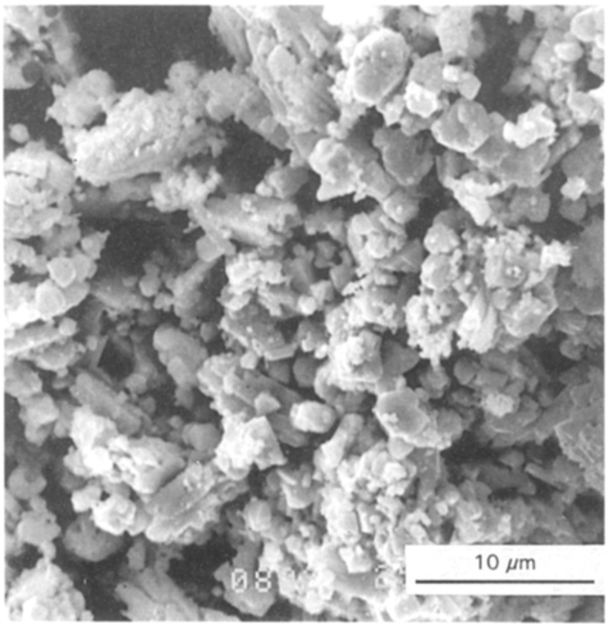

Figure 9 SEM photograph of cured paste fracture surface formed at 145 °C for 7 h; PbO_2/lead powder: 1/0.11.

various heating times in Fig. 10 show a new phase amount corresponding with toughness variations and disappearing in those samples of 5 and 7 h of heating times.

The charging and discharging characteristics of high toughness samples (PbO_2/lead: 1/0/11) formed at 145 °C for 2 h was examined while comparing with a traditional plate of the same shape at 30 °C under the charging and discharging conditions of 0.105 A and 0.25 A of electric current, 1.1 g cm^{-3} and 1.3 g cm^{-3} of H_2SO_4 specific gravity, respectively. The initial discharging time was short, however, the discharging time needed after the initial charging and discharging cycle became same as shown in Fig. 11.

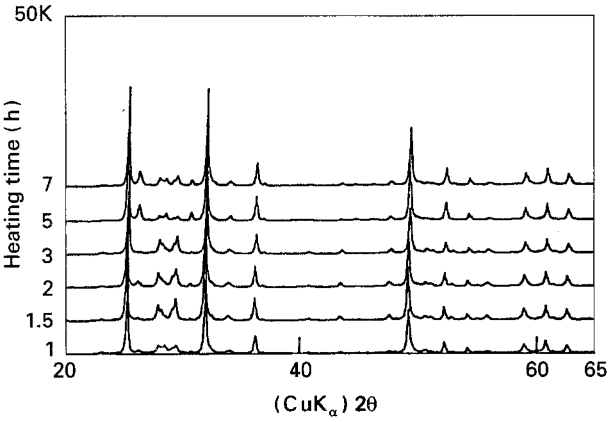

Figure 10 XRD profiles of cured pastes with time formed at 145 °C, PbO_2/lead powder: 1/0.11.

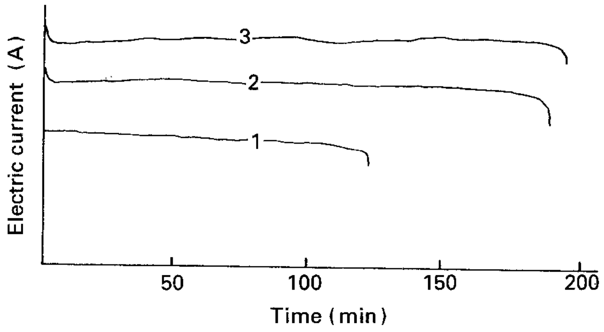

Figure 11 Discharging time of the positive plate, formed at 145 °C for 2 h; PbO_2/lead powder: 1/0.11.

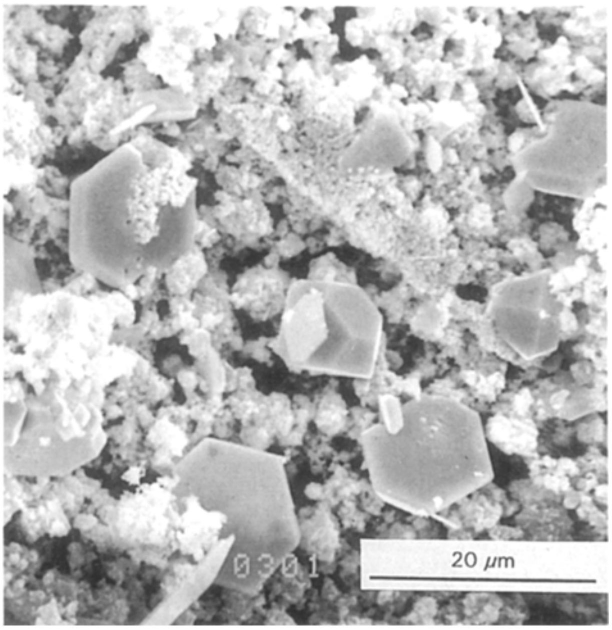

Figure 12 SEM photographs of interface between grid and cured paste formed at 145 °C for 2 h; PbO_2/lead powder: 1/0.11.

Fig. 12 shows a SEM photograph of intersurface position among paste (PbO_2/lead powder: 1/0.11) and grid formed under hydrothermal conditions of 145 °C for 2 h. The large crystals as shown in Fig. 12 are PbO formed by redox reaction paste and grid. These materials may act as a binding among paste and grid.

4. Conclusions

1. The mixing paste of PbO_2 and lead powder easily formed the tough body on lead alloy grid under hydrothermal conditions of 140–150 °C.

2. The binding material of needle-shape basic lead oxide hydroxide hydrate was formed among β-PbO_2 and lead powder.

3. The same characteristics were shown in charge and discharge compared with the traditional lead acid battery positive plate.

4. The new process of making a lead acid battery positive plate was proposed by using of β-PbO_2 and lead powder under a hydrothermal method. This process has some advantages as a simple process without forming and in the reuse of scrap batteries.

References

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