30%, whereas it can range between approximately 30% and 75% if the acid is stratified. This measurement only allows a lower limit to be estimated. A measurement of the acid density above the electrodes can lead to appreciable errors in determining the state of charge and thus in associated operation-management measures.

18.4.7.4.2 Sulphation

When the electrodes are discharged, the active masses, PbO_2 and Pb, are transformed into $PbSO_4$. The size of the sulphate formed depends on the strength of the discharge current – high discharge currents result in small sulphate crystals. If a battery is not recharged soon after its discharge, the sulphate crystals grow as a result of recrystallisation processes. The rate of recrystallisation is linearly correlated with the solubility of sulphate ions. Unfortunately, the solubility of sulphate ions increases with decreasing acid concentration [15]. Therefore, periods of low states of charge (and hence low acid concentrations and high sulphate solubility) harm the battery by accelerating the growth of large sulphate crystals. During subsequent charging, large sulphate crystals with their relatively smaller active surface are re-dissolved more slowly than smaller ones, so that sulphate crystals are still present when charging is nearly finished. Figure 18.18 illustrates that for the same volume, small crystals have a larger surface area than large ones (two-dimensional representation of the three-dimensional effect).

During the course of the operation, these remaining sulphate crystals can accumulate, reducing the active mass and thus the accessible capacity [23]. Sulphation can be reduced to a minimum if each discharging process is rapidly followed by sufficiently complete charging. The effect of acid stratification is that complete charging is seldom achieved for the lower part of the electrode, so that strong sulphation occurs there. This sulphation effect can be clearly seen in the cross-sections of Figure 18.19.

As a result of sulphation, the amount of active material available for normal charging and discharging operations decreases. This reduces the capacity, and the voltage during discharge is also shifted to lower values. If sulphation is too pronounced (as in the lower section shown in Figure 18.19), larger areas of the electrodes can become completely inactive.

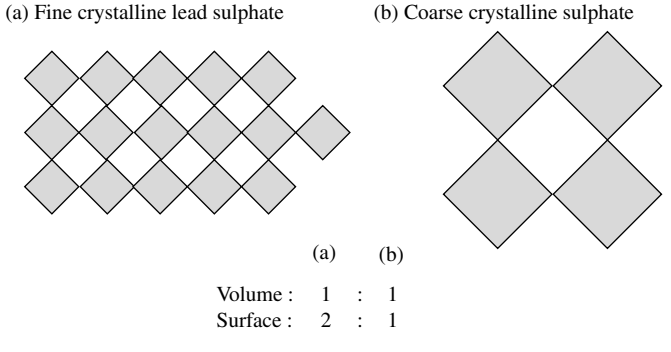

Figure 18.18 An example illustrating the effect of the crystal size on the active surface area of the electrodes. Mass ratio a:b = 1:1, surface area ratio a:b = 2:1