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Growth and kinetic studies of lead carbonate whiskers in silica gel

K MOHANAN PILLAI and M A ITTYACHEN
Department of Physics, University of Kerala, Kariavattom, Trivandrum 695 581

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Abstract. Lead carbonate whiskers were grown by diffusion of ammonium carbonate in the silica gel charged with lead nitrate. It is found that low pH is preferred to the whisker growth. In addition to straight whiskers gently curved whiskers are also found. Curving of whiskers is found to be maximum at high concentration of carbonate ions. Growth kinetics of whiskers are studied by changing the parameters of gel growth. It is found that the parabolic relationship between dimension and growth period is obeyed in this.

Keywords. Lead carbonate whisker; gel growth; crystals with different morphology; kinetics study.

1. Introduction

The appearance of whiskers has been observed both in the course of chemical reactions in gaseous (Brenner 1956; Pbefferkorn 1955) and liquid phases (Sears 1955) and during electrolysis. Whiskers have been of scientific interest as their strength approaches the theoretical value for perfect crystals (Herring and Galt 1952). Gel growth developed by Henisch *et al* (1965) is used for the growth technique of whiskers in our experiment. We report in this paper the growth and kinetics of lead carbonate whiskers and other twinned forms.

1.1. *Experimental techniques and observations*

The growth experiment was conducted in a test tube of length 15 cm and diameter 2·75 cm. $Pb(NO_3)_2$ was incorporated in sodium silicate solution of density 1·03 and pH 4·5 adjusted by acetic acid. After the gel was completely set, $(NH_4)_2CO_3$ was poured over the gel surface.

As soon as $(NH_4)_2CO_3$ was poured a white band was formed on the gel surface. On close examination of the white band microwhiskers of thickness nearly 10 μm were observed. Within 30 min, whiskers of thickness nearly 30 to 50 μm developed from the white band. This was about 3·5 mm long as shown in figure 1. Three distinct regions can be observed in the gel column after the cessation of growth as shown in figure 2. In regions 2 and 3 twinned crystals are formed. Description of crystals found in these regions are given in the table. As the concentrations of $(NH_4)_2CO_3$ is increased the whiskers became very thin and more bend. After attaining a certain length the whiskers were found to thicken. The tips of whiskers were found to be more thick. Thickening of whiskers was retarded at high concentrations of CO_3 ions and at high pH.

Table 1. Description of crystals formed in different regions

pH	Region	Description of crystals
4·5	1	Straight and curved whiskers
	2	Crossed and contact twinned crystals
	3	Twinned sixlings elongated along *c*-axis forming stout hexagons with rounded terminations
7-8	Liesegang rings	Interpenetrated needle-like crystals in groups

Experiments were conducted to see the effect of pH on the growth of these crystals. At pH above 4·5 star like whiskers were formed while the number of twinned forms at regions 2 and 3 increased considerably. This may be due to the increase in nucleation centres at high pH values. Above a pH value of 6 there is a danger of production of lead silicate. Below 4·5 pH the number of crystals in regions 2 and 3 considerably decreased and below 4 only region 1 remains. At very low pH clusters and groups of microcrystalline recticulated networks were formed. This may be due to the distruction of the gel due to the production of CO_2 and subsequent increase in flow of carbonate ions. Liesegang rings (Liesegang 1926) were formed when $Pb(NO_3)_2$ was placed over a gel of pH between 7 and 8 containing $(NH_4)_2CO_3$. Description of crystals found in these rings are given in the table. Some irregular forms were formed below the rings. This may be due to the inclusion of more silica at high pH.

2. Growth kinetics of whiskers

Growth kinetics of $PbCO_3$ whiskers in silica gel were studied by changing the growth parameters.

2.1 *The variation of age of gels*

Gels of different ages were prepared by allowing the gel containing $Pb(NO_3)_2$ to set in open air for different times. For all other experiments the growth apparatus is tightly closed. Growth rates were measured after $(NH_4)_2CO_3$ solution was placed on the surface of the gel. It was found that as the age of the gel increased growth rate decreased. Figure 3 shows the relation between square of the length and time.

2.2. *The variation of concentration of* $Pb(NO_3)_2$

Experiments were conducted by changing the concentrations of $Pb(NO_3)_2$ alone. It is interesting to note that growth rate decreased as the concentration of $Pb(NO_3)_2$ increased. Parabolic relation between length and time is given in figure 4.

2.3. *The variation of concentration of* $(NH_4)_2CO_3$

Growth rate measurements were repeated by altering the concentration of $(NH_4)_2CO_3$ alone. It was found that as the concentration of $(NH_4)_2CO_3$ increased growth rate also increased. Parabolic relation between length and time is shown in figure 5.

Figure 1. Lead carbonate whiskers (× 25)

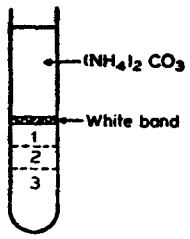

Figure 2. Growth apparatus

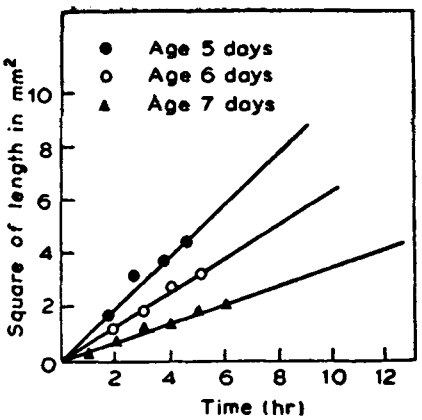

Figure 3. Plot of square of the length of whiskers vs time of growth for whiskers grown in gels of different ages

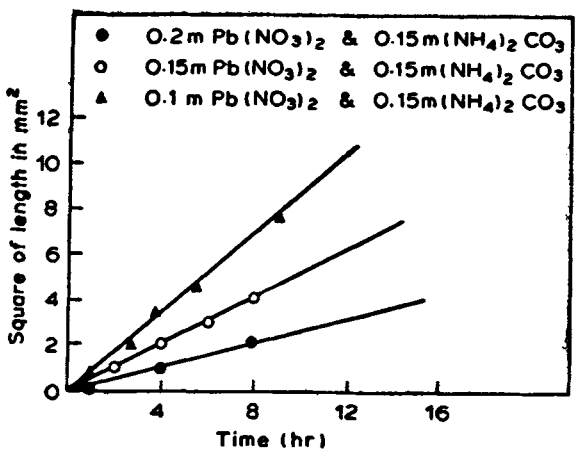

Figure 4. Plot of square of the length of whiskers vs time of growth for whiskers grown in gels of different lead nitrate concentrations.

2.4. *The variation of pH of gels*

The pH value of the gel is varied by using different volumes of 9·1% acetic acid and 16·7% nitric acid keeping the total volume the same. Growth rate measurements showed that growth rate decreased as the pH decreased. Figure 6 shows relation between square of length and time.

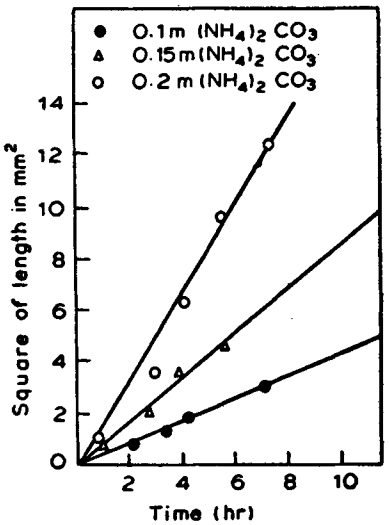

Figure 5. Plot of square of the length of whiskers vs time of growth for whiskers at different $(NH_4)_2CO_3$ concentrations.

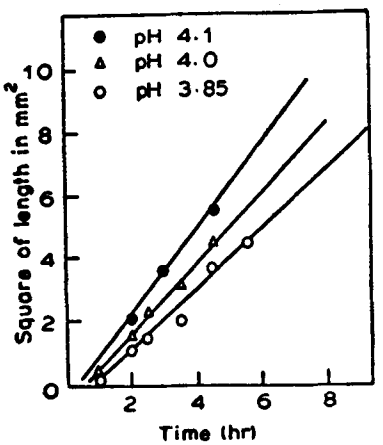

Figure 6. Plot of square of the length of whiskers vs time of growth for whiskers grown in gels of various pH values.

3. Discussion

In systems which depend on the diffusion of one reagent through a gel charged with another, the average crystal growth rate is greater near the top of the diffusion column where the concentration gradient is high. This high concentration favours the growth of lead carbonate whiskers (Hamamura and Nagakura 1976). Lead carbonate is formed by the reaction of lead nitrate and ammonium carbonate according to the relation

$$Pb(NO_3)_2 + (NH_4)_2CO_3 \rightarrow PbCO_3 + 2NH_4NO_3.$$

Lead carbonate crystallizes in the orthorhombic form in which twinning is most common. This may be due to the irregularities introduced in the early stage of its development and change in the supply of the nutrients towards the surface of the crystal at the latter stage (Dana 1958).

As the age of the gel increases the density of the gel increases due to water evaporation. Also, due to water evaporation the gel shrinks (Liaw and Faust 1972). These factors reduce diffusion of ions, hence the growth rate. Increasing concentration of $Pb(NO_3)_2$ in gel increases the density of the gel. Also high lead ion concentration favours the whiskers to thicken. Thus growth rate decreases as the concentration of of $Pb(NO_3)_2$ increases.

Growth in gel is a diffusion controlled process. Therefore as the rate of diffusion increases growth rate also must increase. This is what we observed in the case of higher concentration of $(NH_4)_2CO_3$. As the acidity of the medium increases the lead ions predominate over the carbonate ions which favours the thickening of whiskers. So the growth rate decreases as pH decreases.

4. Conclusion

High concentration of $(NH_4)_2CO_3$ and low pH favours the growth of $PbCO_3$ whiskers. Square of the length of the whisker against time gives a straight line graph in all conditions of growth. Thus parabolic kinetics of one dimensional diffusion controlled process is verified.

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