Chapter 1

Introduction

General knowledge about periodic precipitation

Periodic precipitation(1) is a generic term for processes of material deposition which occurs intermittently in terms of time or space or both. Such processes represent a special case of a fashionable topic: oscillatory reactions, with practical implications in geology, crystal growth, and materials preparation. The term "periodic" is actually a piece of literary license, and should be interpreted with caution. Periodicity should not be understood in the sense that it demands a temporal period, i.e. a constant time interval, something that the phenomena here under discussion indeed fail to show. These phenomena are nevertheless periodic, in the same sence in which (say) a frequency-modulated wave can be described as periodic, i.e., periodic in space.

The phenomenon of periodic precipitation was discovered by Liesegang(2) in 1896, so it is known as "Liesegang rings". Liesegang observed that when a drop of concentrated silver nitrate solution was placed on a gel containing potassium dichromate, the silver dichromate was not precipitated uniformly. The precipitation occured in a set of rings. These regions were separated by clear zones which were void of precipitate. Fig.1.1 gives examples drawn from the work of Hatschek(3).

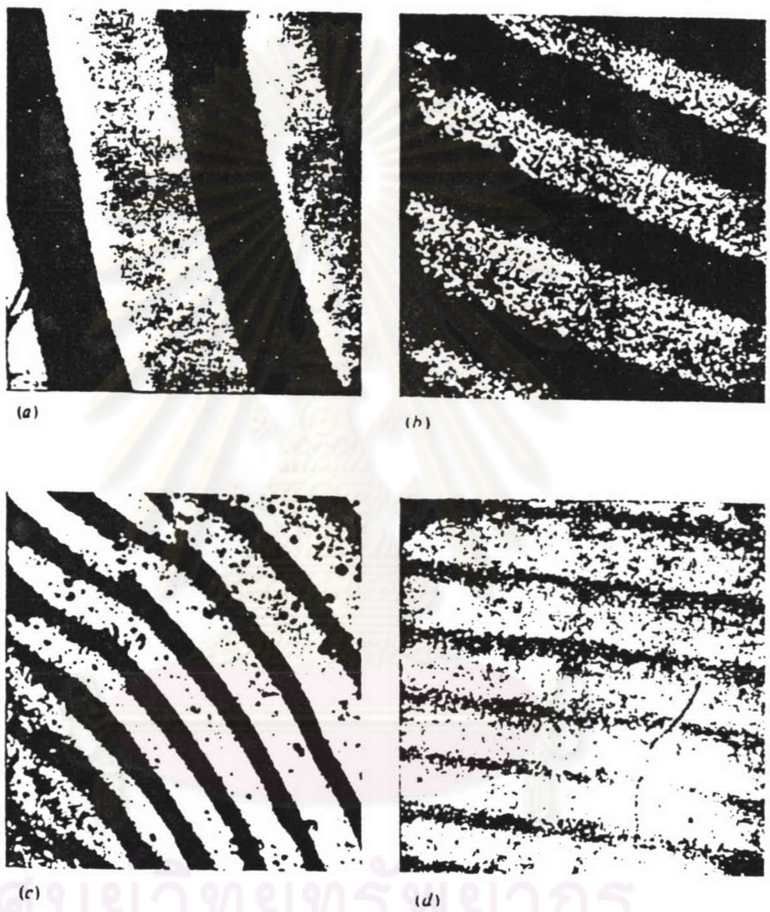

Fig.1.1 Concentric ring systems in agar,

(a) silver chromate (wet) x 100,

(b) lead iodide (wet) x 100 ,

(c) lead iodide (after drying) x 50 ,

(d) lead chromate (wet) x 50 .

Liesegang rings can occur in a variety of media, such as agar gel(4-8), gelation(9), alumina gel(10)and silica gel(11). It is important that the reagent or electrolyte solution can diffuse in the media (preferably inert environment), and in due course react with one another to produce periodic precipitate bands or rings each consisting of insoluble (or only spatialy soluble) clusters or crystals. Periodicity in the precipitates is produced by combination of localized supersaturation and diffusion velocities of reacting ionic species. Crystals and Liesegang rings in gels are often found in nature. It is thought that they may be the precursors to banded agates, gold veins in quartz rock, crystalline material in animal tissue, and even gallstones. Few attempts have been reported to make the phenomenon available as the design of composite material.

Motivation

At present, composite materials are used for many applications, for example, structural, magnetic, optical and electrical conduction because their properties can be tailored over a range of values based on the properties and geometric arrangement of the phases in composites, which have to be controlled during fabrication or processing. Although composite materials displaying highly directional properties are often desirable, they are difficult to process by conventional fabrication. Only lately, it has been demonstrated that the periodic precipitation technique can be used as an alternative processing route to more conventional methods to prepare multilayer structure composite(12). Such systems would combine otherwise exclusive properties, such as transparency to light and good electric conductivity. Also we may choose the precipitated compound as a base for unique electric, dielectric, photoelectric, magnetic and optical properties. Based on the above ideas, we tried to prepare new glass composite materials with Liesegang rings of metal or metal compounds incorporated in the glass matrix, which has never been made before. This makes the glass have exclusive properties, such as transparent and high electric conductivity or anisotropic property. In addition, the preparation multilayer glass composite material by this technique are expected to have low firing shrinkage and can be fabricated in various shapes. A drying step is normally not required. This technique can also decrease costs because the glass powder is less expensive than pure reagents used in sol-gel processes. Condensation takes place via viscous sintering. The sinter temperature is fairly low (below 700 °C). So, it is easy to control.

Viscosity and thermal expansion can also be controlled by selecting the composition of the employed glass. Unfortunately, there is very little information on how to control the Liesegang rings, and how to render it useful to material preparation routes. Heretofore, there have been a number of attempts to explain Liesegang formations and to quantify geometric relationships between gel and precipitate. The theories have met with only limited success in that none of the theories is consistent with all of the experimental observations, because the formation of periodic precipitates is dependent on a vast number of factors, mostly interrelated in a complex manner. Examples are supersaturation and ionic equilibria, pore size distribution of the gel and diffusion coefficients of the reactants, etc. In addition, solubility product of the precipitate, concentration of outer and inner electrolyte, pH, temperature and surface properties of the medium are important factors. So, in this thesis work we study how to prepare Liesegang rings of metals or metal compounds in a matrix of glass and agar gel as media by the technique of periodic precipitation and sol-gel preparation in such a way that no major obstacles left for the sintering process. The report will show that the preparation of suitable Liesegang ring systems alone is a demanding task already. This task is rendered even more difficult by the restriction imposed by the envisaged sintering process.

Objective

The main objective of the thesis is the establishment of a new preparation route i.e., the combination of the steps of gel preparation, generation of periodic precipitates of metal or metal compound in the medium of agar-gel mixed with glass powder, and viscous sintering within a single preparation route. The focus is laid on the steps of gel preparation and the generation of suitable precipitates. The envisaged sinter step enters the considerations only in so far as it poses restrictions on the ways available for gel preparation and precipitation. The sinter step itself is not an object of investigation of the presented work, but of another thesis performed in parallel by a fellow student. The function of the envisaged composite material is high electrical conductivity within a glassy matrix. The target precipitate is copper in the form of a compound which can be reduced to metallic copper upon heat treatment.

Scope of thesis work

1. Study the gel preparation method of a glass powder and agar gel matrix.

2. Study the ratios of glass powder to agar gel that results in homogeneous distribution and can form Liesegang rings of copper compound (copper oxalate) within the gel. In this thesis, only one kind of glass is used because the glass acts as a space-filling medium only.

3. Find the chemical to treat or coat the surface of the glass powder in order to give its surface hydrophobic properties or a favorable morphology for precipitation.

4. Study the effect of concentrations of electrolyte solutions on periodic precipitation in gel. The systems of electrolyte solution are copper nitrate ($Cu(NO_3)_2$) and ammonium oxalate ($(NH_4)_2C_2O_4$).

5. Study other factors that effect to periodic precipitation such as pH, temperature, volume of reservoir electrolyte, shape and size of the preform and particle size of the glass powder.

6. Pre-tests on the behavior upon heat treatment.

7. Pre-test on the decomposition of the precipitates.

8. Characterization of the interface between precipitates band and glass by scanning electron microscope.

9. Characterization of the microstructure of precipitate by light microscope.

Literature survey

The progress in the understanding of the mechanism of periodic precipitation is well documented(13-21). Yet, until now the process is not understood to the extent that trial-and-error research can be substituted by a more systematic approach. Attempts to render the mechanism to some useful application in materials science focus on the spatial non-random distributions of metallic or non-metallic phase in gels(4-8) and polymer films(22). Eventually, the ordering effect of a strong magnetic field on para- and ferromagnetic particles in a matrix(23) is used.

The theories and hypothesis(13-21) that explain the periodic precipitation formation are based on supersaturation, nucleation and coagulation. In addition(24-27) was studied about diffusion and diffusion coefficients of the ions during the precipitation. (4-8) was studied about the many other factors that influence periodic precipitation, such as pH,temperature,electrical field, light etc.. But until now, no theory or hypothesis can predict the distinct pattern of the periodic precipitation, such as, the distance between the bands and the position of the bands. When the medium or the ions or the nature of precipitate change, the conditions for periodic precipitation change, too. In (28) it was found that the periodic precipitation in systems of agar gel occured more easily and distinctly than in silica gels.

The system used is a glass powder uniformly dispersed in an agar gel matrix. The agar gel matrix exclusively serves as a transport medium for the electrolyte solutions. The periodic precipitation is scheduled to take place within the agar gel phase and in-between the glass grains. In this precursor stage, the glass grains act as space fillers only, and eventually display undesirable heterogeneous nucleation effects the suppression of which is a major challenge of this thesis. In a heat treatment step, all reminders of the agar gel phase-except for the precipitated rings - have to be removed completely. In a final sinter step (not an objective of this thesis) the rings shall be incorporated into the glass matrix by viscous flow.