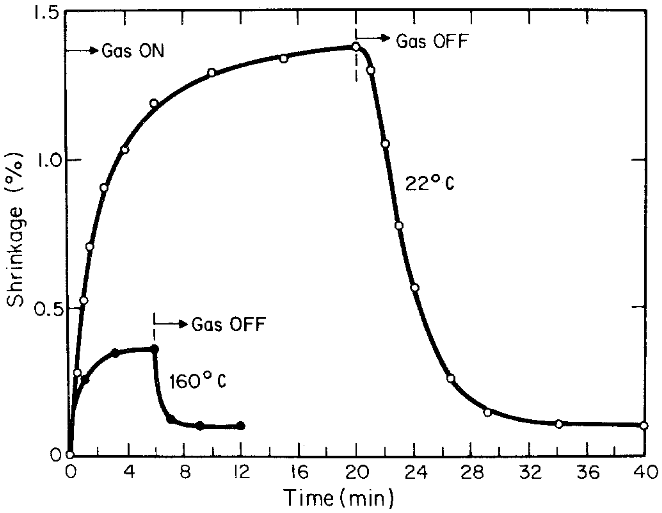

Figure 3 Effect of relative humidity on isothermal length of stabilized Monsanto acrylic at 22° and 160° C.

consequences in processing. As the temperature of a stabilized fibre is cycled about 90 to 100° C, the length of the fibre changes dramatically. Hence when a fibre is cooled from the reaction temperature, it expands in length. On a molecular level, the process may be envisioned as follows: polar groups which bind molecular segments in the polymer are solvated by the water, and Van der Waal's bonds are formed between the polymer and the water. In this way the polymer is allowed to relax or swell, leading to fibre extension. Any model of the stabilized material must, therefore, have extensive secondary bonding.

In summary, the strong secondary forces between molecular segments in stabilized acrylic fibres make the material very hygroscopic. Upon exposure to moisture the stabilized acrylic fibres rapidly equilibrate with a gain in moisture of about 8 wt% and concurrently elongate about 1.5%. As they exist in the laboratory, the stabilized fibres can therefore be regarded as plasticized material.

Acknowledgements

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Au thin films with nm-sized pores made from Au–Ge eutectic alloy films

Microporous membranes and filters have been developed for use in various fields, e.g. medicine, drug manufacture, air pollution, and food industries. These devices are made from metals, ceramics, and polymeric materials. Desorbo and Cline [1] developed porous metal filters produced by selective etching of the rod phase of a directionally solidified eutectic alloy and a two-stage replica process used to produce porous thin films.

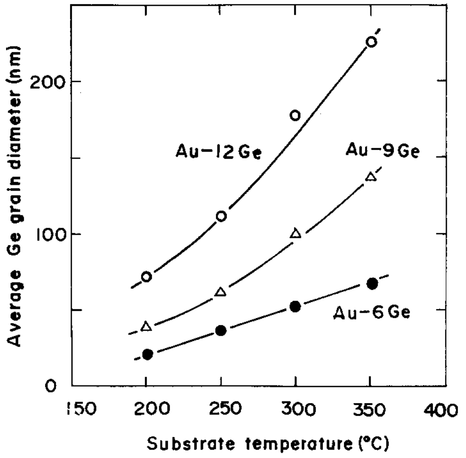

Figure 1 Substrate temperature and composition dependencies of the average Ge grain diameter of 0.1 μm Au–Ge eutectic films evaporated onto the substrate.

In this work, a thin porous film of Au has been examined by selective etching of island-like Ge grains in vacuum evaporated Au–Ge eutectic alloy films [2]. The films have comparatively uniform nm-sized pores. The size is controlled by changing the evaporation temperature and composition of the eutectic alloy film.

The ingots for evaporation were prepared by melting Au and Ge in a quartz crucible. Then the eutectic alloy films were evaporated by resistance heating of the ingots in a vacuum of 10^{-6} Torr. The substrate temperature was 100 to 300° C. To obtain thin eutectic films, a NaCl single crystal was used as a substrate. The evaporated film thicknesses were 50 to 500 nm. After evaporating, the eutectic alloy films were separated from the NaCl substrate in distilled water. The floating films on the water surface were scooped up with a gold mesh. Then the Ge grains in the films were selectively removed by an etchant of $HF:HNO_3:I_2:H_2O$ in the ratio of 1:2:1:2. where I_2 is a saturated solution in CH_3COOH. The pores of the films were observed by means of transmission electron microscope.

The average grain diameter of Ge in eutectic films varies with composition, substrate temperature, and film thickness. Substrate temperature and composition dependencies of the average Ge grain diameter of 0.1 μm films is shown in Fig. 1. The grain diameter increases with the Au content of the films.

An example of the porous film after selective etching of Ge grains in 0.1 μm Au–9 wt% Ge hypo-eutectic film evaporation rated at 300° C is shown in Fig. 2. Bright areas in the matrix Au are portions in which the Ge grains were selectively removed by the etchant. The pore diameter is 20 to 200 nm and the density is approximately 10^9 cm^{-2}. It is clear that the Ge grains were removed completely. Therefore, it is possible to obtain porous Au films whose pore diameter is controllable, by controlling substrate temperature, film thickness, and composition.

Porous Au film prepared by selective etching of Ge grains in a Au–12 wt% Ge eutectic film 0.3 μm thick is shown in Fig. 3. Similar pores to the above can be observed. In the Au–Ge alloy film, since Ge grains grow normally to the substrate surface,

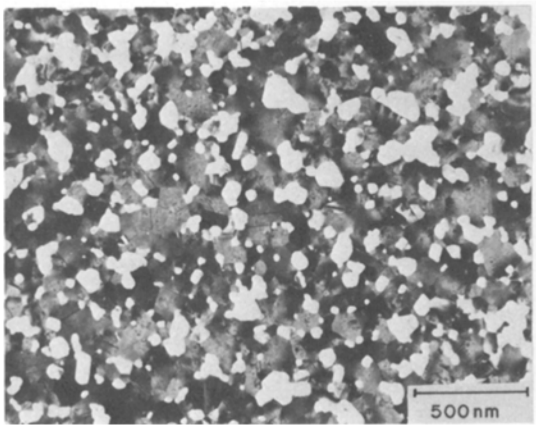

Figure 2 Au porous thin film after selective etching of Ge grains in 0.1 μm Au–9 wt% Ge hypo-eutectic film evaporated at 300° C.

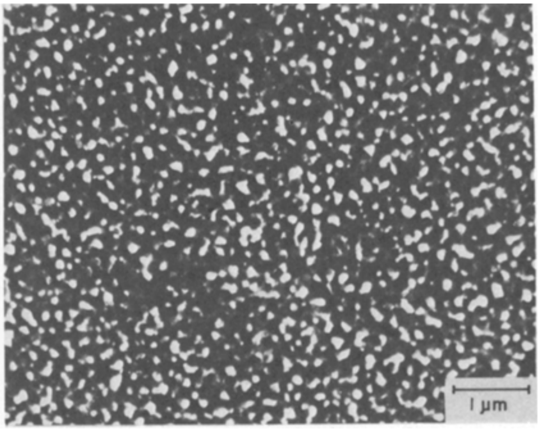

Figure 3 Porous Au thin film prepared by selective etching of Ge grains in Au–12 wt% Ge eutectic film 0.3 μm thick evaporated at 300° C.

two-phase alloy films with column-like growth are obtained. Therefore, it is possible to prepare porous Au films in a range where Ge grains grow in a column from the substrate surface to the film surface.

The porous thin metal films were developed using the selective etching method used for two-phase evaporated alloy films. It is possible to apply this technique to other evaporated eutectic systems, e.g. Au–Si, Ag–Ge, Ag–Si, Al–Si.

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Comments on "Thermochemical effects on the formation of Ca_3SiO_5"

Fluxes are normally present during the manufacture of Portland cement. One of the important functions of the Al_2O_3 and Fe_2O_3 contents is to promote chemical combination in the presence of a reactive liquid. It is however, essential that the presence of a flux should not greatly reduce the quantities of Ca_2SiO_4 and especially of Ca_3SiO_5 which are developed during firing. Phase studies have proven to be very helpful in elucidating the role of Fe_2O_3 and Al_2O_3 [1] and the information inherent in these studies is shown to be directly relevant to calculating the optimum batch proportions [2]. Not suprisingly, these studies have been extended to other potential fluxes firstly because they may be present in appreciable quantities in cement raw materials and secondly because they might possibly be added with a view to reducing the energy required to burn the cement.

The contribution by Ghosh [3] is thus interesting, but it fails to acknowledge the wealth of information which has accumulated in the literature concerning the action of P, Cr, S and F as fluxes. Most of his observations are explained by this body of information.

The system $CaO–P_2O_5–SiO_2$ has been studied in considerable detail [4]. Tricalcium silicate does not form extensive solid solutions containing P_2O_5, whereas Ca_2SiO_4 does. One consequence of this is reflected in the subsolidus phase equilibria: with increasing P_2O_5 content, the stable phase assemblage rapidly alters, becoming a two-phase mixture of CaO and a $Ca_2SiO_4–Ca_3(PO_4)_2$ solid solution. For practical purposes, the formation of Ca_3SiO_5 is suppressed at P_2O_5 contents greater than ~ 2.5% P_2O_5. This behaviour is reflected in more complex systems, with the result that P_2O_5 is generally recognized to be an undesirable constituent because it reduces the potential Ca_3SiO_5 content of the clinker.

Phase data for "CrO_3" are not quite so straightforward to interpret. This arises largely from the multiplicity of oxidation states exhibited by chromium. CrO_3 itself has a low melting point and is rather volatile. Thus, chemical analyses of fired mixtures made with CrO_3 are required to demonstrate that excessive loss has not occurred by volatilization. At higher temperatures, "CrO_3" undergoes spontaneous loss of oxygen in the presence of CaO. Studies of the action of Cr oxide on calcium silicates [5] show that under oxidizing conditions, chromium is readily soluble as Cr^{5+} in Ca_2SiO_4. Thus, its behaviour is similar to that of P^{5+}. If however, the chromium containing preparations are heated under even mildly reducing conditions, most of the chromium is reduced to Cr^{3+}. Trivalent chromium in small amounts probably behaves like Fe^{3+}. Failure to distinguish between the different behaviour of Cr in its various oxidation states have lead to much confusion in the literature regarding the role of chromium in clinkering. Under oxidizing conditions it will, like P^{5+}, reduce the potential Ca_3SiO_5 content.

Sulphates are not appreciably soluble in either Ca_3SiO_5 or Ca_2SiO_4. But upon heating $CaSO_4 \cdot 2H_2O$, (after initial loss of water) it decomposes at temperatures above ~ 1050° C to yield one solid phase (CaO) and two gaseous phases (SO_2 and O_2). The condensed portions of the system are thereby enriched in CaO which

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