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 $\sim 2.5\%$ 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 $\sim 1050°C$ 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

helps to account for the relatively large quantities of CaO observed by Ghosh. Phase equilibria in the $CaO-SiO_2-CaSO_4$ system are further complicated by the appearance of a silicosulphate phase [6] whose stability is sensitive to traces of atmospheric moisture, even at temperatures as high as $1050°$ C [7].

Fluorides have long been recognized as an effective flux for the formation of Ca_3SiO_5. A comprehensive review [8] summarizes the fundamental data and practical uses of fluoride fluxes.

The widespread use of fluxes in cement making presents a challenge to the scientist to explain their action on a systematic basis. Since cement clinker closely approaches equilibrium during its firing, it is essential to consider the equilibrium phase distribution as well as the kinetics of reaction. Moreover, as the complexity of the relevant system is increased by addition of more components, it becomes essential to make use of existing information if the action of the flux is to be interpreted in a systematic physicochemical manner.

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Internal stress dependence of the hardness of crystallized glasses

Stryjak and McMillan [1] recently reported hardness values of a partly crystallized silicate glass increasing linearly with the volume fraction and the grain size (d) of the crystallites developed, i.e. a d^{+1} dependence. An interesting aspect of their data that they did not address was that as the glass begins to crystallize, hardness values were lower than the parent glass. Only when the volume per cent of crystallization was $\sim 15\%$ did the linear increase in hardness with d begin to raise hardness values above that of the parent glass. The Stryjak and McMillan proposed mechanism of grain boundary deformation to justify the d^{+1} hardness dependence does not appear applicable to their specimens for two reasons. First, the d^{+1} dependence results from creep processes that are very unlikely to be operative at the rate needed for room temperature hardness indents. Second, this mechanism fails to address why (a) such a dependence occurs instead of the usual $d^{-1/2}$ dependence observed for ceramics [2],

and (b) the hardness of crystallized bodies actually can be less than that of the parent glass.

The purpose of this note is to propose an alternate explanation that addresses the above initial drop in hardness and includes the normal $d^{-1/2}$ dependence expected for the crystallites. The approach is to consider two aspects of the partially crystallized bodies. First, it is suggested that the linear dependence of the hardness on the volume fraction crystallite reflects the crystallized glasses following a rule of mixture combination of the hardness of the glass matrix and the crystallites, i.e.

$$H = (1 - \beta)H_c + \beta H_g \qquad (1)$$

where H is the hardness of the composite, β is the volume fraction of glass, H_c is the hardness contribution of the crystalline phase and H_g is the hardness of the glass matrix. Note that Stryjak and McMillan showed a direct relation between the volume fraction of crystals $(1 - \beta)$ and d, e.g. see their Fig. 10 and Table I here. Thus, correlation of $(1 - \beta)$ and d provides an explanation of their observed d^{+1} dependence of hardness.