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PHASE SEPARATION BEHAVIOUR OF SPECIAL BASE GLASSES - A CONTRIBUTION TO THE DEVELOPMENT OF BIOACTIVE GLASS CERAMICS

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Résumé - La description du processus de séparation de phases dans les verres des systèmes $\text{CaO} - \text{SiO}_2 - \text{P}_2\text{O}_5$ et $\text{MgO} - \text{Al}_2\text{O}_3 - \text{Na}_2\text{O} / \text{K}_2\text{O} - \text{F} - \text{CaO} - \text{P}_2\text{O}_5$ est une condition préliminaire au développement de céramiques vitreuses bioactives. Une méthode de contrôle totalement nouvelle de la cristallisation d'un verre phosphaté pur, sans séparation de phase, a été mise au point, sur la base d'une élimination automatique du phénomène de sursaturation.

Abstract - The described phase separation process in glasses of the system $\text{CaO} - \text{SiO}_2 - \text{P}_2\text{O}_5$ and $\text{MgO} - \text{Al}_2\text{O}_3 - \text{SiO}_2 - \text{Na}_2\text{O} / \text{K}_2\text{O} - \text{F} - \text{CaO} - \text{P}_2\text{O}_5$ is a precondition of all development of bioactive glass ceramics. A completely different way of controlled crystallization in a pure phosphate glass without phase separation has been found by a spontaneous elimination of supersaturation.

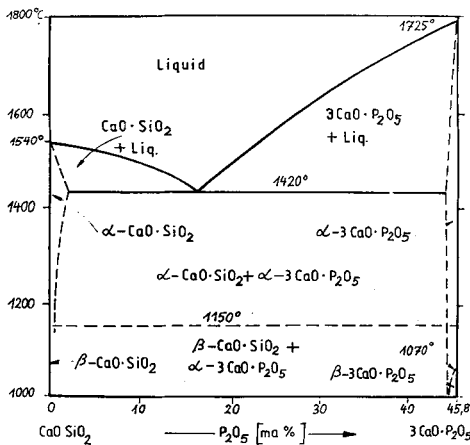
I - INTRODUCTION

In the past ten years, medicine has progressed remarkably in the field of organ substitution. Inorganic materials have been used to a growing extent. A remarkable advancement was achieved by L. Hench /1-2/, who coated the steel or sinter corundum implant with a thin surface layer of bioactive glass. The layer mainly contained phosphate components, which were akin to the apatite material of the bone structure and thus established bioactivity. A better solution was aimed at by the development of solid bioglass ceramics containing phosphate or apatite crystals /3-6/. They are more bone-like in composition than are metals and sinter corundum, and therefore they are more or less bioactive, i.e. they lead to a firm bond with the bone. Except sinter glass ceramics /7/, which are made by the powder method, all known glass ceramics are developed and produced by way of controlled phase separation processes in the initial base glasses. Phase separation phenomena are caused by the formation of stable molecular structural groups and their enrichment in certain regions. As a rule, this will considerably facilitate crystal nucleation in the droplet phase, as the critical nucleus size can be reached with less than the full amount of the activation energy that would be necessary in case of a base glass of homogeneous structure /8/. In base glasses to be converted into a bioglass ceramic, phase separation has to be controlled in such a way that the bioactive apatite crystal phase is produced in one microglass phase during annealing. In the other microglass phase, another silicatic crystal phase is usually separated, which has a decisive influence on other properties of the resulting glass ceramic, such as mechanical strength, chemical solubility, machineability etc. The study of phase separation processes in glasses used in the development of bioglass ceramics is the subject of the present report.

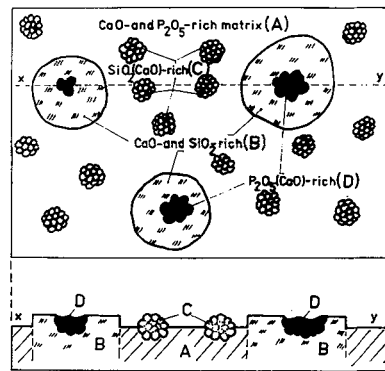
II - PHASE SEPARATION BEHAVIOUR OF SELECTED GLASSES OF THE $\text{CaO-P}_2\text{O}_5\text{-SiO}_2$ SYSTEM

Since CaO , P_2O_5 and SiO_2 are components of almost all bioglass ceramics known, it is important that the phase separation behaviour of selected glasses of that system be known. All glasses studied lay on a straight line connecting calcium metasilicate ($\text{CaO}\cdot\text{SiO}_2$) and calcium orthophosphate ($3\text{CaO}\cdot\text{P}_2\text{O}_5$), i.e. just outside the miscibility gap in the ternary system $\text{CaO-P}_2\text{O}_5\text{-SiO}_2$ /9/.

Fig. 1 shows the related pseudobinary equilibrium diagram of $\text{CaO}\cdot\text{SiO}_2\text{-}3\text{CaO}\cdot\text{P}_2\text{O}_5$ /10/, which is essential for understanding the phase separation behaviour of corresponding glasses. The system is eutectic and its "edge miscibility" is low, i.e. the amount of calcium metasilicate dissolved and taken up in the calcium orthophosphate crystal phase is low, and the same applies vice versa. These relationships are reflected in the phase separation behaviour of corresponding glasses. The schematic drawing of Fig. 2 serves to explain the results of examination by electron microscopy. On the P_2O_5 -rich side of the pseudobinary glass system, we have a matrix glass phase rich in CaO and P_2O_5 (A), in which a CaO - and SiO_2 -rich droplet phase (B) is separated.



1



A = CaO - and P_2O_5 -rich matrix phase
 B = CaO - and SiO_2 -rich phase
 C = $\text{SiO}_2(\text{CaO})$ -rich phase
 D = $\text{P}_2\text{O}_5(\text{CaO})$ -rich phase

2

Fig. 1 - Pseudobinary system $\text{CaO}\cdot\text{SiO}_2\text{-}3\text{CaO}\cdot\text{P}_2\text{O}_5$ /10/.

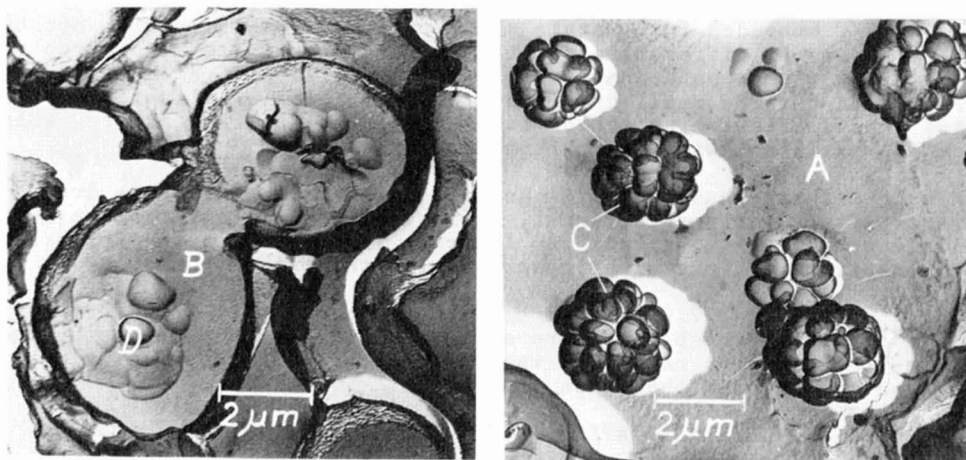
Fig. 2 - Phase separation behaviour (schematic) of a base glass of the pseudobinary system $\text{CaO}\cdot\text{SiO}_2\text{-}3\text{CaO}\cdot\text{P}_2\text{O}_5$.

In a P_2O_5 -rich base glass (according to Fig. 2), a certain cooling or subsequent annealing process will, because of the resultant non-equilibria, cause further secondary unmixing to take place in steps in the two phases separated during the primary process. In accordance with the edge miscibilities occurring in the pseudobinary system (Fig. 1) at higher temperatures, the dissolved portion of SiO_2 and CaO in the phosphate-rich matrix phase and the dissolved portion of P_2O_5 and CaO in the SiO_2 - and CaO -rich droplet phase are separated as smaller droplets. This produces a base glass consisting of four glass microphases of different compositions. An interesting observation made for the first time

two secondary droplet phases form mulberry-like aggregates. This seems to indicate that the glass already contains well-developed, stable structural elements of metasilicate and orthophosphate, which are about to aggregate in larger unmixing regions.

Fig. 3a and b are electron micrographs of such a glass. The large primary droplet phase B (see Fig. 2 and 3a), rich in SiO_2 and CaO , is less attacked. The P_2O_5 - and CaO -rich droplet phase D^c contained in it suffers less corrosion than the matrix phase A which is allied to it. This is another clue to the fact that the droplet phase D already contains a large proportion of orthophosphate structural elements, which are more resistant to citric acid than a normal phosphate glass.

Fig. 3a and b are micrographs of the mulberry-like droplet aggregates formed in both primary phases by secondary phase separation. A comparison of Fig. 3b (phase C) and Fig. 3a (phase D) reveals a distinct difference in etching behaviour. The findings have also been confirmed by phase analysis by means of the electron-beam microprobe. If such P_2O_5 -rich base glasses having the described phase separation behaviour are transformed into a glass ceramic, a controlled separation of hydroxyl apatite and wollastonite as main crystal phases can be achieved, and it is only now that we come to understand properly the kinetic processes of nucleation and crystallization.



3a

3b

Fig. 3a-b - Electron micrograph (Pt-Ir-C replica method) of glass after a week surface etching with 2 % citric acid for 30 seconds (compare with Fig. 2). Mulberry-like droplet aggregates formed in both primary phases by secondary phase separation.

III - PHASE SEPARATION AND CRYSTALLIZATION BEHAVIOUR OF BASE GLASSES OF THE SYSTEM $\text{CaO-P}_2\text{O}_5\text{-MgO-Al}_2\text{O}_3\text{-SiO}_2\text{-Na}_2\text{O/K}_2\text{O-F}$

As expounded in an earlier publication /11/, base glasses of the system $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2$ with different dopings can be employed for developing new glass ceramics having most differing combinations of properties, e.g. such having

- very high mechanical flex-cracking resistance,
- metal-like machineability,
- magnetic properties plus machineability,
- and others.

In all cases, the base glass is a two-phase one, with silicatic droplets embedded in an SiO_2 -rich matrix. Enriched in the droplet phase are Mg^{2+} , Al^{3+} and the doping elements. If this glass is subjected to a certain thermal treatment, it will separate fluorophlogopite mica crystals $\text{NaMg}_3/\text{AlSi}_3\text{O}_{10}\text{F}_2$ as main crystal phase in the droplet phase.

As mica crystal cleave easily along the 001 plane, the resulting glass ceramic is machineable, i.e. it can, like a metal, be sawn, drilled, turned, milled, tapped etc. without breaking as normal ceramics would. In the base glass just described gets additional dopes of 10 to 29 mole-% of CaO and 2 to 9 mole-% of P_2O_5 and has a composition of 19 - 54 SiO_2 , 8 - 15 Al_2O_3 , 2 - 21 MgO , 3²⁻⁵ $\text{Na}_2\text{O/K}_2\text{O}$, 3 - 23 F^- , 10 - 34 CaO , 2²⁻ 10 mole-% P_2O_5 , a three-phase base glass results, as shown in Fig. 4 /12/. Embedded in a matrix glass phase very rich in SiO_2 are two droplet phases of different composition and droplet size. The large droplets are a phosphate phase with enrichments of CaO , MgO , Al_2O_3 , $\text{K}_2\text{O/Na}_2\text{O}$ and F^- . The small droplets are the original, silicatic unmixing phase, likewise enriched with MgO , Al_2O_3 , $\text{Na}_2\text{O/K}_2\text{O}$ and F^- , which is still coexistent with the phosphate droplet phase.

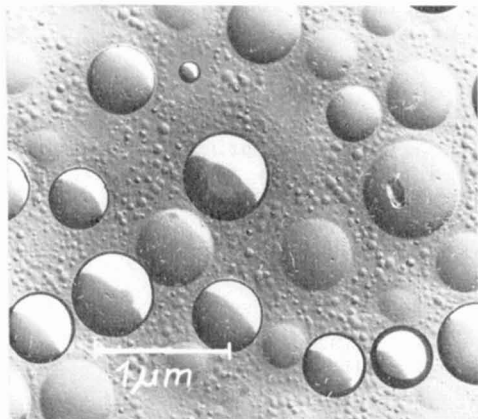
When such a three-phase glass is annealed, the large phosphate droplets segregate fluorapatite. The small, silicatic droplets still contain sufficient Mg^{2+} , Al^{3+} , alkali and fluorine ions to allow the formation of phlogopite mica crystal by reaction with the matrix phase.

In Fig. 5 the large, P_2O_5 -rich droplet regions begin to transform into apatite crystals, whose faces are already visible on the droplets. The apatite-to-phlogopite ratio and the ratio between the residual glass phase and the crystal phases can be varied.

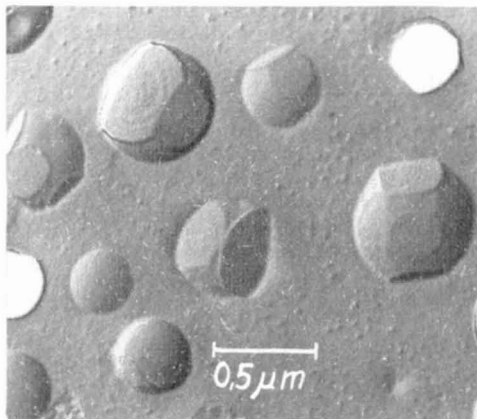
IV - CONTROLLED CRYSTALLIZATION IN GLASSES NOT TENDING TO PHASE SEPARATION

Latest results of our basic research, have shown that under certain conditions it is possible to effect controlled volume crystallization in base glasses of homogeneous structure without phase separation, and thus to make these glasses available to the development of bioglass ceramics. These are pure phosphate glasses in which the spontaneous elimination of supersaturation with certain components leads to a base structure which looks quite similar to a phase separation but has nothing to do with it.

The phenomenon is a spontaneous primary nucleation throughout the glass volume. Nuclei in the ellipsoids obviously release the formation of the main crystal phase by way of epitaxial interactions. In Fig. 6, this phase is shown in its initial stage as ellipsoidal spherulites and may



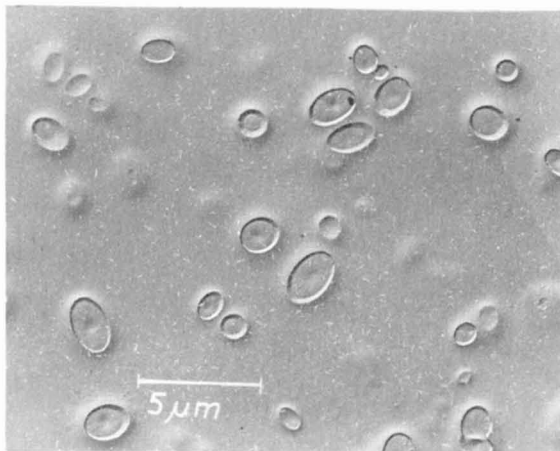
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5

Fig. 4 - Base glass of the system $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2\text{-Na}_2\text{O/K}_2\text{O-F}$ doped with CaO and P_2O_5 . Separation of two droplet phases of different composition in the SiO_2 -rich matrix (electron micrograph of a replica).

Fig. 5 - Three phase glass as in Fig. 4 with the large P_2O_5 -rich droplets beginning to transform into apatite crystal (electron micrograph of a replica).



6

Fig. 6 - Beginning controlled nucleation and crystallization in a pure phosphate glass of homogenous structure, by means of spontaneous elimination of supersaturation phenomena (electron micrograph).

be mistaken as phase separation. From the three selected examples treated here it is obvious that in the successful development of new bioglass ceramics for use in medicine, the more profound exploration of phase separation, or of the microstructuring processes during the cooling of a glass melt, plays a key role.

V - CONCLUSION

The key to the goal-directed development of new glass-ceramic materials is the control of the microstructure formation processes in the basic glasses. As a rule, this concerns the control of phase separation but it has been found for the first time that controlled crystallization can also be achieved in glasses of homogeneous structure by the spontaneous elimination of supersaturation phenomena.

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