

# LEUCITE PORCELAIN

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## INTRODUCTION

A number of properties of potassium and cesium aluminosilicates suitable for utilization in technical practice have been discovered during the last fifteen years. It was above all the possibility of immobilising radioactive cesium  $^{137}\text{Cs}$  because its fixing into the structure of borosilicate glass involves big difficulties, particularly due to extractability of cesium out of the materials. Tests have been carried out with aluminosilicates, phosphates, titanates, and various zeolites; however, the best results were obtained with pollucite ( $\text{CsAlSi}_2\text{O}_6$ ). Its high melting temperature (above  $1900^\circ\text{C}$ ), relatively low density ( $3.3 \text{ g/cm}^3$ ) and a relatively low thermal expansion coefficient ensure a good resistance to thermal shocks. A low creep at  $1400 - 1500^\circ\text{C}$  and chemical inertness allow materials suitable for high-temperature parts of combustion engines, gas turbines and the like to be prepared.

However, dental prosthetics appears to be the most significant field of application. The way was found how to improve the properties of dental porcelain, in particular its fused adhesion to metals and fracture toughness. The innovation is based on the properties of leucite ( $\text{KAlSi}_2\text{O}_6$ ) whose presence in porcelain allows its thermal expansion to be adjusted to that of metals, so that the suppression of changes occurring during the cooling down of the product lead to enhanced fracture toughness of the porcelain.

### Utilization in dental prosthetics

Use of porcelain in dental prosthetics was already known in the 18th century [1]. In principle, a thin layer of the porcelain mix (quartz, feldspar, kaolin) was applied in paste form onto the roughened surface of a metallic skeleton and then fired at a suitable temperature, usually  $900 - 980^\circ\text{C}$ , at which sintering took place, and on cooling down the ceramic material

achieved an aesthetically satisfactory appearance, i.e. translucence, colour shade and also satisfactory strength. This technological process has therefore been known for a long time, but the principles of weldability with metal and the causes of brittleness of the product have been understood only not far ago. This fact can be regarded as the main reason why nowadays polyacrylates reinforced with a metallic structure are increasingly used in dental prosthetics in spite of a number of more advantageous properties of porcelain (hardness, colour fastness, biological tolerance, resistance to the oral environment, and also durability). The problem of reliable weldability between ceramics and metals has been satisfactorily examined by Hahn and Teuchert [2] who showed that the primary requirement is to reduce the difference in thermal expansion coefficients of the ceramic material and the metal. In place of the mix used in the manufacture of conventional feldspar porcelain they have chosen a composition corresponding to the region of primary crystallization of leucite in the system  $\text{K}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$  and demonstrated that leucite crystallized during the cooling of the product raises the thermal expansion coefficient of porcelain to a value close to the expansion of metal ( $13 - 15 \times 10^{-6} \text{ K}^{-1}$ ). At the same time they found that admixtures of lithium, rubidium and cesium promote crystallization, which is suppressed by sodium admixtures. On this basis, which represented a leap forward in the development of dental porcelain, it was eventually possible to prepare leucite porcelain which is readily fusible with many metals. This is borne out by a number of patents [3 - 5], and also by the launching of industrial production of the raw material mix for stomatological laboratories.

Further development of leucite porcelain was influenced by several significant studies. Morena [6] found that glasses containing dispersed crystals of leucite exhibit higher fracture toughness than the same glasses free from leucite crystals. Mackert [7] and also

Denry [8] discovered that in the vicinity of leucite crystals in porcelain there were microcracks whose origin they ascribed to the difference between thermal expansion of leucite and that of the glass matrix. On the basis of these findings, Rasmussen [9] assumed that the mechanism of increased fracture toughness of leucite porcelain could be similar to that of ZTA composites (Zirconium Toughened Alumina) [10]. It has been proved that their high fracture toughness is due to martensitic transformation of metastable tetragonal  $ZrO_2$  to its monoclinic form. Rasmussen supported his hypothesis by the plausible convincing evidence for the fact that the transformation of metastable cubic leucite in porcelain may be initiated by stress in a mechanically loaded material. This hypothesis had subsequently turned the research to another direction, namely at seeking a material exhibiting not only fusibility with metals, but at the same time also a high fracture toughness. It has been proved that leucite porcelain containing 6.2vol.% of leucite in its vitreous matrix achieves a fracture toughness higher by up to 60% than the classical feldspar porcelain [11].

A completely new field of study aimed at finding new structural materials has thus been opened for the materials science. To understand the behaviour of leucite, it was first necessary to study in depth its structure and its behaviour in the course of phase transformations.

#### Crystal structure and phase transformations of leucite

The structure of leucite represents a continuous three-dimensional skeleton formed by  $(Si,Al)O_4$  tetrahedra, each of which shares all its oxygens with its neighbours [12, 13]. The tetrahedra are arranged into four-, six- and eight-member rings, where the six-member ones form a sequence of parallel layers, passed through by open channels in the perpendicular direction. Potassium cations are placed in the channels. The structure of leucite is stable above the temperature of 893 K. It is cubic, characterized the spatial group Ia3d, and the elementary cell contains 48 tetrahedra and 16 potassium cations.

On cooling down the cubic structure is transformed into a tetragonal one. This conversion is rapid, reversible and continuous (transformation of the 2nd order). The change in the volume and size of the elementary cell in terms of temperature is shown by figures 1a and b.

The cubic structure of leucite has the significant property of being extremely tolerant with respect to change in composition.  $K^+$  cations are readily replaceable for  $Rb^+$  or  $Cs^+$ , but also aluminium cations in the tetrahedral can be easily substituted with those of boron or iron [14]. By the substitution of alkali cations the stability of the cubic modification is shifted towards lower temperatures and the size of the elementary cell grows.

The conversion of cubic leucite into the tetragonal modification involves deformation of the six-member

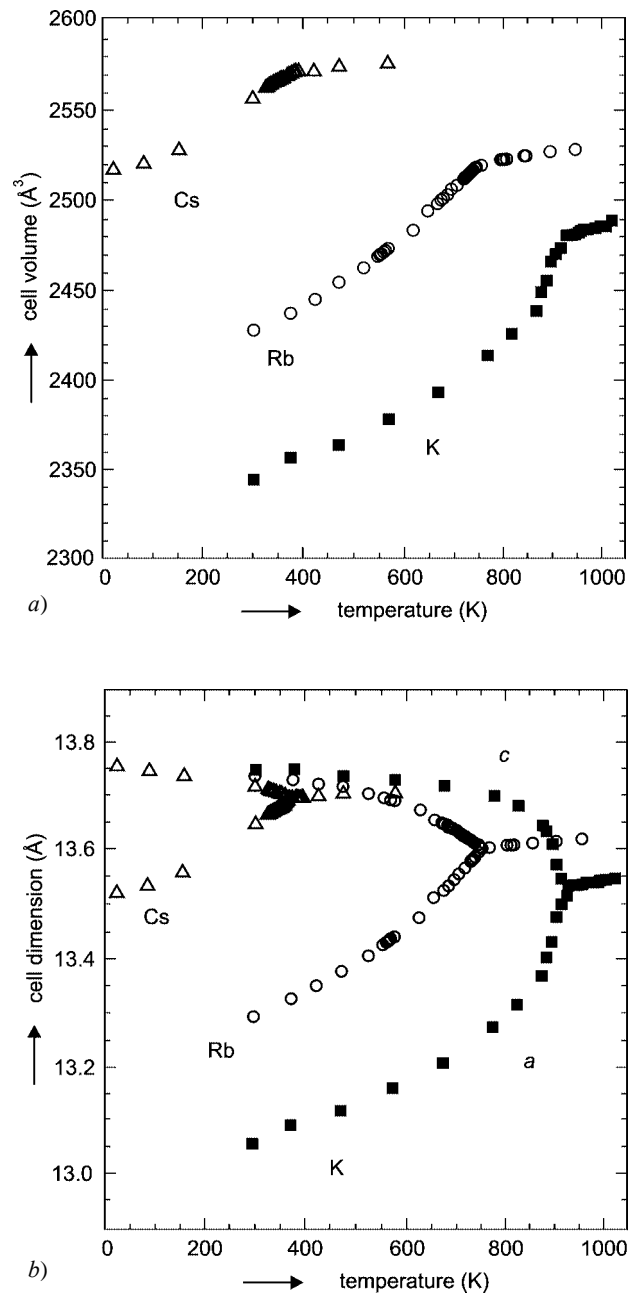


Figure 1. Temperature dependence of a) volume of the elementary cell, b) dimensions of the elementary cell.

tetrahedron layers, as established by Palmer [13] on the basis of neutron diffraction.

The transformation is martensitic, that is anisotropic and athermal, proceeds at the speed of sound in solids and exhibits temperature hystereses. It proceeds diffusion-free, by the slipping or twinning mechanism, during which processes the atoms retain their neighbours and move over a distance that is smaller than their original mutual one. In the case of leucite the martensitic transformation is facilitated by slippage of the six-member tetrahedron ring planes.

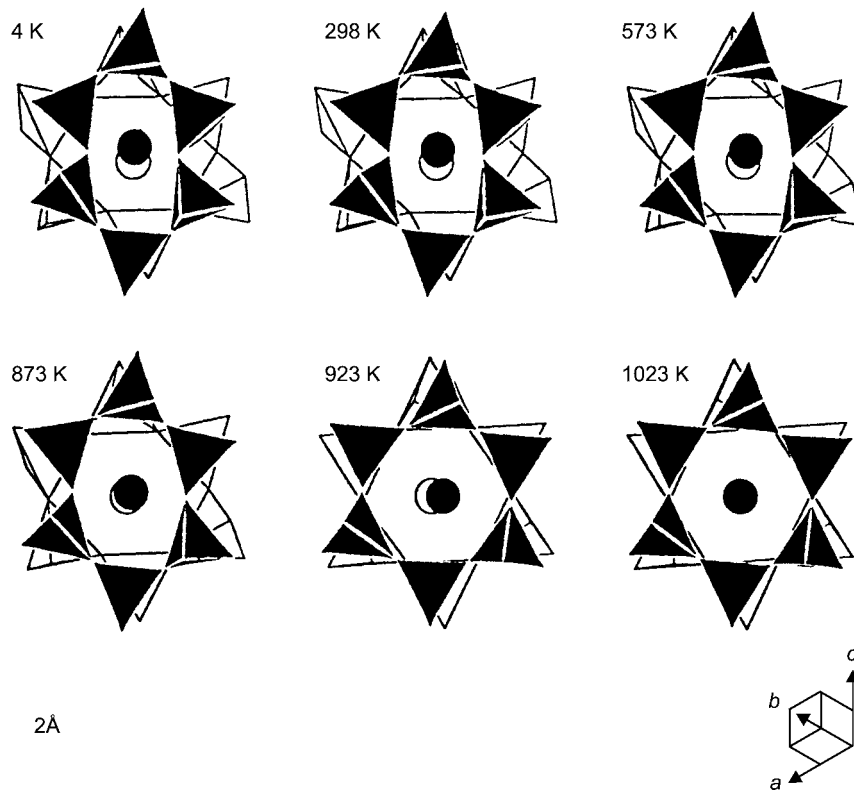


Figure 2. Temperature dependence of the structure of channels and of the placing of potassium ions.

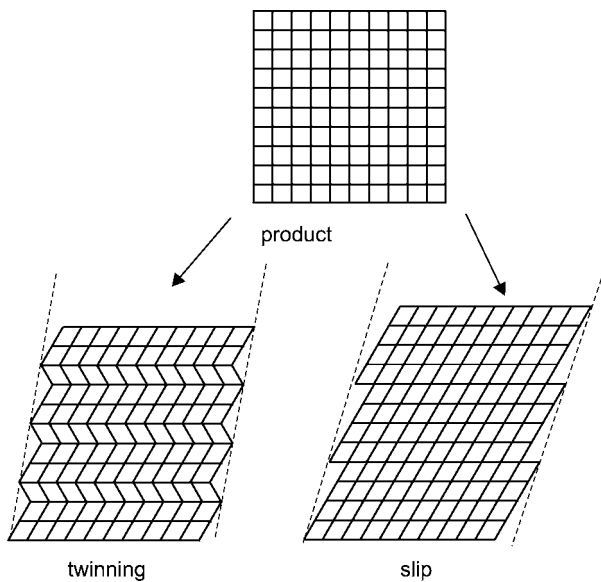


Figure 3. Two mechanisms of martensitic transformation: twinning and slipping.

On the basis of a similarity between martensitic transformation of leucite with that of  $ZrO_2$  it may be assumed that the application of leucite represents a promising and so far non-utilized way of preparing new structural materials. A prerequisite for this is of course

a better understanding of the mechanisms of promoting fracture toughness, about which very little is so far known in contrast to the ZTA materials.

#### The actual aims of research

The problem of fusion joining of porcelain with metals can be regarded as a satisfactorily resolved one. However, attainment of a satisfactory fracture toughness of leucite porcelain has so far remained an open issue, both from the standpoint of dependence of fracture toughness on the microstructure of the material, as well as from that of viable technology.

A great problem is represented by the fact that nucleation and growth of leucite crystals from melt, on which the present technology of leucite porcelain manufacture is based, are extraordinarily slow processes requiring very long holding periods on firing [15]. The same problem arises in connection with the firing of precursors prepared by the sol-gel method [16] or by decomposition of zeolites of suitable composition [17]. It is also difficult to control these processes so as to produce a homogeneous dispersion of leucite crystals in the vitreous matrix, i.e. a microstructure that with ZTA materials has been found optimal in terms of fracture toughness. As shown by Hölland [18], nucleation of leucite in glass takes place at the surface only, and it may be assumed that this might also be the case of the other precursors mentioned.

A viable way of resolving the problems might be offered by hydrothermal synthesis of leucite.

It was this method that has been proved successful in the preparation of pollucite [19, 20, 21] at a temperature of 220°C and with a holding period of the order of tens of minutes. Control of nucleation [22] and crystal growth under hydrothermal conditions was studied in detail in connection with the synthesis of zeolites [23, 24]. It may be assumed that this method could allow also leucite with a particle size of the order of tens nanometres to be synthesized, and subsequently used in preparing, with a suitable matrix, a composite material whose fracture toughness (again due to similarity with ZTA materials) should attain values exceeding several times those of exhibiting by contemporary leucite porcelain.

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