STRUCTURE ASSESSMENT BY X-RAY DIFRACTOMETRY FOR CERAMIC MATERIALS USED IN ORAL PROSTHETIC SYSTEMS

Maria URSACHE, Adina Oana ARMENCIA
University of Medicine and Pharmacy of Iasi, Dental Medicine Faculty, ROMANIA
adinaarmencia@yahoo.com

ABSTRACT
The paper presents a difractometric analysis on two types of ceramics nowadays available on the market and frequently used in restorative dentistry: InLine (IVOCLAR) and Hera-Ceram (HAEREUS KULZER). The diffractograms obtained by projecting the x-ray beam on the ceramic surface allowed establishing the structural characteristics that could influence the tribological behaviour of certain ceramic materials by determining the crystalline parameters and/or amorphous network and correlate the results to the wear coefficient values of the concerned materials. This non-destructive method that characterise materials’ structure establishes several correlations between the macroscopic properties and their atomic structure.

KEYWORDS: difractometry, ceramic, crystalline parameters.

INTRODUCTION
The properties a restorative material should include several such as those concerning the structure and surface quality (roughness, surface free energy, surface tension, damping, hydrophobicity, hydrophily, electrostatic interactions and microhardness) and they play a major clinical role, generally determining the material’s selection [2, 3].

The physico-chemical properties of ceramics are strongly related to their crystalline phases and the X-ray beam diffraction can be used for analysing the crystalline structure of the ceramic materials. Moreover, a X-ray diffractogram could offer information on the structural and crystalline parameters, as well as on the amorphous fraction of every type of ceramic material [2, 3, 4].

EXPERIMENTAL RESEARCH MATERIAL AND METHOD
The aim of the study was to determine the structural characteristics that could influence the tribological behaviour of certain ceramic materials by determining the crystalline and/or amorphous network of the concerned materials.

Using the ceramic materials, study specimens were prepared as disks of 25 mm radius and 2 mm thickness (0.5 mm metal base and 1.5 mm the ceramic aesthetic component).

Two types of ceramics nowadays available on the market and frequently employed in the restorative dentistry represented by the InLine (IVOCLAR) and HeraCeram (HERAEUS KULZER) materials (fig. 1) were used in order to assess their crystalline or/and the amorphous structural characteristics.
The following parameters were taken into account when manufacturing the specimens:
- micrometric or crystalline granules sizes,
- specimen thickness,
- preferential orientation,
- the possibility of deformatons’ occurring during cold working of the metallic base,
- specimen surface flatness on which the X-ray beam will be focused.

In order to obtain a proper focalization, the specimens were produced with a thin, strongly absorbent surface. The specimen thickness, \( t \), necessary for obtaining maximum intensity peaks must obey the following formula:

\[
t \geq \frac{3.2 \cdot \rho \cdot \sin \theta}{\rho' \cdot \mu}
\]  

where:
- \( \mu \) is the linear absorption coefficient as the fraction of a beam of radiation absorbed per unit thickness of the absorber,
- \( \rho \) and \( \rho' \) are the densities of the studied materials, given in the same unit,
- \( \theta \) – diffraction angle.

For having good and reliable results, the thickness \( t \) must be much higher than that one calculated with the above-mentioned formula. The actual amount of diffraction, which is approximately equal to the multiplication between the samples surface irradiated area and the X-ray penetration depth into the sample, depends on the linear absorption coefficient.

The samples were characterised with the help of X-ray diffractometry, using a diffractometer DRON 2, a Cu anticathode being used. The X-ray corresponding radiations were within the range of 1.54056 Å and 1.54182Å, as issued by the X-ray generator tube. The Cu K\( \alpha \) radiations were projected on the samples surface at different irradiation incidences; all the diffractograms were obtained by scanning the samples with a variable diffraction angle between 5° and 65°.

The records were done in a step-by-step procedure, with a 0.05° pass and a 4 seconds scanning time.

For the small angles region, the authors selected a system of registration with a 0.02 seconds pass and a 4 seconds absorption time. The maximum diffraction position in the diffractograms was identified according to the ASTM (American Society for Testing Materials) files guidelines, published under the aegis of the JCPDS (Joint Committee for Powder Diffraction Standards).

RESULTS

Figure 2 shows the diffractogram obtained by projecting the X-ray beam on the HeraCeram ceramic surface. It is noted that the HeraCeram is a two-phase material, which has a crystalline phase embedded in an amorphous phase. It is a material rich in crystalline phase, which will influence its mechanical properties. The diffraction peak height is closely related to the crystalline phase. The more crystalline plans, the higher and narrower the peak is, as shown in figure 2.

Figure 3 shows the diffractogram of the ceramic material.

The InLine ceramic has a reduced amount of crystalline phase (small diffraction peaks) within the
abundant amorphous phase, and a hardness value slightly superior to the HeraCeram ceramic.

**DISCUSSIONS**

The diffractographic analysis shows that the HeraCeram ceramic contains crystals with a large part in the tetragonal structure and a small fraction in the cubic structure. This variation is strongly related to the different orientation of the microcrystals in the cubic granules. The same analysis also emphasizes the diffraction peaks, which correspond to certain roughness peaks that will favour the material transfer (as described in further studies [1, 3]). The appearance of peaks characteristic to the presence of aluminium in the material structure, suggests the partial decomposition in the crystalline network (especially characteristic of the material HeraCeram as compared to the dental material InLine). The transfer layer from the “valleys” of the diffraction diagram characterises the roughness reduction within the wear traces. If the amount of crystalline phase of the ceramic material is very small (such as for ceramic InLine), there is a possibility of not being identified, a smaller percentage of 5% being considered a very small amount in order to expose the crystalline structure of analysed ceramic material [5, 6].

Additionally, the microcrystals orientation may influence the friction and wear coefficient values as many crystals can act as charge particles within the matrix glass ceramic material. The amount of crystals in the HeraCeram ceramic is much higher than the same quantity in the InLine ceramic, which explains the different wear behaviour of the two studied ceramic materials (results that are consistent with those presented in the literature). However, the presence of amorphous fraction offers superior mechanical properties for the ceramic material. As the degree of amorphous state is greater, the hardness of the material is better, but also its resistance to severe wear process. Also, the resistance to acid attacks in the oral environment is higher.

Basically, the degree of wear of these ceramic materials will depend on the homogeneity of the crystalline phase distribution in the amorphous matrix [6, 7]. It is known that a homogeneous distribution favours the initiation and propagation of cracks in the mass of a material with low resistance to acid attack (as it is observed in HeraCeram diffractograms). If crystalline phases are uniformly distributed, the degree of damage is reduced with increased reliability of the tribosystem (as InLine appropriate pottery, although crystalline fraction is reduced). Matrix glass is the glass-ceramic dental silicate, an inorganic product of fusion that has been cooled to a rigid state without crystallize. The polymerization increases the viscosity very quickly, eventually forming a very rigid three-dimensional network.

This explains the different behaviour of other types of ceramics, in which the main component is silica (D SING, VM13).

Added in increased quantities, it makes opaque the aluminium and ceramic resistance in rolling decreases, making it more brittle, more exposed to fatigue damaging (any pottery HeraCeram).

Aluminium ceramics, although having a composition similar to those with silicon, are less resistant. This leads to lower resistance to fracture (i.e., bending and compression), because propagation favours the crazing process. Worn material rate decreases with increasing silica concentration. As a result, the material becomes more resistant to wear. In the case of aluminous ceramics, the increased concentration of aluminium has a negative effect on the abrasion resistance [4, 5, 8]. The relationship between the coefficient of wear, the microhardness and the presence of crystalline or amorphous phases, although it is known, however, requires further research.

It is known that structural changes (which may be evidenced by X-ray diffraction) act as the limiting factor influencing the fatigue and wear resistance of materials in general, and in particular of ceramic materials, therefore, it is needed a special attention in understanding the mechanisms underlying structural changes that occur during their use in the oral environment, as a means of substitution of hard tooth structure.

Different mechanical properties are determined by different structures, which in turn are dependent on changes which occur in the crystallization of the surface. It is known that changes in structure and morphology of crystalline and amorphous phases of surface and deep layers influence hardness, property which, in turn, is closely connected to the tribological behaviour of ceramic material [4, 7, 8]. Basically, anisotropy (crystalline alignment dependency) influences the hardness of ceramics, property which, in turn, affects their resistance to wear (as revealed by the study performed by the authors).

**CONCLUSIONS**

The dependence character of the $\tau$ absorption coefficient for the $\lambda$ wavelength plays an important role in the structural analysis and provides the possibility of a radiation and filter selection in the processes of studying crystals. Although a two-phase material, the material CeramHera will have a low resistance, the microcrystals within its structure offering relatively low mechanical properties to the material. An appropriate hardness associated with proper resistance is the consequence of the amorphous
fraction presence in the bulk material. It is the case of the InLine ceramics.

Most non-destructive methods that could be used for characterising materials establish several correlations between the macroscopic properties and their atomic structure.

REFERENCES