The sintering furnace. The ignored component in the CAD/CAM system.
The quality of the high-temperature oven used for densification of zirconium oxide is gaining importance due to material innovations. Innovative, highly translucent types of zirconium oxide open up new possibilities – however, require suitable sintering conditions.

Dental zirconium oxide has been used clinically for over 20 years. It has become established as a high-strength and durable framework material. In recent years, many industrial manufacturers of ZrO_2 milling blanks have concentrated on increasing the translucency of the material. New chemical raw material variants and improved finishing techniques allow blanks to be produced that combine high pressure resistance (>900 MPa) with greater translucency. Liquid-based colouring systems are used for the creation of tooth shades allowing whitening of the incisal third. Furthermore, pre-coloured blanks in tooth shades are available. These materials are suitable for use as general frameworks for every bridge length and particularly for monolithic (fully anatomic) crowns and bridge prostheses without ceramic veneers in the posterior tooth area. The transparency of the latest generation of monolithic zirconium oxide is approaching that of glass ceramics. This new material group achieves minimal light refraction and reduced light scattering through a hybrid microstructure of cubic and tetragonal crystals, leading to even greater translucency. The spectrum of indications for monolithic prostheses can be extended to the front teeth and smile line area.

For the aesthetics of the veneered pieces of monolithic constructions to approximate the natural teeth, it is essential to master the shade precision and reproducibility. This can be incredibly difficult with the innovative, highly-translucent zirconium oxides. Beside the utilised colouring system and its correct use, the sintering process in particular has significant influence over the shade and opacity. During the shrinkage process and the consolidation of the material in the furnace, the result can be negatively influenced by various effects. To make the sintering process controllable, it is helpful to understand these effects. The selection of the furnace concept and knowledge of the precision in relation to the end temperature and heating rate are crucial.

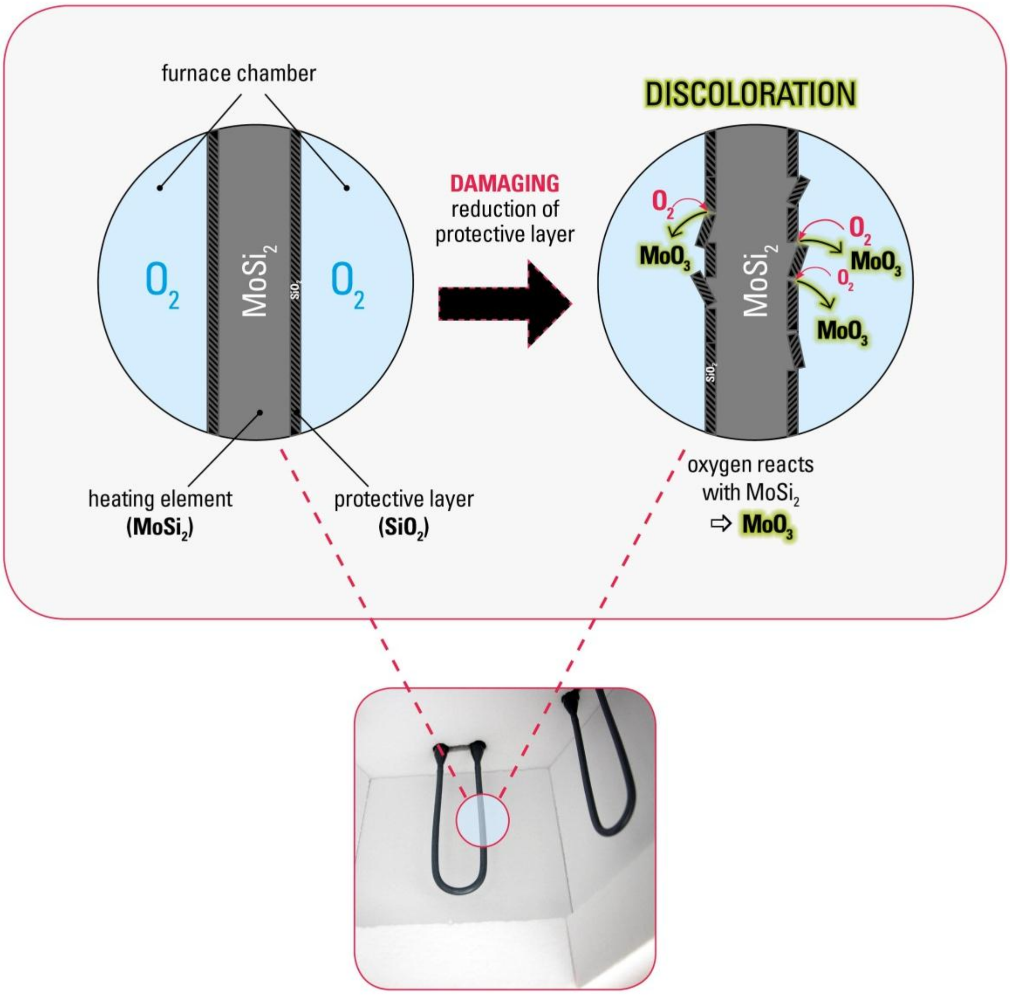
Discoloration

The high-temperature furnaces on offer for use in the dental sector fall essentially into two categories, distinguished by their integrated heating elements. The standard heating elements are made of molybdenum disilicide ($MoSi_2$) and silicon carbide (SiC).Undesired discolouration can take place with $MoSi_{2.}$ This is yellow-green on white, un-coloured zirconium oxide pieces (***Fig. 1***).

Fig. 1: Right crown: green-yellow discolouration caused by MoO_3 h

The discolourations are created by the release of MoO_3 (molybdenum (VI) trioxide) from the heating elements. If MoO_3 comes into contact with the chromophoric oxides in the colouring liquid, or one of the pre-coloured blanks, there is a mixing reaction, which can considerably distort the desired tooth colour. Intact heating elements made of $MoSi_2$ are encased in a protective layer of SiO_2 (silicon dioxide), which prevents this discolouration. If one considers the temperature behaviour of $MoSi_2$ heating elements, then reactions can be found in two temperature zones. In the lower zone of about 400-600 °C and in the upper zone range of about 1000 °C-1600 °C (depending on the furnace manufacturer). If one passes through the lower temperature zone at low speed, this can lead to pest oxidation during which reaction with oxygen primarily forms the undesirable MoO_3. At higher temperature, SiO_2 forms as a protective layer and this prevents or slows down the pest oxidation (***Fig. 2***).

Fig. 2: Representation of the resulting discolouration caused by the MoSi2 heating element ("pest oxidation"). The heating element depletes itself over time



The SiO_2 protective layer is under low residual compressive stress. If the stress becomes too high, e.g. through the continuous growth of the layer, then this eventually cracks and flakes can occur, and this will lead again to the creation of MoO_3 in the next heating phase. Cleaning cycles with rapid heating and long dwell times at high temperature can repair this protective layer (observe the furnace manufacturer's information). Several cycles may be necessary for sufficient repair, depending on the extent of the damage. The use of ZrO_2-based cleaning powders can also help to free the furnace chamber of MoO_3 residues. As both the pest oxidation and the protective layer need the heating element in order to form, this becomes increasingly depleted through continuous use. Therefore, the number of possible repairs and the functionality of the heating element are limited. Ultimately, an exchange of the heating element is essential. These discolouration effects are not seen with SiC-operated furnaces. Therefore, anyone wanting to eliminate a negative variable in his process, should make some enquires before investing in furnaces with SiC heating elements.

Influence of temperature on colour and translucency

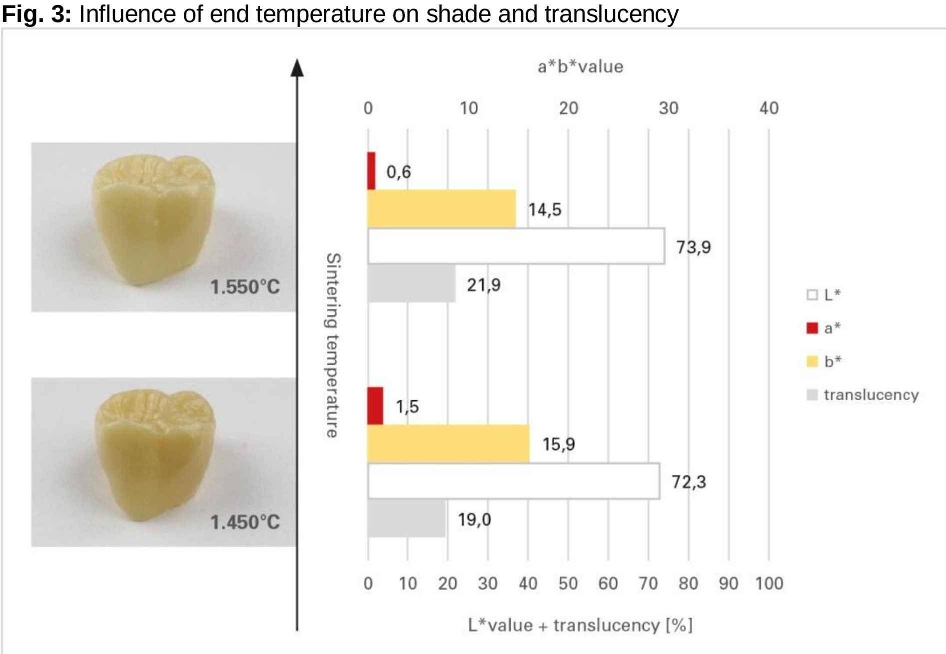
A zirconium oxide construction requires a specific amount of thermal energy in order to form an optimum structure. The incident light interacts with this structure, bringing about absorption and reflection of specific light wavelengths, whereby finally a particular colour effect is created. If the structure is significantly altered, the visual appearance of the material is also altered as a result. A stable sintering process is therefore a precondition for reproducible colour results.

Increasing grain growth is seen with **increasing sinter temperature** and the corresponding increase in the thermal energy input. In a structure with large grains, the light is less refracted and scattered, as there are fewer grain boundaries. This leads to increased translucency of the material.

But the chroma of the piece also changes, as the chromophoric dopants / ions are differently incorporated into the material structure leading to an altered reaction with the incident light.

Figure 3 shows crowns made from a highly-translucent zirconium oxide (3Y TZP-LA) coloured to shade A3.5.corresponding to Vita®. The sintering followed a standard sintering process (approx. 8 h) at varying sintering temperatures. The values of the shade and translucency measurements are presented in the diagram above. The measurement and description of the colours was performed using the L*a*b* system (cie Lab). This describes a three-dimensional colour space in which the brightness value L* and the colour coordinated a* (+a red / -a green) and b* (+b yellow / -b blue) of all the colours in the hue and chroma / saturation are represented by numbers.

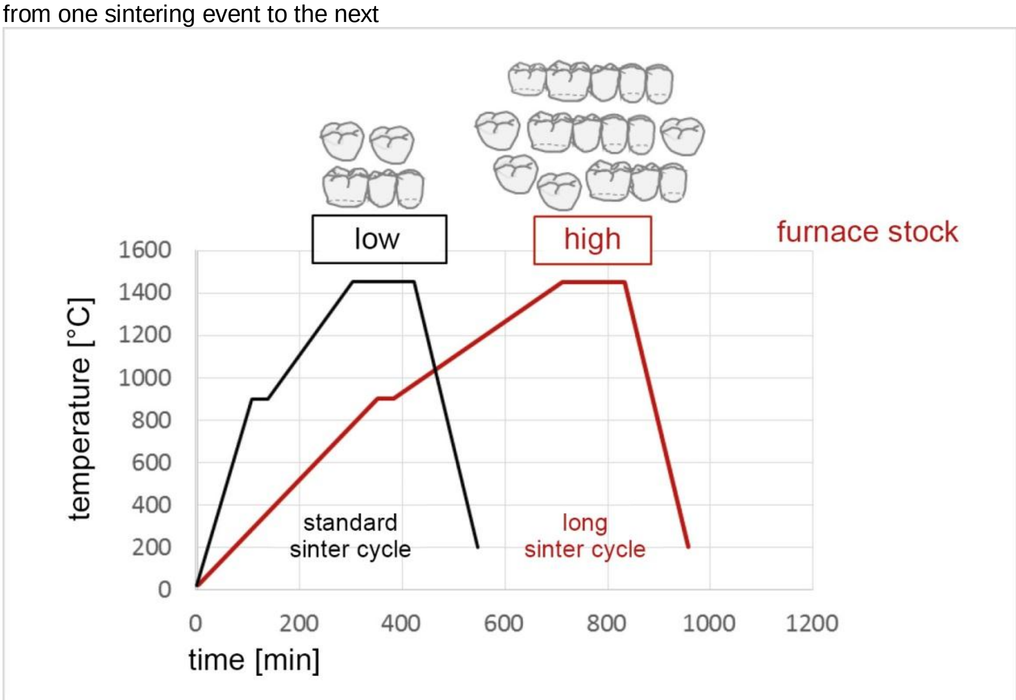
Fig. 3: Influence of end temperature on shade and translucency



From the diagram it can be assumed that the translucency increases by around 3 % with a rise in sinter temperature of 100 °C. At the same time, however, the hue also changes considerably as can be seen in the figures. The white value L* increases, while the red (a*) and the yellow (b*) percentages drop. The Vita® A shade series is defined as reddish-brownish. If the red / yellow chroma is lost, then correspondingly this differs from the target tooth shade.
So here the precision of the furnace in relation to the exact end temperature and energy distribution is required. A possibly way to determine the firing precision are tests with PTC rings. The PTCR (process temperature control ring) is a ceramic ring which shrinks during a special sinter cycle proportionally to the heat input. The furnace end-temperature can be determined from the final dimension of the ring with a precision of +/- 10°C using temperature tables. If a significant deviation is found between the furnace temperature and the programmed / expected sinter temperature using the PTCR control firing, then recalibration of the furnace is recommended.

In addition to the sintering end temperature, **the loading of the furnace** has an important influence on the resulting colour. In a fully loaded furnace, every single item has considerable less thermal energy available than in a comparable sinter cycle with a low furnace load. This can lead to substantial difference in the translucence and colour. To guarantee the reproducibility of the optical qualities, using a sintering program with a longer heating phase with a high furnace load and / or solid pieces is therefore recommended ***(Fig. 4)***.

Fig. 4: Increased furnace use for more pieces or sintering aids (dishes or supporting plates) absorbs more energy, which then is not available for the individual parts. Slower heating rates can help to achieve a uniform result from one sintering event to the next



Here, the use of a SiC oven can also have a positive effect. As it is not necessary to cover the work in SiC furnaces to prevent the individual pieces from discolouration, the furnace load is often smaller. The ceramic cover also absorbs energy which is then not available to the individual, shielded pieces for perfect sintering.
The aspects presented here can only shed light on a few influencing factors. Anyone wishing to improve their colouration results should request an elaborate consultation from his zirconium oxide and furnace suppliers. The colour fidelity and reproducibility can be improved with a well adjusted sintering process.