Hot Alone won't Do the Trick!

The sinter furnace for zirconia ceramics in respect of heating with molybdenum disilicide heating elements ($MoSi_2$) and high temperature insulation based on polycrystalline alumina wool (PCW) provides a solution for dental ceramics.

Introduction

The providers of CAD/CAM-systems for the production of full-ceramic restorations based on zirconia (ZrO_2) use a sinter furnace in addition to a scanner and a cutting/grinding machine. The requirements to processing of such materials have increased continually, along with the growing diversity of the zirconia round blanks and color liquids. In addition to materials characteristics that are to ensure the longest possible service life of the work, the visual impression of crowns, bridges, abutments, supra-constructions, etc., plays an essential role.

Translucent, highly translucent and fully colored round blanks have been developed in addition to the white ones in the course of the last years to improve this impression. Additionally, the market offers a growing number of color liquids from various providers to adjust the color of the zirconia to the patient's tooth color. This has clearly changed the requirements in particular to sinter furnaces in the last years. Apart from this, the temperature range is growing and the ZrO_2-works are sintered faster and faster. Temperatures for zirconia ceramics from below 1400 °C to above 1600 °C may be possible in future. The duration of the sintering cycle ranges from less than 15 min for individual crowns to overnight firings for complete restorations. The materials that are installed in the furnaces are exposed to extreme temperature changes for years.

Additionally, transport of the furnaces to the mechanical parts puts a considerable strain on the electronics system and not least the heating elements and insulation of the high temperature furnace. Such furnaces are often transported across several thousand kilometers with different means of transport by the furnace manufacturer before they reach their destinations.

Keywords
sinter furnace, $MoSi_2$ heating elements, dental ceramics, zirconia ceramics

Fig. 1
$MoSi_2$ heating element

Heating elements

About 5000–7000 furnaces for sintering zirconia are produced every year at the moment. The numbers are rising. There are two different heating element types that are installed in the dental furnaces on the market to achieve the extremely high temperatures, usually in excess of 1400 °C . By far the largest share of the furnaces on the market is built with molybdenum disilicide ($MoSi_2$) heating elements. In some few cases, silicon carbide (SiC) heating elements will be used. These two element types differ in their properties in addition to the entirely different basic materials.

SiC heating elements are usually used up to a temperature of 1530 °C as recommended by the furnace manufacturers. A firing cycle will take several hours. $MoSi_2$ heating elements can be used up to a temperature of 1750 °C, depending on the quality and furnace type. The maximum application temperature of these heating elements therefore is clearly above that of SiC heating elements. Additionally, the surface load, which means the power [W] that can be emitted per square centimeter [cm^2] is more than twice that of SiC, at above 25 W/cm^2. This permits much faster heating-up rates, to much higher application temperatures. Heating to 1550 °C in less than 15 min is possible.

MolyCom®-Hyper 1800 ($MoSi_2$) heating elements that have been used on the international dental market since 2005 have turned out to be much longer-lived than SiC elements in continuous tests and according to the experience of various fur-

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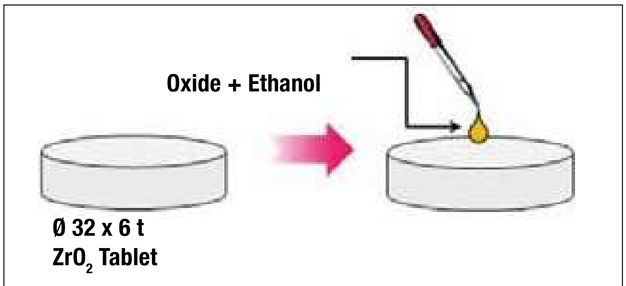
Fig. 2
Example of discolored teeth



Sintering conditions:
Material: yttrium-partially stabilized zirconia
Sintering temperature: 1500 °C (2732 °F) with 5 K/min heating up
Soaking time: 3 h

Fig. 3
Sample preparation

nace manufacturers. SiC elements usually need to be replaced after just a few hundred cycles due to the strong change of resistance, which corresponds to a service life of approx. 1–2 years at common use. MolyCom®-Hyper 1800 elements (Fig. 1) in contrast have been operated for more than 2500 cycles without any failure or need for exchange. Exchange of the defective element is usually sufficient in $MoSi_2$ heating elements. In contrast to this, all parts of the SiC elements must be exchanged in one due to the strongly impaired resistance.

Discoloration of zirconia

It is often said that zirconia works suffer discolorations from molybdenum (VI) oxide (MoO_3), which can be released by $MoSi_2$ heating elements. This is not accurate. Fig. 2 shows an example.

MoO_3 is released by oxidation of $MoSi_2$ at temperatures of 400–600 °C. Usually, the $MoSi_2$ heating elements form a protective SiO_2 layer on the surface that prevents oxidation of the basic material. The MoO_3 can be released when the SiO_2 layer grows too thick and spalling results. Formation of a too-thick SiO_2 layer is mostly prevented by additives in MolyCom®-Hyper 1800 elements. If spalling occurs anyway, regeneration firing at temperatures of 1450 °C for several hours can be the solution. No products should be in the furnace for this.

Examinations have shown that MoO_3 does not discolor zirconia. For this, many different oxides were dissolved in a liquid and dripped onto zirconia samples as shown in Fig. 3. As the samples in Fig. 4 show, the zirconia samples that were treated with MoO_3 showed no discoloration in the zirconia after sintering. Samples treated with Al_2O_3, SiO_2, Cr_2O_3, MgO and in particular Fe_2O_3 showed discolorations – some of them considerable. This shows that the release of these oxides can considerably contribute to discoloration of ZrO_2. MoO_3, however, does not. The visual impression was confirmed by a colorimeter, as can be seen in Fig. 5.

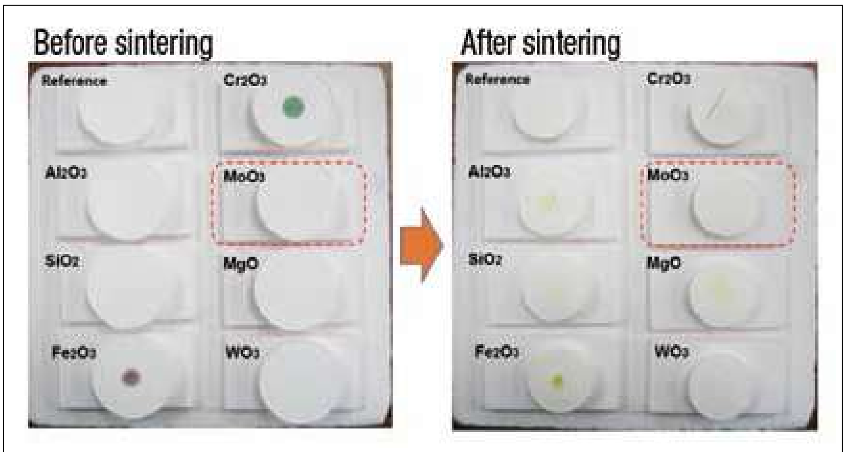
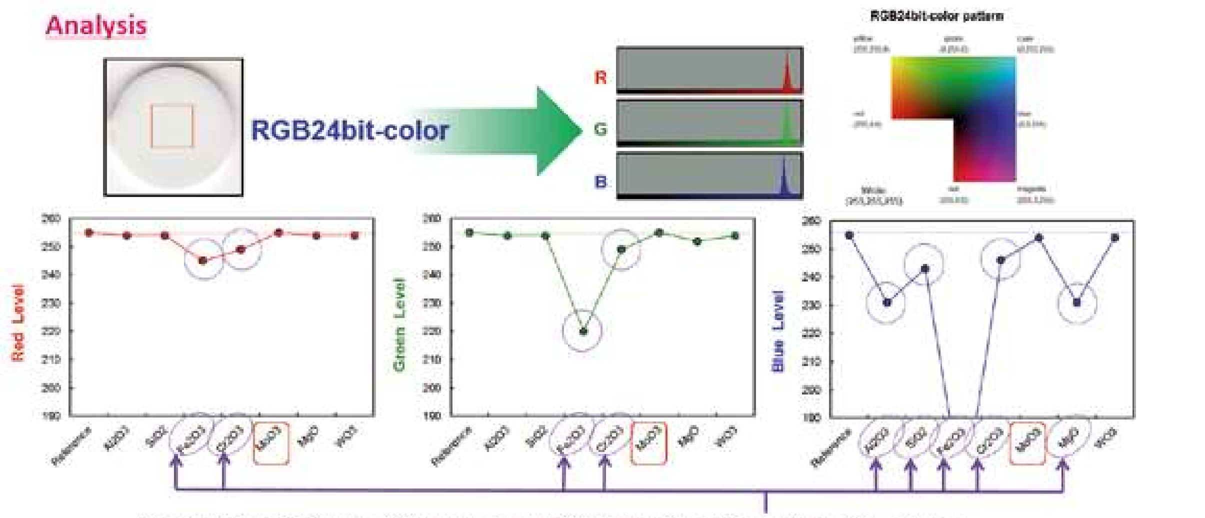


Fig. 4
Test with several oxides on ZrO_2-samples

These discolorations occur when heating elements of standard $MoSi_2$ qualities are used in zirconia furnaces. MolyCom®-Hyper 1800 heating elements are highly pure heating elements that have a much lower degree of contamination than standard elements. This makes it possible to nearly entirely exclude contaminations. For even stricter requirements, MolyCom®-Hyper 1800 Super Clean elements can be used, which have an even lower degree of contamination. Fig. 6 shows samples after sintering with different $MoSi_2$ heating element types. To increase contamination, the samples were sintered at temperatures of 1630 °C and 1680 °C, which is far above the usual range for ZrO_2. It can be seen clearly that the standard heating elements of $MoSi_2$ led to much stronger contamination of the ZrO_2 samples.

If we additionally compare the chemical analysis of the heating elements (Tab. 1), the standard heating elements show a much higher degree of contamination, in particular by iron oxide. No contamination could be measured at use of the MolyCom®-Hyper 1800 elements up to a temperature of 1630 °C. No contamination was measured for MolyCom®-Hyper 1800 Super Clean elements up to 1680 °C.

Additionally, a contaminated zirconia sample (shown in the analysis in Fig. 7) on the surface was analyzed with a secondary ion mass spectrometry (SIMS). As the analysis



Discoloration of different oxides proved, especially iron oxide. MoO_3 shows no discoloration.

Fig. 5
Proof of the color change by RGB 24 Bit color colorimeter

Tab. 1 Chemical analysis of $MoSi_2$ heating elements

[ppm]	Al	Fe	Mg	Ca	Ti	Na	K	Cr	Ni	Mn
Standard $MoSi_2$ heating elements	3500	1200	740	560	114	104	95	53	43	13
MolyCom-Hyper	<10	590	<10	<10	<10	<10	<10	20	11	<10
MolyCom-Hyper Super Clean	<10	90	<10	<10	<10	<10	<10	<10	<10	<10

shows, increased contents of iron oxide could be documented in the sample up to a depth of 0,15 µm. While the degree of contamination is very low, it has a considerable visual effect.
The vapor pressures of many different oxides at the surface temperatures of the $MoSi_2$ heating elements in the furnace were additionally calculated with Fact Sage. They are shown in Fig. 8.
It becomes evident that MoO_3, tungsten (VI) oxide (WO_3) and iron oxide have high vapor pressures at the application temperatures in the dental furnace. MoO_3 does not need to be considered in this, since it has already been documented that it will not discolor ZrO_2. Other oxides, such as Al_2O_3 have much lower vapor pressures and therefore do not contribute to contamination. Again, it becomes evident that the iron oxide is the essential factor that contributes to contamination of the ZrO_2.

Color liquids

Color liquids are often used to color the ZrO_2 ceramics. They contain metal salts and other compounds dissolved in a liquid. Acids were once commonly used for this. Today, most of the available liquids are water-based. Liquids that will form many different oxides during firing, such as Fe_2O_3, CuO, MnO, Co_2O_3, Bi_2O_3, ZrO_2, V_2O_3, CrO_2 and others, are used to discolor the material. The ZrO_2 blank is either soaked in them or painted with them. Sufficient drying of the blank after this is very important. This is often not observed sufficiently. If liquid remains in the blank, it will evaporate while firing and dissolved compounds will spread in the furnace, contaminating it. This affects the heating elements as well as the insulation and may cause severe contamination of the furnace, which in turn will discolor the subsequent ZrO_2 works.

Furthermore, the inside of the furnace and the $MoSi_2$ heating elements will be additionally stressed since the protective layer of SiO_2 will be destroyed, which in turn will reduce service life. To avoid this, products can be fired in a closed saggar, which is called an UltraSaggar – ZTA 1600. A material of zirconia toughened alumina (ZTA) has proven valuable for this. It can be used even at heating-up rates of up to 100 K/min. Tests were performed, with ZrO_2 samples being fired in a closed saggar as well as on top of it in a contaminated furnace. The color differences between the samples were considerable, as shown in Fig. 9.

Insulation

Very high demands are posed to insulation of a sintering furnace. The material is subject to extreme temperature changes and must resist temperatures of up to 1600 °C.

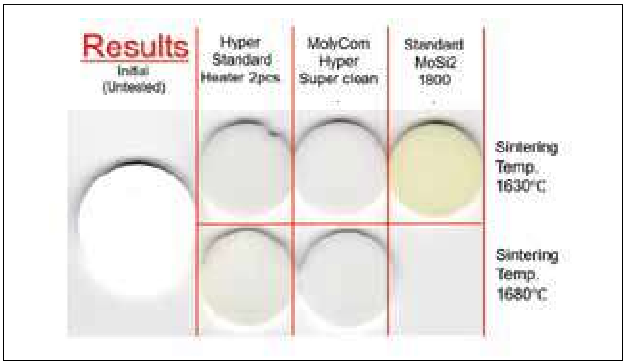


Fig. 6
Color changes from different heating element qualities

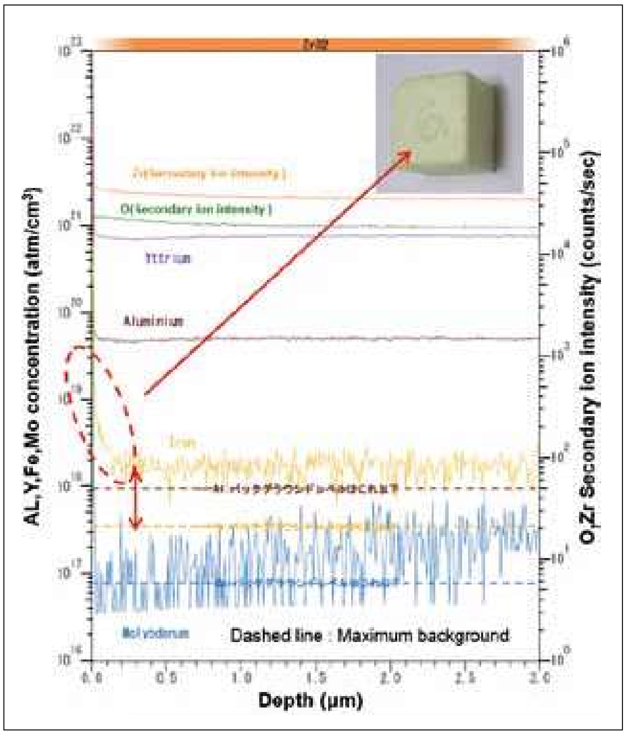


Fig. 7
Secondary ion mass spectrometry (SIMS) of a contaminated ZrO_2 sample

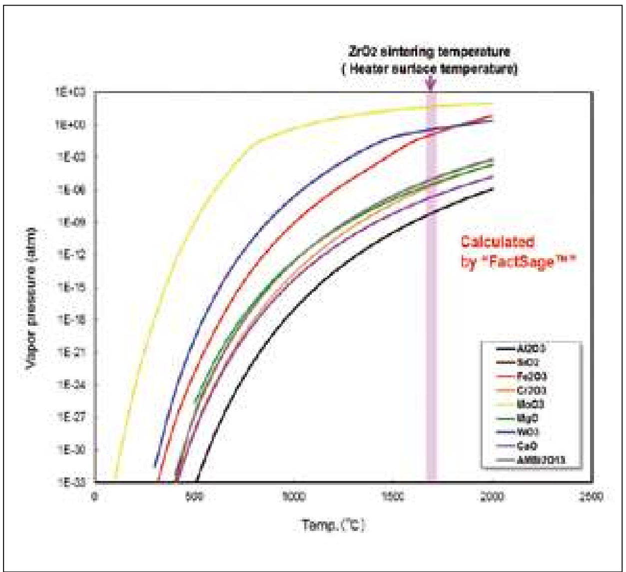


Fig. 8
Vapor pressure of different oxides at surface temperature of heating elements in use

Fig. 9
Sample 24 was sintered on a closed saggar (muffle); sample 17 was inside the saggar in the same firing run in a contaminated furnace

On the other hand, furnace manufacturers must observe very precise production accuracy. UltraBoards have proven their worth for this. These are insulation boards based on polycrystalline alumina wool (PCW). The outstanding thermal shock resistance and the low heat capacity permits even the fastest firing cycles at <30 min. It is recommended not to use insulation boards with refractory ceramic fibers (RCF), since they pose a health concern.

In addition to this, a newly developed recipe permitted development of a nearly dust-free UltraBoard/UltraVac 1750/400PS (RCF-free) that also withstands difficult transports without any significant abrasion. The insulation structure has to be considered in this as well. Backup insulation with an extremely low heat transmission factor permits using much thinner insulations than when using conventional refractory ceramic fibers.

Apart from board materials, the company offers complete furnace sets adjusted to the specific requirements of the dental market in cooperation with its customers for more than 10 years. Complex geometries with insulation materials that can be used up to 1800 °C including the supply of necessary heating elements can be implemented.