Novel Zirconate Based Moulds for the Investment Casting of Titanium Alloy Melts

L. Freitag, St. Schafföner, N. Lippert, Chr. Faßauer, C. Legner, U. E. Klotz, Chr. G. Aneziris

Dedicated to the 10th Anniversary of refractories WORLDFORUM

Investment casting allows the near net shape production of complex cast parts, but the investment casting of high melting and highly reactive titanium alloy melts is very difficult. Calcium zirconate (CaZrO$_3$) is a novel ceramic refractory material, which is particularly stable in a highly reducing atmosphere and in contact with extremely reducing titanium alloy melts such as Ti6Al4V. Besides the refractory, the choice of the binder is equally important because conventional silicate binders significantly impair the corrosion resistance. Although there have been successful attempts to develop CaZrO$_3$ investment casting moulds, silica-free CaZrO$_3$ investment casting moulds using a water-based binder have not yet been reported.

For the first time, graded CaZrO$_3$ investment casting moulds using a silica-free water-based binder system were successfully produced [1]. Moreover, the chemical, physical, thermo-mechanical and microstructural properties of the moulds were described. A combination of fine-grained primary coats and coarse-grained secondary coats resulted in a high surface quality as well as sufficient mechanical stability of the moulds. Investment casting of Ti6Al4V led to an exceptionally low hardness increase of the cast part, suggesting that only a slight corrosion reaction took place. Thus, the silica-free CaZrO$_3$ investment casting moulds contributed to an improved investment casting of titanium alloys.

1 Introduction

Titanium alloys are key materials in aerospace as well as in biomedical and chemical industries due to their high strength combined with a low density and an excellent corrosion resistance. Investment casting allows the near net shaping of complex cast parts, using a ceramic refractory mould, which is produced by the lost-wax process, and filling it with the liquid metal melt. After solidifying, the ceramic mould is removed by breaking the shell. Fig. 1 provides a general model of the ceramic coats produced by dip-coating and stuccoing on the wax pattern. Due to the high reactivity and the high melting point of titanium alloy melts, much research was done to identify a suitable refractory material [1–7]. Yet, conventional refractories such as Al$_2$O$_3$, SiO$_2$, ZrO$_2$, CaO

![Fig. 1 Model of the coats on the wax pattern [1] (the coats are produced by dip-coating and stuccoing)](image-url)
and Y2O3 were not sufficiently corrosion resistant and had further drawbacks. Recently, calcium zirconate (CaZrO3), a novel refrac-
tory material with a high melting point of 2368 °C, was successfully evaluated in contact with titanium alloy melts [1, 3, 4]. The production of CaZrO3 investment cast-
ing moulds was reported by Kim et al. [2], but was not yet presented in detail. Thus, investment casting moulds based on CaZrO3 and a silica-free binder were developed and extensively described. Instead of silica bind-
ers, which remain in the mould and impair the corrosion resistance, a temporary binder based on a polymer dispersion was used. Required mould properties include corrosion resistance, thermal shock resistance, creep resistance, sufficient strength in green and sintered state, sufficient permeability and high surface quality. A graded composition of coatings combines the surface quality of a fine-grained facecoat with the high creep re-
sistance and stability of coarse-grained sec-
toary coats and might even lead to an im-
proved thermal shock resistance by different thermal expansion coefficients of the coats.

2 Experimental

2.1 Slip production

First, stable coarse-grained and fine-grained CaZrO3 slips with a maximum particle size of 1 mm (S1) and 0.5 mm (S0.5), respectively, were developed [1]. The used raw materials were fused CaZrO3 (Imerys Fused Minerals Murg GmbH/DE) and CaZrO3 produced by solid state reaction synthesis similar to Schafföner et al. [7] for the finest particle fraction. To ensure a good flowability and to minimise the water demand, the particle size distribution of the slips was optimised based on the model of Funk and Dinger with a distribution modulus of q = 0.22. The batches are summarized in Tab. 1.

To improve the stability of the slips, xanthan gum (Axialt RH 50 MD, C.H. Erbslöh GmbH & Co. KG/DE) and food grade guar gum (Axilat RH 50 MD, C.H. Erbslöh GmbH & Co. KG/DE) were added to the solids. The amount of stabilizers was slightly higher for S1 due to the coarser grains. Moreover, the content of solids in the slips was adjusted as high as possible (>90 %) to ensure a good wetting behav-

To begin with, distilled water was mixed with the dispersing and wetting additive (BYK LP-C 22134, BYK-Chemie GmbH/DE) and the defoamer (BYK LP-C 22787, BYK-Chemie GmbH/DE). This mixture was added to the solids followed by 5 min stirring with a high shearing laboratory mixer (RZR 2102 control, Heidolph Instruments GmbH & Co. KG/DE). Then, the polymer dispersion binder (BYK LP-C 22893, BYK-Chemie GmbH/DE) was added as a temporary binder and fi-

Having prepared stable slips, which were shear-thinning and slightly thixotropic as described in a previous study [1], cylindrical wax patterns (height: 80 mm, diameter: 10 mm) consisting of Aqua Green Flake Wax (Freeman Manufacturing & Supply Company, Avon/US) were dipped into the ceramic slurry for 10 s, and were then stuc-

ted after draining of the excessive slip for 30 s. The stucco material was fused CaZrO3 with a particle size of 0.5–1 mm, and 0–0.5 mm after each dip-coating with S1 and S0.5, respectively. For the stuccoing process a modified siev-
ing machine was used. The wax patterns were attached to a screw driller and a sufficient amount of the stucco material placed on a sieve. Dur-

Tab. 1 Composition of the coarse-grained slip S1 and the fine-grained slip S0.5

<table>
<thead>
<tr>
<th>Product Name</th>
<th>Raw Material</th>
<th>Grain Size</th>
<th>( d_{50} ) [µm]</th>
<th>( S_1 ) [mass-%]</th>
<th>( S_{0.5} ) [mass-%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Imerys fused CaZrO3</td>
<td>CaZrO3</td>
<td>1–0.5 mm</td>
<td>848.4</td>
<td>25</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.5–0.0 mm</td>
<td>167.2</td>
<td>30</td>
<td>59</td>
</tr>
<tr>
<td></td>
<td></td>
<td>−45 µm</td>
<td>12,61</td>
<td>25</td>
<td>12</td>
</tr>
<tr>
<td>Stoichiometric synthesis</td>
<td>synthesized</td>
<td>2.14</td>
<td>20</td>
<td>29</td>
<td></td>
</tr>
<tr>
<td>Axialt RH 50 MD</td>
<td>Xanthan gum</td>
<td>Mass relative to dry mass</td>
<td>0.05</td>
<td>0.02</td>
<td></td>
</tr>
<tr>
<td>Food grade guar gum</td>
<td>Guar gum</td>
<td></td>
<td>0.05</td>
<td>0.02</td>
<td></td>
</tr>
<tr>
<td>Water</td>
<td>H2O</td>
<td></td>
<td>6.38</td>
<td>6.73</td>
<td></td>
</tr>
<tr>
<td>BYK LP-C 22134</td>
<td>Dispersing and wetting additive</td>
<td></td>
<td>2</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>BYK LP-C 22787</td>
<td>Defoamer</td>
<td></td>
<td>0.05</td>
<td>0.05</td>
<td></td>
</tr>
<tr>
<td>BYK LP-C 22893</td>
<td>Binder</td>
<td></td>
<td>4</td>
<td>4</td>
<td></td>
</tr>
</tbody>
</table>

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Later on, the coated samples were carefully dried at a temperature of 30 °C and a relative humidity of 60 % in a climate chamber (KPK 3533/15, Neutron Klimasimulation GmbH/DE). The drying times after the first coating and the next coatings were 2 h or 5 h, respectively. After the last coating step, the samples were dried for 7 d in the cli-

2.3 Mould properties

The shell thickness in the green state was evaluated prior to dewaxing. Thereby, 5 moulds of each composition were mea-

After sintering, 5 samples of each composition were investigated regarding their apparent porosity using the Archimedes method based on the standard DIN EN 993–1 with water as the immersion me-

Moreover, the pore size distribution

of one sample of each composition was determined using mercury porosimetry (AutoPore V 9600, Micromeritics GmbH/DE). These properties were investigated because they are related to the permeability of the mould, an important property, which is hard to measure for the original samples.

The thermal shock experiments were conducted by heating the samples in a preheated oven for 30 min and subsequent quenching in water. Regarding the heating temperature, preliminary experiments were carried out. The standard DIN EN 993-11 suggests 950 °C as the testing temperature, however, this program led to a too heavy destruction of the samples. Finally, 650 °C was determined as a suitable temperature which allowed the comparative evaluation of the moulds.

Furthermore, the cold modulus of rupture of a minimum of 10 samples with and without thermal shock exposure, respectively, was determined. Thus, the cylindrical hollow samples were exposed to a three point flexural test (TIRAtest 28100, TIRA GmbH/DE). The length of the support span was 3 cm, the testing velocity was 2 mm/min. Depending on the shell thickness of the samples, the maximum bending force was evaluated in order to estimate the influences of shell thickness and thermal shock exposure. Finally, the surface, microstructure and bonding of the samples was examined by a field emission scanning electron microscope (SEM) (XL30FEG, FEI Company/NL).

3 Results and discussion

3.1 Mould properties

After successful dewaxing and sintering, the surface of the moulds was homogeneous and smooth (Fig. 2). The properties of the investigated moulds are summarized in Tab. 2. Regarding the thickness of the moulds before firing, the average standard deviation was 6,2 %. Considering the manual coating process and the high maximum grain size, these variations are tolerable, so the shell thickness can still be seen as relatively homogeneous. The green shell thickness of all coarse-grained and graded moulds after 5 coats was 6,3 ± 0,5 mm. Generally, the shell thickness varied only slightly, but in most cases an increasing number of S0,5 front coats tended to result in a thinner shell. Surprisingly, this was not the case for 3 coats of S0,5, as the shell thickness slightly increased. A possible reason might be the much better wetting behaviour of the slip S0,5, which was adjusted to minimize draining, especially for the primary coat on the wax pattern. This slip might be less ap-

<table>
<thead>
<tr>
<th>Coats</th>
<th>Primary Coats of $S_{0,5}$</th>
<th>Thickness (Green) [mm]</th>
<th>Apparent Porosity [%]</th>
<th>Median Pore Diameter [µm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>0</td>
<td>4,5 ± 0,2</td>
<td>23,7 ± 0,4</td>
<td>16,0</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>3,8 ± 0,2</td>
<td>25,8 ± 0,4</td>
<td>21,6</td>
</tr>
<tr>
<td>3</td>
<td>2</td>
<td>2,9 ± 0,2</td>
<td>24,2 ± 2,6</td>
<td>10,6</td>
</tr>
<tr>
<td>3</td>
<td>3</td>
<td>3,8 ± 0,2</td>
<td>29,7 ± 0,0</td>
<td>19,7</td>
</tr>
<tr>
<td>5</td>
<td>0</td>
<td>7,2 ± 0,5</td>
<td>22,9 ± 0,5</td>
<td>12,0</td>
</tr>
<tr>
<td>5</td>
<td>1</td>
<td>6,5 ± 0,2</td>
<td>23,7 ± 0,3</td>
<td>19,7</td>
</tr>
<tr>
<td>5</td>
<td>2</td>
<td>5,6 ± 0,6</td>
<td>22,6 ± 0,2</td>
<td>19,1</td>
</tr>
<tr>
<td>5</td>
<td>3</td>
<td>6,9 ± 0,4</td>
<td>27,1 ± 0,2</td>
<td>19,8</td>
</tr>
<tr>
<td>7</td>
<td>0</td>
<td>10,4 ± 0,5</td>
<td>23,5 ± 1,3</td>
<td>15,5</td>
</tr>
<tr>
<td>7</td>
<td>1</td>
<td>9,2 ± 1,0</td>
<td>22,6 ± 0,5</td>
<td>17,1</td>
</tr>
<tr>
<td>7</td>
<td>2</td>
<td>8,1 ± 0,4</td>
<td>21,8 ± 0,1</td>
<td>18,0</td>
</tr>
<tr>
<td>7</td>
<td>3</td>
<td>10,1 ± 0,5</td>
<td>26,8 ± 0,3</td>
<td>21,6</td>
</tr>
</tbody>
</table>
appropriate for the secondary coats because draining is necessary to cover the increasing surface while the stability is mainly provided by the coarser grains of S₁.

The average apparent porosity of the coarse-grained and graded CaZrO₃ investment casting moulds of 23.4 ± 0.9 % and 23.2 ± 1.5 %, respectively, did not significantly differ. Presumably, there were two interactive effects on the apparent porosity. The higher maximum grain size of S₁ might increase the apparent porosity but it appears that the broader grain size distribution also led to a denser packing and therefore to a decrease of the apparent porosity. Nevertheless, the values are regarded as beneficial for the corrosion resistance as well as the thermal shock resistance and are in the typical range for refractories [9].

In addition, the relatively high apparent porosity combined with the large median pore diameter of the coarse-grained and the graded samples of 14.5 ± 2.2 µm and 16.6 ± 3.6 µm, respectively, might contribute to an improved permeability of the mould. However, the pore size should not be too high in order to avoid a critical drop in strength [9].

After thermal shock with 650 °C as the testing temperature, no samples with 3, 5 or 7 coats respectively were completely destroyed. The degree of impairment decreased with increasing shell thickness. All tested samples with 7 coats remained undamaged, whereas most samples with 3 coats were damaged to varying degrees. Some of these samples, however, exhibited small previous cracks from dewaxing. Regarding the samples with 5 coats, 80 % of the samples were undamaged and only 20 % were slightly damaged.

During investment casting, thermal shock occurs as rapid heating, not as cooling. Yet, rapid cooling is more critical in case of ceramic materials, so if the material withstands rapid cooling, it usually also withstands rapid heating [9].

Fig. 3 displays the bending force [N] of the different samples as a function of the shell thickness [mm]. Despite a certain variation, there is a linear increase of the bending force with increasing shell thickness both for the samples without and with thermal shock exposure. In case of the thermally shocked samples, the slope is smaller, which can be explained when the effect of the shell thickness is taken into account. In all cases, a minimum shell thickness is required to provide stability. Applying only 3 coats might not be sufficient. However, with increasing shell thickness the difference between the samples with and without thermal shock exposure becomes bigger, which is generally due to the drop in strength after thermal shock. This drop becomes more apparent as the shell thickness increases because the temperature gradient increases. Therefore, the shell thickness should not be unnecessarily high. In this case, a shell thick-
ness of 6–10 mm and about 5 coats of the slip system might be stable enough without generating a large temperature gradient. Moreover, the microstructure of a graded CaZrO$_3$ investment casting mould (2 fine-grained primary coats, 3 coarse-grained secondary coats) is presented in Fig. 4–5. Fig. 4 illustrates the build-up of the coats. Comparing the fine-grained structure of the inner surface and the fine-grained front coats and the coarse grains of the coarse-grained coats, the contrast is remarkable. Nevertheless, an excellent bonding between the different coats was observed. The coarse grains are embedded in a fine-grained matrix. This composition contributed to a porous matrix and thus presumably to an improved permeability. Fig. 5 reveals the inner surface of the graded CaZrO$_3$ investment casting mould with 2 fine-grained primary coats. A uniform matrix of fine grains is apparent, which contains some small pores. This combination of an even inner surface and open porosity is considered as beneficial for investment casting.

3.2 Investment casting

After investment casting using a coarse-grained CaZrO$_3$ investment casting mould with 3 coats, a cast part with a mainly smooth and shiny surface (Fig. 6) was obtained. Due to the coarse grains of $S_1$, some rough parts are also visible. The mould withstood the thermal shock during casting and could be easily removed. As can be seen in Fig. 7, the surface hardness of the final cast part was 324–360 HV0.1. Compared to the starting material hardness of 312 HV0.1, the hardness increased only slightly and no alpha case occurred. This is in line with the smooth and shiny appearance of the cast part. Kim et al. [1] reported similar low hardness values for silica-free CaZrO$_3$ moulds and much higher values for Al$_2$O$_3$ and ZrO$_2$ moulds in contact with Ti6Al4V. Consequently, it can be considered that only a slight corrosion reaction took place.

Tab. 3 presents the chemical analysis of the cast part by glow discharge optical emission spectroscopy (GDOES). The impurities measured by GDOES were lower than the ASTM B348 specifications and also lower than the data described by Schafföner et al. [4] for melting Ti6Al4V in CaZrO$_3$ crucibles, which was supported by the beneficial low hardness values. Yet, there are limitations regarding these comparisons. Due to the shape, only the core of the cast part was chemically analysed, so the impurity contents on the surface might be slightly higher. Furthermore, it has to be considered that melting experiments in crucibles are characterized by longer contact times and melt movements during vacuum induction melting, which considerably increases corrosion [2].

4 Conclusions

- Generally, the slips were thixotropic and shear-thinning, which suggests sufficient stability and suitability for dip-coating. The coarse-grained slip also exhibited a stability-providing yield point.
- Silica-free coarse-grained and graded CaZrO$_3$ investment casting moulds with a...
sufficient shell thickness were successfully produced.

- The high apparent porosity and the large median pore diameter might imply a good permeability.

- The microstructure investigated by SEM is characterized by a good bonding of coating layers and stucco as well as a porous matrix that results from coarse grains embedded in a fine-grained network. The use of the fine-grained slip for the first coating considerably improved the quality of the inner surface.

- The hardness increase on the surface of the final Ti6Al4V cast part was exceptionally low, suggesting that only a slight corrosion reaction occurred. These results indicate the high potential of silica-free CaZrO₃ investment casting moulds to replace conventional silica-containing investment casting moulds as a novel corrosion resistant material for the investment casting of titanium alloy melts.

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**References**


