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Original Article

Functional coatings for titanium casting molds using the replica technique

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ABSTRACT

The quality of titanium cast parts depends not only on the corrosion reaction of the mold in contact with the titanium alloy melt, but also on the dimensional accuracy and the surface quality of the investment casting mold. Usually, the ceramic mold is produced by dip-coating. This contribution investigated the coating properties of green calcium zirconate ($CaZrO_3$) coatings produced by the replica technique. Thus, the effect of different coating slurries as well as different coating technologies on important coating properties was analyzed. In all cases, centrifuging and spraying produced thinner coatings compared to dip-coating. Using an appropriate coating slip, particularly centrifuging revealed a cohesive homogeneous coating surface and is therefore a promising technology for the production of functional coatings for titanium casting molds.

1. Introduction

Investment casting of titanium and its alloys enables the near net shaping of complex cast parts such as turbine blades, jewelry or hip replacement joints. Due to their excellent strength, low density and high biocompatibility, especially titanium alloys meet the constantly increasing demands of chemical, biomedical and aerospace industries [1]. The main challenge in titanium metallurgy is the high reactivity of titanium alloy melts in contact with nearly every ceramic refractory material. Usually a heavy corrosion reaction causes a hard and brittle oxygen-enriched surface called alpha case, which impairs the surface quality as well as the mechanical properties of the cast parts [1–4].

Recent investigations have revealed the high corrosion resistance of the novel ceramic refractory material calcium zirconate ($CaZrO_3$) in contact with titanium alloy melts, especially Ti6Al4V [5–7]. Investment casting molds based on a silica-free $CaZrO_3$ slurry reduced the corrosion reaction considerably [7].

The production of investment casting molds by the lost-wax process is state of the art [1,8]. For this purpose, a wax model is repeatedly dip-coated into a ceramic slurry and then sprinkled with ceramic stucco. After sufficient drying between each coating step and after final coating, dewaxing and sintering of the mold take place. Usually, the inner surface of the obtained ceramic mold determines the surface quality of the final cast part, which is eventually produced by casting the metal melt into the mold. The replica technique by Schwartzwalder—a similar technology in the way a model is replicated—describes the processing of macroporous ceramic foam filters [9], which has become an established technology for molten metal filtration [10–13]. Important process steps include the coating of a polymeric foam with ceramic slurry, drying, burning out the foam and final sintering. Different coating technologies such as centrifuging and spraying are used to reproduce the complex structure [11–16].

Rising demands on the surface quality as well as increasing complexity of investment cast products require new coating technologies. On the one hand, dip-coating as an established coating technique for the lost-wax process offers a uniform and homogeneous coating, but it is limited regarding coating thickness and wettability of complex and small parts of the wax model. On the other hand, spraying is another well-known technology with advantages such as selective application, reduced drying times and thin functional coatings. Similarly, centrifuging allows to produce thinner coatings than dip-coating.

Using this technique, functional coatings such as thin primary coats with improved surface quality as well as final coats, which create strengthening compressive stresses by shrinkage, can be applied [17,18]. A model of a graded composition of functional coatings is displayed in Fig. 1. Although these techniques would offer a selective adjustment of coating properties, they have not yet been investigated to produce functionalized investment casting molds by the lost-wax process.

Coating properties such as wetting behavior, homogeneity and thickness are controlled by the rheology of the slurry and the processing parameters. As a rule, the slurry has to be shear-thinning and thixotropic. A yield point is also beneficial to prevent excessive dripping of the applied coating [19,20]. For spraying, the geometry of the nozzle and the spraying parameters are important [19,21]. Centrifuging is adjusted by the dipping time as well as the time and the rotational

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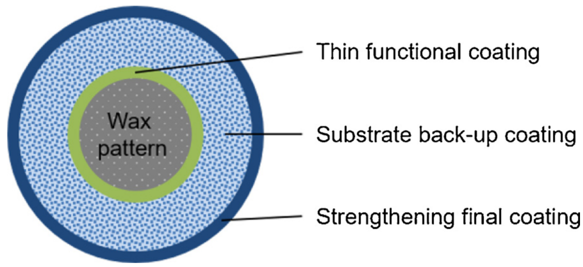

Fig. 1. Model of graded composition of investment casting molds using functional coatings.

speed during centrifuging.

The aim of the study was to develop a $CaZrO_3$ coating slip with suitable rheology and coating behavior to produce thin coatings by spraying and centrifuging. Applying the slip on wax models by spraying, centrifuging or dip-coating, adhesion and cohesion of the coatings, the homogeneity as well as the applied coating mass and the coating thickness were evaluated and compared. Moreover, the microstructure of selected dry green coatings was investigated by scanning electron microscopy (SEM) and X-ray computed tomography (XCT).

2. Materials and methods

In the present study, a fine-grained coating slip based on $CaZrO_3$ with a maximum grain size of 45 µm was developed. In order to compare different coating slips and coating technologies, rheological investigations as well as coating experiments using slurries with varying composition (solids and xanthan gum content, type of binder) were conducted. The chosen additives were already used successfully for $CaZrO_3$ dip-coating slips in a previous study [7]. All additives are water-based and therefore environmentally friendly and nonhazardous to health.

The investigated coating technologies were spraying, centrifuging and conventional dip-coating as a reference. Thereby, the aim was to obtain significantly thinner homogeneous coatings by spraying and centrifuging compared to dip-coating. For improved accuracy of the coating experiments, a 3^2 full factorial experimental design was applied with the two factors coating slip (X_1) and coating technology (X_2), each at three levels (see Table 1). Factorial designs are superior to one-factor-at-a-time experiments since they allow to investigate the main effects as well as the interaction effects of factors on the response variable [22].

2.1. Slip production

The compositions of the slips are presented in Table 2. In all experiments $CaZrO_3$ raw materials produced by electric arc melting (Imerys Fused Minerals Murg GmbH, Germany) and by stoichiometric solid state synthesis were used. The solid state synthesis was conducted exactly as described in a previous paper [7] by dry mixing, uniaxial pressing, sintering and milling.

In a next step, xanthan gum (Axilat RH 50 MD, C.H. Erbslöh GmbH & Co. KG, Germany) was dissolved in deionized water and then allowed to rest for 2 h to ensure proper hydration. Xanthan gum is a polysaccharide well-known for its stabilizing and shear-thinning properties even at low concentrations [11,23–25]. Aiming for a processable slip with a high solids content, an amount of xanthan gum as low as 0.05% or 0.1% relative to the solids was used, modifying the rheology of the slip without causing an overly increased viscosity or water demand.

Table 1
Factors of the 3^2 full factorial experimental design.

Factor	Identifier	Low level (−1)	Intermediate level (0)	High level (+1)
Coating slip	X_1	A	B	C
Coating technology	X_2	Dip-coating	Centrifuging	Spraying

Table 2
Composition of the coating slips.

Product name	Raw material	Grain size fraction	A (wt.%)	B (wt.%)	C (wt.%)
Imerys fused $CaZrO_3$	$CaZrO_3$	−45 µm	70	70	70
Stoichiometric synthesis	$CaZrO_3$	2.14 µm (d_{50})	30	30	30
Axilat RH 50 MD	Xanthan gum		0.05	0.1	0.1
Water	H_2O	mass relative to	14	15	15
BYK LP-C 22134	Dispersing agent	solids mass	2	2	2
BYK LP-C 22787	Defoamer		0.05	0.05	0.05
BYK LP-C 22893	Binder		4	4	0
BYK LP-C 22346	Binder		0	0	4

Subsequently, the xanthan gum solution was mixed with a deflocculant based on a structured copolymer (BYK LP-C 22134, BYK-Chemie GmbH, Germany) and a silicone-free defoamer (BYK LP-C 22787, BYK-Chemie GmbH, Germany). The liquid mixture was then added to the solids, followed by 5 min stirring at a shear rate of 900 min^{-1} with a high shearing laboratory mixer (RZR 2102 control, Heidolph Instruments GmbH & Co. KG, Germany). Finally, an aqueous urethane-acrylate dispersion binder (BYK LP-C 22893, BYK-Chemie GmbH, Germany) for slips A and B or a solution of an acrylate copolymer (BYK LP-C 22346, BYK-Chemie GmbH, Germany) for slip C was added and the slip was subsequently mixed again for 5 min at 900 min^{-1}. For improved homogeneity, the slip was mixed in a ball mill for at least 12 h. Finally it was mixed again for 5 min using the high shearing laboratory mixer.

2.2. Dip-coating

Wax models are usually used for the production of investment casting molds [1]. For all coating experiments, cylindrical wax models (height: 80 mm, diameter: 10 mm) consisting of Aqua Green Flake Wax (Freeman Manufacturing & Supply Company, USA) were used. In addition to the simple cylindrical wax models, a complex jewelry casting model was coated to demonstrate the suitability of the coating process for the desired shape.

Dip-coating—a standard coating process for the production of investment casting molds [1]—was applied as a reference coating technology. Therefore, the wax model was dipped manually into the ceramic slurry for exactly 10 s in order to ensure complete wetting of all parts, followed by carefully withdrawing the model and draining of the excess slip for precisely 30 s.

2.3. Centrifuging

Regarding centrifuging essentially the same wax models, i.e. simple and complex cylindrical models, were used. First, a dip-coating step was performed exactly as described above, but with reduced drain time of only 10 s in order to minimize solidifying and drying effects, which might impair the homogeneous centrifuging of the slurry [20]. An additional centrifuging step followed to remove excess slurry. Thereby, the coated model was placed on a rotating disk fixed to a high shearing laboratory mixer (RZR 2102 control, Heidolph Instruments GmbH & Co. KG, Germany) with a distance of 4 cm from the axis of rotation (see also