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The casting of titanium based alloys is a complex and expensive procedure, due to their high melting temperature and chemical reactivity with oxygen at $T > 600^{\circ}\text{C}$. Hence, molten titanium easily reacts with crucibles and mold components during casting. Therefore, the whole process is done in vacuum or inert gas atmosphere, e.g. in cold crucible arc casting machines under argon atmosphere. However, conventional techniques can be also used for titanium casting, but require some adjustments regarding crucible and investment material. A couple of crucible materials are commercially available with supposedly suitable properties for titanium casting. The aim of this study was to assess the suitability of selected commercial ceramic crucibles for the investment casting of Ti6Al4V for jewelry purposes. A commercial vacuum tilt casting machine and a centrifugal casting machine were employed to cast the alloy in copper molds or in refractory investment shells. The form filling of the shell, the crucible and the investment reactions were assessed by microstructural investigation, chemical analysis and hardness profiles of the as-cast items as a function of shell temperature. The reaction of the alloy strongly depended on the crucible material, the coating of the crucibles and the temperature of the ceramic shell. Optimum results were achieved with yttria and yttria coated alumina crucibles. Improvement of the materials and process costs are necessary to allow the competitive casting of jewelry made from titanium alloys.

Investment casting of Ti alloys by induction melting

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INTRODUCTION

Titanium based alloys are highly versatile due to their interesting properties such as high corrosion resistance, good mechanical properties, high biocompatibility and low density. Ti6Al4V is the most widely used titanium alloy. It is characterized by good machinability and excellent mechanical properties. Intermetallic NiTi alloys with B2 structure are used in many medical applications are based on this alloy, particularly stents, due to their super elasticity and its shape memory properties. Titanium aluminides based on γ -TiAl are of increasing interest for gas turbine applications. However, the high reactivity of titanium containing alloys hampers their castability. Conventionally, cold crucible arc melting under argon atmosphere is employed for titanium alloys, because it is characterized by the absence of crucible contamination with the melt [1-3]. However, this process shows some typical disadvantages such as low superheating and inhomogeneous temperature of the melt due to the cold crucible and therefore limited form filling of the mold.

Investment casting with induction melting could be an alternative casting method especially for small and filigree parts typically used in jewelry and medical applications, but the high reactivity of titanium alloys with the crucible in the liquid state represents a serious limit for this process. Based on consideration of the Gibbs free energy of formation of several refractories, yttria, calcia, thoria and beryllia offer the highest chemical stability towards titanium melts [1, 4]. Thoria and beryllia are less suitable because of their radioactivity and toxicity. Calcia suffers from its strong alkaline reaction with humidity. Crucible materials can react with the melt in various ways [4]: dissolving in the liquid metal (e.g. alumina, zirconia, titania, graphite), reducing by the liquid metal forming a volatile or solid reaction product with the melt (e.g. alumina, titania, graphite) or melting or evaporating below the melting point of the metal (e.g. quartz). Yttria and calcia would be suitable refractories for titanium alloy casting for their thermodynamic stability but both suffer from their low thermal-shock resistance and their reaction with humidity, respectively. For this reason research activities are concentrating on graded crucibles with melt-facing yttria or calcia coatings [5-12]. Aluminium titanate (Al_2TiO_5) is of interest as crucible matrix, if a stable coating of yttria or zirconia can be used, because of its low modulus of elasticity and very low heat conductivity combined with low thermal expansion and high thermal shock resistance [13]. In this study four commercially available ceramic crucible materials were selected and tested in melting and casting trials with Ti6Al4V. Graphite crucibles were used as a reference as they frequently used in industrial practice [14]. The scope of this work was to evaluate the properties of parts that were cast with different commercial crucibles, with respect to the requirements in jewelry and medical applications.

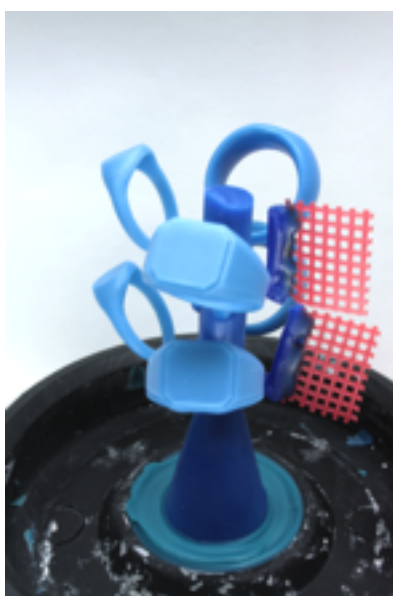
EXPERIMENTS

Four different commercial refractory crucibles, which were recommended for titanium casting by the manufacturers, were tested by casting Ti6Al4V (Ti Grade 5). Type A is zirconia coated quartz crucible. Quartz has a high thermal shock resistance but also shows a high reactivity with titanium. Zirconia shows high chemical and physical stability at high temperatures, but it is not inert regarding titanium. Type B is a yttria coated aluminum titanate (Al_2TiO_5) crucible (Al_2O_3 : 52,3 wt. %; TiO_2 : 41,2 wt. %; MgO : 6,0 wt. %; other: 0,5 wt. %) with an open porosity of 10-16%. Crucible Type C is a refractory material produced by the shell preparation technique. The melt facing layers are consisting of yttria whereas the final layers are consisting of alumina. Crucible type D was cold isostatically pressed and sintered from pure yttria powder resulting in some residual porosity. Machined and polished high quality graphite crucibles (Tokai Carbon, grade G347S) with a very low ash content of 50-100ppm were used for comparison with the ceramic crucibles. The long-term chemical and mechanical stability of each crucible type was tested at least twice by repeated use in the below described casting experiments.

A series of casting experiments was carried out in a 15kW vacuum tilt casting machine (Indutherm VTC200VTi) and a 10kW vacuum centrifugal casting machine (Topcast TCE10), both equipped with induction heating. An inert gas atmosphere in the casting chamber was established by four times repeated evacuation to < 10-2mbar and backfilling with argon. The metal temperature during heating was monitored by a two-color quotient pyrometer (Maurer QKTRD1085), which was calibrated with the α/β transition temperature (878°C) and the melting temperature of pure titanium (1668°C). Melting and casting trials were carried out with a batch size of 20 - 500g. Different heating rates were applied depending on crucible material and the amount of alloy. Using the same heating power the metal heated slower in graphite crucibles compared to the ceramic ones, because the graphite is conductive and was therefore directly heated while shielding the metal from the electromagnetic field. The casting temperature was about 1850°C .

After casting the trees were water and sand-blasted. Metallographic cross sections of the cast pieces were at prepared using conventional metallographic techniques. Vickers micro hardness profiles (load 0.1 kg) of the ingots were evaluated on the cross-sections in order to identify a possible alpha-case formation. The alpha-case is a surface layer that is enriched in oxygen due to the reaction with the mold. In order to study the crucible-melt interface cross sections of the crucibles were prepared. Identification of the reaction products and their chemical composition was performed by a quantitative SEM-EDX microanalysis using a Zeiss SUPRA scanning electron microscope operating at 15kV equipped with an Oxford Inca EDX system. The chemical composition was measured by glow discharge optical emission spectrometry (GDOES).

In a first step casting trials with copper molds were carried out to analyze the contaminations caused by the crucible. Subsequently casting experiments in ceramic shells were performed using graphite crucibles and those ceramic crucibles (type C and D) that performed best in the trials with Cu molds. Ceramic shell molds of jewelry pieces were prepared basing on the conventional lost wax technique (Figure 1). In a first step the wax pieces were coated with an alumina-magnesia primary layer (J. Morita Europe GmbH, Titavest CB) to minimize the reactivity with the melt. After drying this coating process was repeated several times in order to form a mechanically stable shell. Actually, the Titavest CB investment is intended as dental investment by the manufacturer. Large stable shells cannot be prepared with this material. Therefore, the coated wax tree was put into a flask, which was filled with a standard dental phosphate-bonded investment (Shera, Titan-Easy) and fired according to the manufacturer's recommendation. The flask temperature for casting was varied between 22°C, 200°C and 400°C. The casting conditions were identical to the optimized conditions determined by copper mold casting and each cast required ca. 140g of ingot material. In order to assess the form filling and investment reactions for different casting conditions the tree contained wax parts of varying size and weight: two grid patterns to assess form filling, four light weight rings and two heavier rings that were expected to show higher investment reactions due to prolonged heat exposure. The cast jewelry pieces were ground and polished using conventional jewelry techniques.



Wax tree



Primary yttria coating



Sprinkled with alumina sand and dried

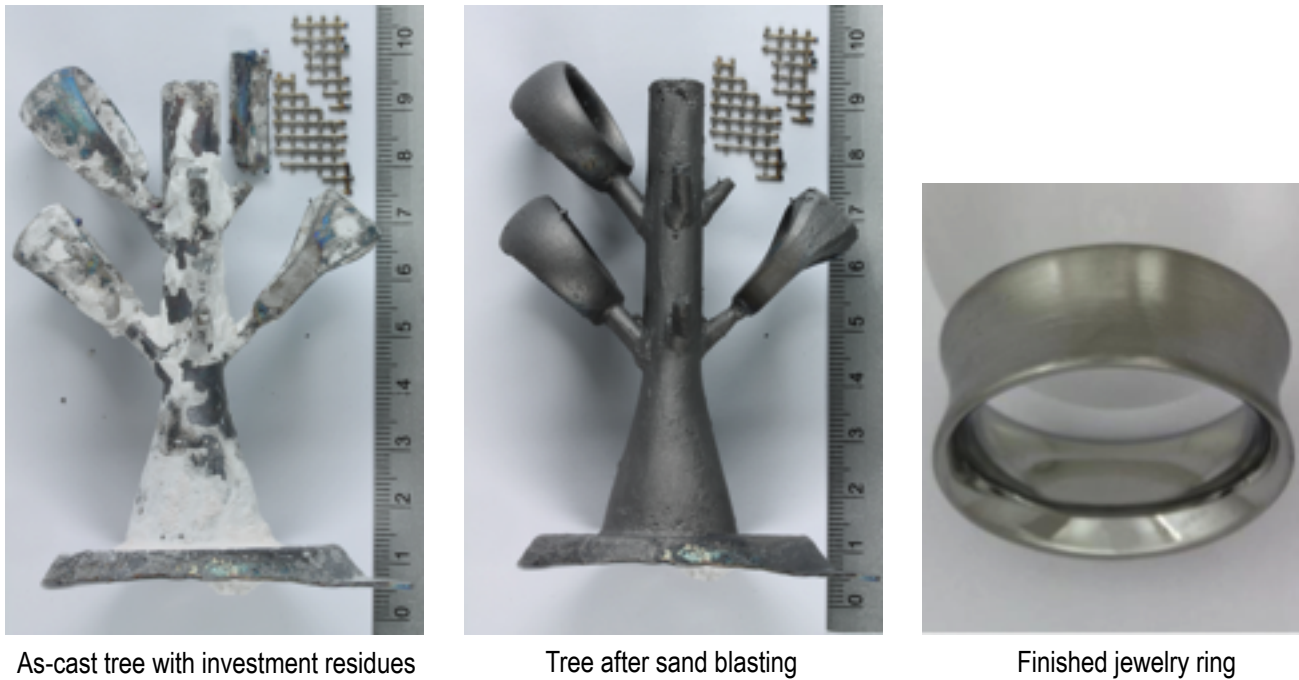


Figure 1 – Process steps of shell preparation and casting from the wax pattern to the finished jewelry

RESULTS AND DISCUSSION

CRUCIBLE REACTIONS

The four crucible materials reacted very differently with the alloy during the melting and casting. Table I gives a summary of the contamination of the melt in comparison to the starting material and the ASTM standard. The hardness profiles measured on metallographic samples are shown in Table II and Table III.

Crucible	Mold	HV1	Ti	Al	V	O	N	Si	Zr	Y	C
A	Cu	1317	Bal.	-	-	3,00	1,30	5-12	0,57	-	0,80
B	Cu	405	Bal.	6,04	3,99	0,30	0,05	0,03	0,01	0,19	0,01
C	Cu	343	Bal.	5,80	3,75	0,21	0,04	0,02	0,01	0,29	0,01
Graphite	Cu	371	Bal.	5,85	3,79	0,08	0,01	0,01	0,01	0,01	1,61
C	Shell,	200°C	Bal.	Bal.	5,86	3,78	0,01	0,01	0,01	0,01	0,01
D	Shell,	400°C	Bal.	Bal.	5,84	4,06	0,01	0,01	0,01	0,01	0,01
		400°C									
Graphite	Shell,	380	Bal.	Bal.	5,61	3,91	0,01	0,01	0,01	0,01	01,30
		400°C									
Starting material	-	312	Bal.	Bal.	6,01	4,26	0,05	-	-	-	0,01
ASTM B367-09	-	-	Bal.	Bal.	5,50	3,50		-	-	0,00	0,1
					-	-				5	
					6,75	4,50					

Table I. Casting trials with Ti6Al4V (except for crucible A, where titanium Grade 2 was used). Vickers hardness HV 1 (bulk value) and chemical analyses in mass percent (GDOES) compared to the standard ASTM B367-09 and the starting material.

Crucible A (zirconia coated quartz) strongly reacted with the melt as soon as complete melting was achieved. Such reaction was indicated by a sudden increase of the temperature of the melt. EDX measurements indicated the formation of titanium oxide and titanium silicides. The original zirconia coating was completely dissolved. As a consequence of this reaction the hardness increased to over 1300 HV 1 and the ingot became very brittle. Very high silicon and oxygen contents were found in the cast sample (Table I). Due to the reaction and the high hardness crucible A is not at all suitable for titanium casting.

Crucible B (yttria coated aluminum titanate) showed much less reaction, however, the yttria coating of the crucible was completely dissolved after a single use of the crucible. The crucible shows the tendency to crack, which limits the number of repeatable castings, even after re-coating with yttria. The hardness of the as-cast material is about 400 HV 1 and therefore significantly enhanced compared to the starting material (Table I). The composition shows increased levels of aluminum compared to the samples cast in crucible C and D, and elevated levels of oxygen and yttrium stemming from the dissolved yttria coating. The oxygen content is about a factor of two compared to the starting material and exceeds the limits according to the ASTM standards. In conclusion, for titanium rich alloys aluminum titanate crucibles were found to be not suitable despite their yttria coatings. They might be suitable for alloys with lower titanium content.

Crucible C was built using a ceramic shell preparation process and is showing high porosity (Figure 2a, b). The yttria coating of this crucible, shown as a bright layer in Figure 2c, is much thicker compared to the coatings of crucibles A and B. Like all other crucibles, deep cracks were detected in type C, preventing re-use. The melt penetrates the pores in the yttria layer and the crucible bulk up to a depth of 2 mm. During solidification and cooling such penetration can result in a delamination of the yttria layer implying that such crucibles can usually only be used for one casting. The surface hardness obtained in copper mold casting was 350-400 HV 0.1 (Table II). The chemical analysis (Table I) shows slightly increased oxygen, nitrogen and yttrium levels compared to the starting materials, but they are still below the ASTM limits.

Table II: Ceramic crucibles: Vickers hardness HV 0.1 as function of the distance from the surface.

Distance from surface	Crucible C/Cu mold	Crucible C/Shell 22°C	Crucible C/Shell 200°C	Crucible C/Shell 400°C
10µm	386	437	551	535
50µm	370	410	415	470
100µm	370	389	356	390
200µm	356	375	356	370
400µm	343	373	355	350

Table III: Graphite crucibles: Vickers hardness HV 0.1 as function of the distance to the surface.

Distance from surface	Crucible C/Cu mold	Crucible C/Shell 22°C	Crucible C/Shell 400°C
10µm	389	420-580	400-490
50µm	398	378-550	430-556
100µm	412	453	465
200µm	395	441	379
400µm	402	373	364

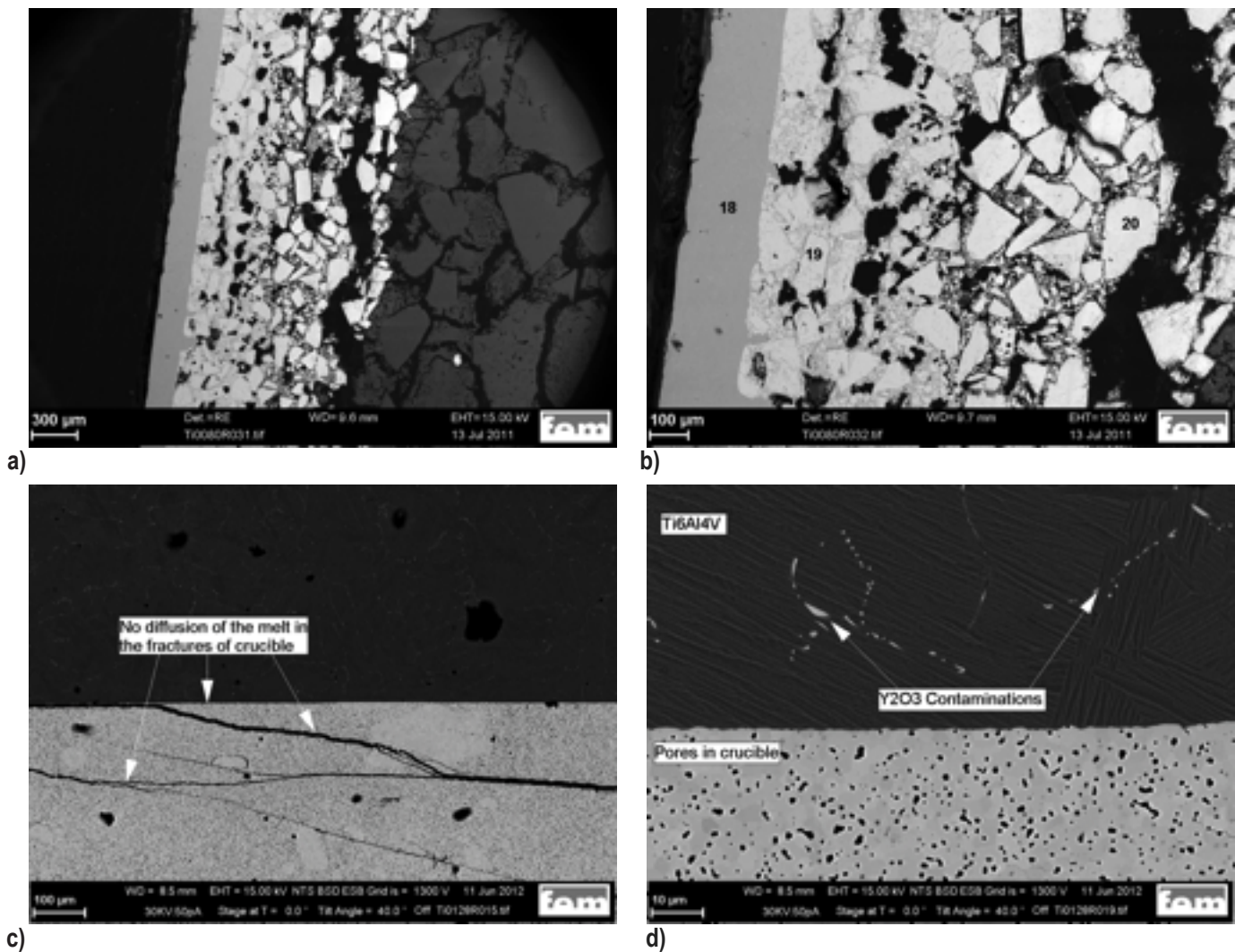


Figure 2: Reaction of the ceramic crucibles C and D with the Ti6Al4V melt.

Crucible D was a bulk yttria crucible without additional coating. It was only used for shell casting. Due to the lower thermal shock resistance the crucible had to be heated slowly. Despite the slow heating and the porous crucible material, significant cracking occurred during melting (Figure 2c). Therefore, the crucible of the given geometry could only be used once or twice. It was observed that the cracks are not filled with melt. Additionally the bottom of the crucible lacks a diffusion zone, unlike the other refractory materials, i.e. a clear division between the ceramic and the melt exists. The bulk hardness of the cast Ti6Al4V rod was 350-400HV_{0.1}. The chemical analysis (Table I) shows a slight increase in oxygen, but the value remains below the limit of the ASTM standard. During melting the liquid metal wets the crucible dissolving and eroding small amounts of yttria, which are then found as interdendritic yttria particles in the cast pieces (Figure 2d and Figure 3c). The eroded yttria particles cause an increased yttrium content, which is higher compared to crucible C, because of the slower heating and thus resulting longer erosion times. The use of yttria crucibles for TiAl casting is described in [12]. The presence of yttria particles is attributed to a combined effect of chemical dissolution of yttria in the TiAl melt and physical erosion of the crucible by the electromagnetic stirring of the melt. Both effects correlate with increasing temperature of the melt and to a lesser extend with increasing melting time. A compromise has to be found for the necessary overheating of the melt to obtain sufficient form filling and for the melting speed and duration to avoid cracking of the thermal shock sensitive yttria crucible.

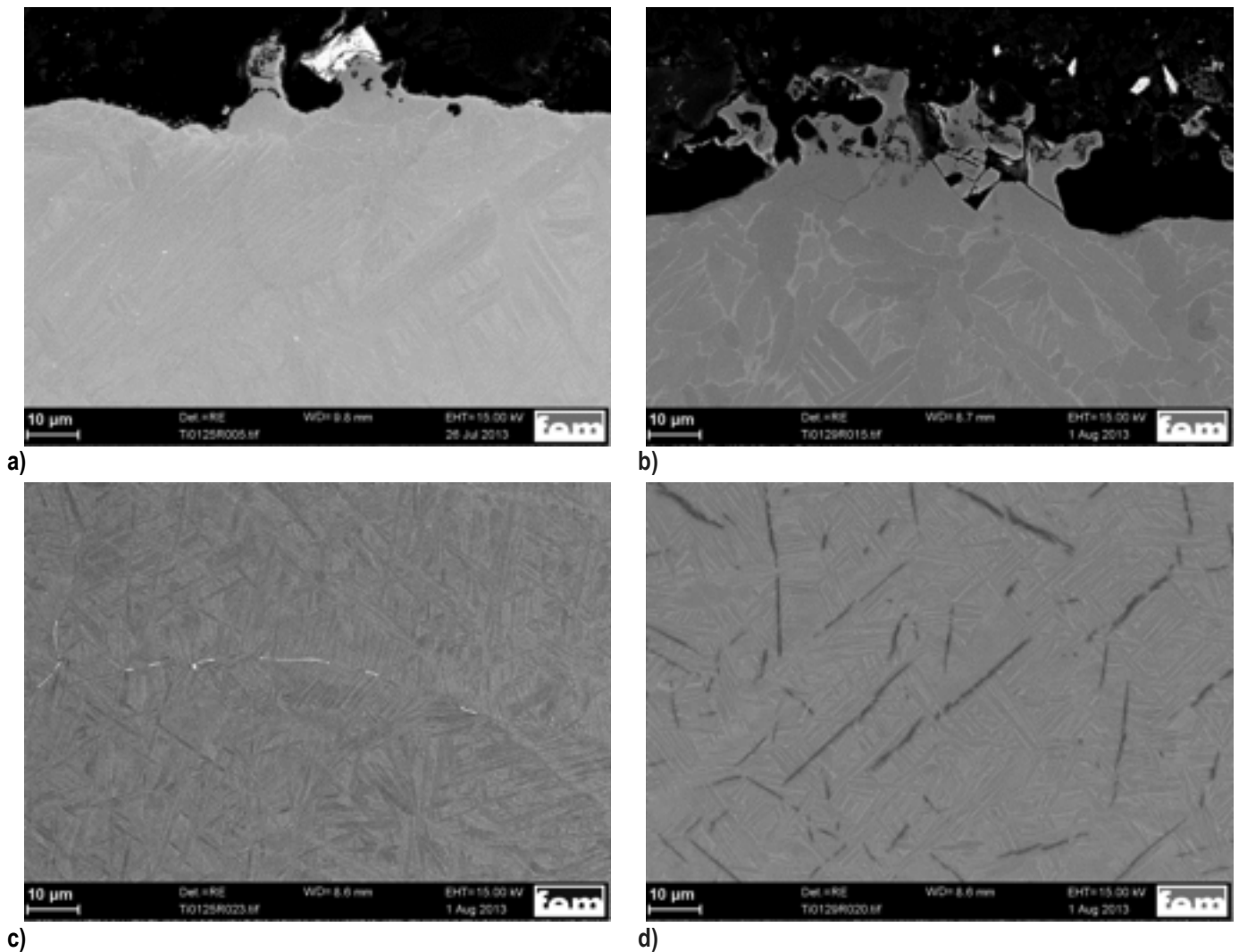


Figure 3: Microstructure of the Ti6Al4V shell castings in the ceramic crucible C (a, c) and a graphite crucible (b, d).

Graphite crucibles are strongly reacting with titanium to form titanium carbide, but can be used many times without cracking. The surface hardness strongly scattered between 400 HV 1 and 600 HV 1 due to the presence of titanium carbide particles (Table III). The bulk hardness ranges from 370-450HV1. The higher carbon content of the copper mold cast explains its higher hardness compared to the shell cast. The hardness strongly depends on the amount of titanium carbide, which can be up to 20vol.%. The amount of titanium carbide strongly depends on melting time and casting temperature and on the crucible surface to alloy mass ratio. Casting smaller quantities usually resulted in higher titanium carbide contamination of the melt and therefore poorer form filling ability and higher hardness. Because of the strong carbide contamination graphite crucibles are no suitable alternative to ceramic crucibles. Anyway they are currently used in industrial practice.

The metallographic and SEM/EDX investigation of interface melt-crucible showed that even though materials with high refractoriness (ZrO_2) and chemical inertness (Y_2O_3) were used, the coated crucibles still caused several practical problems. For example the integrity of the coating could be damaged by thermal stresses. In that case the melt penetrated the cracks and reacted with the bulk material. However, crucible D (pure Y_2O_3), was not wetted by the melt and the cracks were not penetrated. For all crucible types the reaction with the melt is more intensive at the bottom compared to the wall as the total contact time until the metal is completely melted is longer.

SHELL CASTING OF JEWELRY ITEMS

The process steps for shell casting are illustrated in Figure 1. For these casting experiments were used the crucibles C and D, and graphite crucibles as reference.. The quality of the cast was assessed by the achievable form filling, the surface quality and the hardness. For this purpose the tree contained several rings of different sizes and weights and a filigree grid.

During the casting trials the superheating of the melt was varied between 60K and 350K for a shell temperature of 400°C. In none of these cases complete filling of the grid could be achieved, because of a strong reaction with the shell. Some parts even broke from the tree during devesting, which is probably caused by an embrittlement of the ring gate due to shell reactions. The risk of

cracking increased with increasing melt temperature. In order to reduce shell reactions, the shell temperature was reduced to 200°C and 22°C, respectively. This improved the surface quality of the rings significantly. Anyway, the surface of rings was very rough due to residues of the shell that were sticking strongly to the surface. In case of 200°C shell temperature the form filling was not deteriorated. However, at a shell temperature of 22°C a complete form filling could no longer be achieved. For identical casting parameters, centrifugal casting resulted in significantly better form filling compared to tilt casting. The best compromise of form filling and shell reactions was achieved for centrifugal casting with a shell temperature of 200°C. However, it has to be mentioned that the tilt casting machine used in the project was a prototype model. Based on the experience from the project some features to obtain better form filling were later improved in the production model, such as a pre-cast vacuum and a reduced time to apply the overpressure after casting.

Hardness profiles (Table II and Table III) indicated surface hardening in a 50-100µm thick layer. Between 22°C and 200°C the shell temperature correlated with the surface hardness. Thus, for room temperature shells the surface hardening was quite small, a significant surface hardening was observed at shell temperatures of 200°C or above. With graphite crucibles the bulk hardness was generally higher compared to ceramic crucibles due to the formation of titanium carbide. The high surface hardness and the hard investment inclusions made it difficult to finish the jewelry.

The microstructure of the Ti6Al4V casts was investigated at the surface and the center of the rings for the ceramic and the graphite crucibles (Figure 3). In case of the ceramic crucible the typical Widmannstätten structure of $\alpha+\beta$ titanium was found. At the surface α titanium was stabilized by elevated oxygen content. However, a continuous alpha-case layer could not be found. Throughout the cross section, the former β grain boundaries are partially decorated with yttria particles (bright areas in Figure 3). The contaminations have been found in the bulk as well as at the surface of the specimen. The amount of yttria increased with increasing melt temperature and melting time. In case of the graphite crucible a stronger reaction and a thicker alpha-case layer was observed.

Needle-like titanium carbide precipitates were found throughout the complete ring section. The hardness and impurity levels of the Ti6Al4V casts are given in Table I. In both ceramic crucibles the hardness levels and the oxygen contents were comparable to copper mold casting, i.e. no significant further contamination of the melt occurred by the shell.

The effect of different shell coatings was investigated by different authors with differing results. While in [15] alumina shells showed the most significant surface hardening and zirconia shells were showing the lowest hardening, the opposite was observed in [16]. Calcia shells showed the lowest surface hardening in both works, although the surface hardness values of 215 HV and 330 HV differed significantly in [16] and [15], respectively. Both groups used arc-melting, so that crucible reactions can be excluded as an origin of this difference. No information about the shell temperature is given in these papers. However, our results showed that the shell temperature had a significant effect on the resulting hardening. The hardened surface layer of 200-400µm observed in [15, 16] is quite thick compared to our results of 50-100µm. However the bulk hardness is slightly higher in our samples, which were melted in ceramic crucibles. Eventually, the reaction with the crucible material lowers the activity of the titanium melt, which then reacts less with the shell.

Casting trials similar to our experiments, but with much smaller amounts of alloy (18g, ca. one eighth of the present study) are reported in [7]. Among others, the authors also used Titavest investment to prepare small-size flasks and reported a quite similar hardness profile like in the present work. Additional yttria coating of the wax patterns before investment lowered the surface hardness to about 50% (250-300 HV).

SUMMARY AND OUTLOOK

Most jewelry items of titanium are made by mechanical machining, while casting is mainly used for dental parts or larger technical parts. Casting processes, although dedicated to complex and filigree items are not used up to now, because of the challenging and expensive casting process. The adaption of established arc-melting and casting processes from dental industries is challenging, because the filigree jewelry structures require a certain superheating of the melt, which is difficult to achieve by arc-melting. Induction heating in ceramic crucibles is therefore a potential alternative. Casting trials with commercially available crucibles and investment materials showed the feasibility of the investment casting of Ti6Al4V jewelry with the following results:

- High quality yttria or yttria/alumina crucibles are required to obtain sufficient surface quality and reasonable hardness of the castings.
- The alpha case during shell casting was ca. 100µm thick with surface values of about 550-600HV0.1. The finishing of such jewelry is therefore time consuming and expensive.
- The impurity levels of castings of Ti6Al4V remained close to the upper limits of the respective ASTM standards. jewelry
- The use of yttria coatings for crucible and shell resulted in yttria residues in the titanium castings; something that might be tolerable for jewelry, but not in medical or technical castings.

Further work will be required to improve crucible and shell materials and the titanium casting process. Currently the process costs are too high for competitive titanium jewelry production. jewelry

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