Effect of SiO₂ concentration in silica sol on interface reaction during titanium alloy investment casting

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Abstract: Using silica sol as a binder for titanium investment casting is very attractive due to its good stability and reasonable cost as compared with yttrium sol and zirconium sol. However, the mechanism of interface reaction in the related system remains unclear. In this investigation, the interface reaction between Y₂O₃-SiO₂ (Y-Si) shell mold and titanium alloys was studied. A group of shell molds were prepared by using Y₂O₃ sand and silica sol with different contents of SiO₂. Ti-6Al-4V alloy was cast under vacuum by gravity casting through cold crucible induction melting (CCIM) method. Scanning electron microscopy (SEM) and energy dispersive x-ray spectroscopy (EDS) were employed to characterize the micromorphology and composition of the reaction area, respectively. X-ray photoelectron spectroscopy (XPS) was used to confirm the valence state of relevant elements. White light interferometer (WLI) was used to obtain the surface topography of Y-Si shells. The results show that the thickness of reaction layers is below 3 μm when the SiO₂ content of silica sol is below 20wt.%. Whereas, when the SiO₂ content increases to 25wt.%, the thickness of the reaction layer increases sharply to about 15 μm. There is a good balance between chemical inertness and mechanical performance when the SiO₂ content is between 15 and 20wt.%. Moreover, it was found that the distribution of SiO₂ and the roughness at the surface of the shell are the key factors that determine the level of reaction.

Key words: titanium alloy; investment casting; Y₂O₃; silica sol; surface roughness

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With the rapid development of the aerospace industry, the demand for titanium alloy is continuously increasing owing to its excellent impact on the weight reduction of aircraft^[1]. Investment casting is one of the most important and widely used methods in the formation of titanium alloys^[2]. However, the castings suffer from surface defects due to both the physical and chemical interactions between the titanium alloy melt and shell mold^[3].

To guarantee the quality of the casting surface, a shell mold with higher chemical inertness as well as higher compactness is required. Y₂O₃ has become the best choice as a shell mold material due to its excellent inertness against titanium alloy melt as compared to ZrO₂^[4], CaO^[5] and BN^[6] based on Gibbs free energy (ΔG_f) analysis^[7]. Cui^[8] and Zhao^[9] found that the oxygen

enrichment in titanium melt was small when yttria was employed as a molding material.

As a binder, yttrium sol is also the best in inhibiting the reaction between titanium and shell mold. However, the stability of the slurry made by yttrium sol and Y₂O₃ sand is poor^[10], in addition to the high price of this binder. Silica sol is a widely used binder in investment casting which shows superior performance besides being available at a reasonable price. Notwithstanding these advantages, SiO₂ reacts vigorously with titanium melt based on its Gibbs free energy (ΔG_f)^[7]. So, silica sol has been considered not suitable to be used as a shell mold binder in titanium casting for a long time. Frueh^[11] made a systematic study to evaluate the probabilities of silica sol application in shell mold. The result was so abjective that when using silica sol as face coat binder, the Ti/mold reaction would be very severe regardless of the filler materials. Papadopolosk^[12] and Myoung-Gyun^[13] found silica sol in the face coat led to a 100 μm and 220 μm thickness reaction layer, respectively, and new phase Ti₅Si₃ and Ti₃Si might exist in the layer. Horton^[14] devised a way to make titanium parts with good surface

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quality using silica sol as face coat binder which seemed not in accordance with ΔG_f theory^[14]. The results of these reported studies are contradictory and the reaction mechanism between SiO_2 containing ceramic shell and titanium melt remains unclear.

The aim of this study is to verify whether silica sol can be used as a binder for titanium investment casting. A group of shell molds were made using Y_2O_3 sand and silica sol with different contents of SiO_2 , and Ti-6Al-4V alloy was poured into these shell molds. The reaction mechanism between titanium and Y-Si shell mold was also studied

1 Experimental procedure

First, the 30wt.% silica sol was diluted to 10wt.%, 15wt.%, 20wt.% and 25wt.%, respectively, by adding distilled water. The pH value of diluted binder was adjusted to the required value by hydrochloric acid and sodium hydroxide solution. Then the prepared silica sol and Y_2O_3 filler were mixed and fully stirred to make the shell slurries. The slurries with silica sol of different SiO_2 contents were labeled as S1, S2, S3 and S4, the shells made by these slurries were named as K1, K2, K3 and K4, and the casting samples made from these shells were named correspondingly as M1, M2, M3 and M4.

Figure 1(a) shows the design of wax pattern in which twelve 20 mm $\times$ 20 mm $\times$ 6 mm cuboids adhere to a cylinder gate.

The cuboids were coated with the four prepared slurries, i.e., S1, S2, S3 and S4 through brush-painting method and stuccoed with Y_2O_3 particles, thereby forming the face coat. After drying, four back coats were applied. The shell specifications are summarized in Table 1. Figure 1(b) shows the ceramic shell mold after steam dewaxing. Finally, the shell was fired in a box type furnace in air with a heating rate of $10^\circ\text{C}\cdot\text{min}^{-1}$ to $1,050^\circ\text{C}$ and held for 12 h before pouring.

Fig. 1: Design of wax pattern (a) and shell mold (b) after steam dewaxing

Table 1: Shell mold specifications for pouring experiment

Sample	Face coat		Back coat	
	SiO_2 content in silica sol (wt.%)	Filler material	SiO_2 content in silica sol (wt.%)	Filler material
K1	10	Y_2O_3	30	Mullite
K2	15			
K3	20			
K4	25			

The cold crucible levitation melting (CCLM) method was employed in a furnace ZG-2XF that is consisted of a crucible, which can hold 2 kg of pure titanium. The melting of Ti-6Al-4V alloy was conducted under a pressure of 2×10^{-2} Pa, and the pouring temperature of the melt was around $1,700^\circ\text{C}$. The ceramic shell was preheated to about 200°C before pouring.

The 20 mm $\times$ 20 mm $\times$ 6 mm titanium alloy samples for further analysis were cut at the middle in the direction parallel to the cylinder gate by wire electrical discharge machining (WEDM), and then subjected to finishing processes of grinding and polishing. SEM and EDS (MERLIN VP Compact, Carl Zeiss, Jena, Germany) were used to characterize the structure and composition of the reaction layer of the castings. XPS (Hammer's, 250XI, UK) was utilized to confirm the valence state of relevant elements, and WLI (Veeco, Dektak 150, US) was applied to obtain the surface profile of the shell molds.

2 Results and discussion

2.1 Structure, composition and hardness of interface reaction layer

Samples M1, M2 and M3 had relative smooth surfaces and metallic luster while M4 was gray through visual observation. The cross section of the sample was examined by SEM and EDS, as shown in Fig. 2. The EDS line scanning shows that the distribution of Ti and O in M1, M2 and M3 is almost homogeneous and does not change with the depth from the surface to the interior of the samples. The cross-sectional boundary was also flat, indicating that the reaction degree between titanium and shell mold was very mild. It can be seen from the interface topography and metallographic structure in Fig. 2 and Fig. 3, the thickness of reaction layers was limited to $3\ \mu\text{m}$. For the M4 sample with 25wt.% SiO_2 , a reaction layer of about $15\ \mu\text{m}$ thick was identified at the surface

Fig. 2: Cross-sectional micromorphology and elemental distribution of M1 (a), M2 (b), M3 (c) and M4 (d)

Fig. 3: Cross-sectional metallographic structures of M1 (a), M2 (b), M3 (c) and M4 (d)

marked by a higher O and Si content, as shown in Fig. 2(d). The metallographic structure was observed with an optical microscope, as shown in Fig. 3. M1, M2 and M3 had almost the same metallographic structure, the transformed β phases. No obvious reaction layer was found at their surfaces, which was

consistent with the SEM analysis. As for M4, it had the similar transformed β phases, but also a coarse reaction layer of about 15 μm at the surface.

It should be mentioned here that certain Y_2O_3 particle inclusions were also found in M1 (Fig. 4). It implies that when

Fig. 4: Y_2O_3 oxide inclusion at surface (a) and interior (b) of M1

SiO_2 content decreased to 10wt.%, the SiO_2 bond between Y_2O_3 particles was not strong enough to resist the impact of the melt flow. According to the previous study on the strength of Y-Si shell^[15], the green strength and hot strength of Y-Si shell (15wt.%–20wt.% SiO_2 content in silica sol) are around 5–6 MPa, which is better than the 3.5–5.5 MPa of commonly used diacetate zirconium- Y_2O_3 system^[16]. Therefore, sufficient shell mold strength can be achieved with a suitable SiO_2 content.

To obtain a quantitative elemental distribution, a series of spot scanning was conducted and the results are shown in Fig. 5. The element-containing layer includes a reaction layer and a diffusion layer. For M1, M2 and M3, the reaction layer was thin and the

diffusion layer was the main part, while for M4, the reaction layer held a dominant position. As shown in Fig. 5(a), the thickness of the Si-containing layer in M3 and M4 was about 12 μm and 60 μm , respectively. In comparison, the thickness of the Si-containing layer in M1 and M2 was below 5 μm , which is far less than that of M4. From Fig. 5(b) it can be seen that the O-containing layer of M4 consisted of about 15 μm reaction layer and 3–4 μm diffusion layer, while the total O-containing layer for M1, M2 and M3 was all below 5 μm . The Si and O contents in the reaction layer were less than those in the diffusion layer for M4 (Fig. 5). It may be due to the fact that the reaction layer was not as smooth as the diffusion layer, which weakened the reflected signal.

Fig. 5: Change of Si (a) and O (b) contents with an increase in distance from metal surface

Take 105% of the hardness value of the substrate as the critical value of hardened layer, then it can be seen from Fig. 6 that the thickness of the hardened layer of the metal samples are 20 μm , 20 μm , 40 μm and 70 μm for M1, M2, M3 and M4, respectively. The thickness of hardened layer (H_{hard}) is correlated to the thickness of Si-containing layer (H_{Si}), which was 2 μm , 4 μm , 12 μm and 60 μm for M1, M2, M3 and M4, respectively, as shown in Fig. 5(a). The obtained linear fitting equation is $H_{hard} = 0.807H_{Si} + 16.122$ ($R^2=0.9368$). In the Y-Si face shell mold and Ti-6Al-4V system, the diffusion of Si seems to be a contributing factor to the hardened layer during the reaction between Y-Si shell mold and Ti-6Al-4V system.

2.2 XPS analysis of metal surface

According to the SEM analysis, a few new phases were identified. To further confirm the reaction pattern, XPS was

Fig. 6: Microhardness of samples M1, M2, M3 and M4

applied to obtain the valence state of related elements. The sample used in the XPS analysis was M2, and the obtained results are shown in Fig. 7. As can be seen from O1s curve, a major peak at 532.8eV corresponding to the Si-O bond energy of

Fig. 7: XPS curves of O (a), Ti (b), Si (c) and C (d) on sample M2 surface

532.5eV could be found. As for Ti, the 458eV peak corresponds to the $Ti2p_{2/3}$ binding energy of 458.4eV, and the 464eV peak corresponds to $Ti2p_{1/2}$ binding energy of 464.3eV. These results confirm that most of the Ti exists as TiO_2 ; there are also some minor peaks indicating that Ti also exists in other forms. For Si, the peak at 102.5eV corresponds to Si-O binding energy of 102.533eV, which reveals that Si mainly exists in the fired product of the silica sol. At the same time, there are many minor peaks in the Si2p curve signifying that Si also exists in some other forms. As for C, the peak at 284.8eV corresponds to C in $(-Si(CH_3)_2-O)_n$. Based on this analysis, the formed compounds

might be TiO_2 and SiO_2 with a small amount of $(-Si(CH_3)_2-O)_n$. Besides, some amount of Ti-Si might also exist.

2.3 Surface structure analysis of Y-Si shell

To better understand the reaction mechanism, the surface profiles of shell molds were obtained by white light interferometer and the results are shown in Fig. 8. The surface morphology undulation of shell K1 was more severe than that of K4. Figure 9 shows the change of surface roughness with an increase in SiO_2 content. The surface roughness decreased from 2.364 μm to 1.934 μm when SiO_2 content increased from 10 to 25wt.%.

Fig. 8: Surface micro-topography of K1 and K4 by white light interferometer

Fig. 9: Change of shell roughness with an increase in SiO₂ content in silica sol

Figure 10 shows the microphotographs of the shell surfaces obtained by SEM. As for K1, the slopes with almost pure Y₂O₃ surface can be found, as shown in Fig. 10(a), and the Y₂O₃/SiO₂ ratio (area ratio) here was relatively high. However, the slopes of K4 were covered by a layer of small particles as shown in Fig. 10(b), which renders the Y₂O₃/SiO₂ ratio smaller. These particles decreased the surface roughness and altered the wettability with titanium melt at the same time. As shown in Figs. 10(c) and (d), K4 also had a much more compact internal structure; the SiO₂ binder between Y₂O₃ particles formed a continuous three-dimensional space structure. It can be concluded from Figs. 8–10 that the shell surface would be smoother with an increase in SiO₂ content of silica sol.

Fig. 10: Microstructures of K1 (a) and K4 (b) surface and cross-sections of K1 (c) and K4 (d)

2.4 Analysis on reaction mechanism

Based on the analysis of the shell structure above, a scheme on the shell structure was built (Fig. 11). It was a combination of Y₂O₃ particles, SiO₂ particles and pores. Compared with shell mold K1, K4 has a smaller Y₂O₃/SiO₂ ratio on the slope, smaller roughness at the surface and denser structure in the interior of the shell mold.

In this investigation, the direct chemical reaction between Y-Si shell mold and titanium melt was moderate in general. Common oxygen containing α layer and phase transition almost cannot be found. The interface reaction layer showed up as a rough surface.

According to the shell mold structure and interface reaction analysis above, a contact-wetting-reaction model was built. The whole reaction process was divided into three stages: surface contact stage, wetting stage and internal reaction stage. When the melt just contacts the face coat, it would react with SiO₂ at the shell edge, as shown in Fig. 11. No matter the amount of SiO₂, it always had this stage, and the reaction layer thickness, h_1 , was very small and treated as a constant here. Then, the melt moves further, commencing the wetting process during which the melt fills the surface pores on the shell mold. This wetting stage is controlled by both the physical structure and material types at the surface. The reaction layer h_2 of this stage can be

Fig. 11: Microstructures of K1 (a) and K4 (b) surface and cross-sections of K1 (c) and K4 (d)

calculated using the fluid infiltration theory of Washburn^[17] and shown by Eq. (1):

$$h = \sqrt{\frac{\gamma R \cos \theta}{2\eta}} \sqrt{t} \quad (1)$$

where, h - penetrating depth; γ - surface tension; R - pore radius; θ - contact angle; η - melt viscosity; t - time.

Naidich^[18] and Li^[19] proved that titanium melt had poor wettability on Y_2O_3 surface, which was dominated by physical wetting, but extremely good wettability on SiO_2 , which was dominated by reactive wetting. According to Zhu,^[20] during the wetting process of titanium melt on Y-Zr-O ceramic, the contact angle increases, whereas the wettability decreases with an increase in the surface roughness. Based on the surface structure analysis and the references^[18-20], the surface roughness of shell mold K1 was relatively large, which blocked the physical wetting. Besides, the Y_2O_3/SiO_2 ratio on the slope was relatively large, which increased the contact angle and hindered the reactive wetting. According to these two reasons, the wetting stage stopped quickly before the internal reaction stage, and consequently, h_2 was also small. Then the direct reaction between Y_2O_3 and titanium started, which was very mild and ignored here. It explains the slight reaction degree and the smooth metal surface of M1, M2 and M3.

As for M4, things are different. The wetting stage of M4 was promoted and the surface pore on the shell mold was fully filled because of the lower Y_2O_3/SiO_2 ratio and smaller roughness. Then the last stage - internal reaction stage, started inside the shell, forming the reaction layer, h_3 . During this process, the melt contacts directly with the SiO_2 between Y_2O_3 particles inside the shell and reacts with them. Shell K4 had a compact internal structure and a denser SiO_2 space structure. This three-dimensional space structure of SiO_2 will act as a pipe providing the material and energy exchanges between the melt and the SiO_2 inside shell. The reaction continued until the temperature dropped down, whereas the melt viscosity increased to a certain extent forming the reaction layer h_3 . All of the three stages formed the reaction layer [Fig. 2(d) and Fig. 3(d)].

Based on the discussion above, the total thickness of the reaction layer of M1 (H_{M1}) and M4 (H_{M4}) can be calculated with Eq. 2 and Eq. 3, respectively:

$$H_{M1} = h_{1M1} + h_{2M1} = c + \sqrt{\frac{\gamma_1 R_1 \cos \theta_1}{2\eta(T)}} \sqrt{t_1} \quad (2)$$

where, H_{M1} - reaction layer thickness of M1; h_{1M1} - reaction layer thickness of M1 in the contact stage; h_{2M1} - reaction layer thickness of M1 in the wetting stage.

$$\begin{aligned} H_{M4} &= h_{1M4} + h_{2M4} + h_{3M4} \\ &= c + \sqrt{\frac{\gamma_4 R_4 \cos \theta_4}{2\eta(T)}} \sqrt{t_4} + h_{3M4} \end{aligned} \quad (3)$$

where, H_{M4} - reaction layer thickness of M4; h_{1M4} - reaction layer thickness of M4 in the contact stage; h_{2M4} - reaction layer thickness of M4 in the wetting stage; h_{3M4} - reaction layer thickness of M4 in the internal reaction stage.

The obvious increase in the thickness of the reaction layer of M4 (Fig. 2) compared with M1 can be explained by Eq. 2 and Eq. 3. It is because M4 had a fully developed wetting stage ($h_{1M4} > h_{1M1}$) and an extra internal reaction stage ($h_{3M4} > 0$), while the wetting stage of M1 stopped quickly and did not have the third stage.

3 Conclusions

(1) The thickness of the reaction layer was below 3 μm when the SiO_2 content of silica sol was below 20wt.%. It jumped to about 15 μm when the SiO_2 content reached 25wt.%. Besides, Y_2O_3 inclusions became a problem when SiO_2 content decreased to 10wt.%. With a suitable SiO_2 content, Y-Si face coat can be an appropriate combination to cast Ti-6Al-4V with enough of both chemical inertness and strength.

(2) The surface roughness decreased from 2.364 μm to 1.934 μm when the SiO_2 content increased from 10wt.% to 25wt.%. The Y_2O_3/SiO_2 ratio at Y_2O_3 slopes also decreased with an increase in SiO_2 content. Besides, the shell with 25wt.% SiO_2 has a more compact SiO_2 inside structure.

(3) The interface reaction between Ti-6Al-4V and Y-Si face coat can be divided into three stages: surface reaction stage, wetting stage and internal reaction stage. An increase in SiO_2 content intensified the reaction by promoting the wetting stage. If SiO_2 content is low, such as M1 in this study, the reaction will stop at the wetting stage. If the SiO_2 content is high enough, such as M4, it will have a complete wetting stage and an extra internal reaction stage.

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