

Mechanism and Influence of Re-dissolution of Zirconium Diacetate-Yttria Shell for Titanium Investment Casting

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Abstract: The re-dissolution of zirconium diacetate-yttria shell (ZA-Y shell) and its impact were investigated. The re-dissolution rate under moisture condition was measured by a balance. Three-point flexural strength was measured using a universal testing machine, and the fracture index was calculated. The distribution of the surface precipitates was observed by optical microscope, and its morphology and composition were tested using scanning electron microscopy (SEM) combined with energy spectrum analysis (EDS). The composition of the ZA-Y shell was measured by X-ray fluorescence (XRF). The results show that the re-dissolution is limited. The maximum water penetration rate is 2.5% and the dissolution rate is 0.8% within 20 min. The strength decreases by 26% and fracture index reduces to 66%. The surface precipitates are attributed to dissolution of ammonium metatungstate (AMT) and there are two reasons: drastic pressure release or fast drying condition with slow heat dissipation.

Key words: titanium; investment casting; re-dissolution; strength; precipitate

Because of the high pouring temperature and active chemical properties of titanium alloy, the facecoat shell in titanium investment casting must be made with special materials. A widely used facecoat slurry is usually made from zirconium diacetate binder, yttria powder and AMT (ammonium metatungstate) reinforcing agent^[1]. The ZA-Y (zirconium diacetate-yttria) shell generally uses solvent dewaxing^[2], but the toxicity of trichlorethylene is a threat to the workers and the environment, and a safe dewaxing method is necessary.

Autoclave dewaxing is a popular and environmentally friendly method. Compared to other methods such as hot water dewaxing and flash dewaxing, it has advantages for titanium complex structures^[3]: little expansion stress to the shell^[4], and the great heat transfer makes the wax flow out before big expansion; little increase to the internal stress^[5], and the temperature is approximately 180 °C, lower than the decomposition temperature of zirconium diacetate and AMT.

However, the ZA-Y shell will dissolve in moisture environment. With the reduction of water, zirconium diacetate (Fig.1) polymerizes (Fig.2) and the binder gels gradually^[6]. But in moisture environment, the coordination bond break, and the gelled zirconium diacetate dissolves again.

The re-dissolution may change the bonding condition of the shell, thus affecting its strength and surface quality. This would eventually lead to the inclusion defects caused by the peeling of facecoat or surface precipitates, which would significantly affect the quality of titanium castings. In the present paper, the re-dissolution of ZA-Y shell and its impact were studied. Water penetration and re-dissolution rate under water and steam condition were measured. Three-point flexural strength and fracture index under different conditions were compared. The morphology and the composition of the precipitates were investigated and the reasons were analyzed.

1 Experiment

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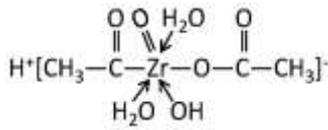


Fig.1 Chemical structure of zirconium diacetate

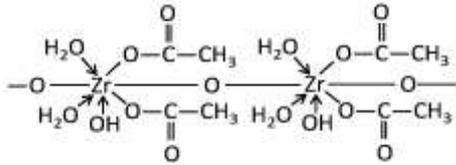


Fig.2 Chemical structure of polymerized zirconium diacetate

Zirconium diacetate binder, yttria powder and AMT were made into a slurry with the proper viscosity to make the ZA-Y layer, using yttria as sand material. Aluminum-silicon based slurry and sand were used to make the aluminum-silicon layer. The ZA-Y shell was made of 8.5 ZA-Y layers (8 layers and 1 seal), and the Y-Al shell was made of 2 ZA-Y layers and 5.5 aluminum-silicone layers. The drying time was 24 h/layer. To avoid the effects of wax infiltration, shells for re-dissolution and strength tests were separated from the wax by hand.

Re-dissolution and water penetration rate were measured with shell of 40 mm × 20 mm × 5 mm. The shell was dried at (105 ± 5) °C to constant weight m_1 , then immersed in (95 ± 5) °C water (to avoid the boiling impact) for a certain time, which was weighed as m_2 and then dried to constant weight m_3 . The re-dissolution rate S and water penetration rate W_m can be calculated by Eqs.(1) and (2):

$$S = \frac{m_1 - m_3}{m_1} \times 100\% \quad (1)$$

$$W_m = \frac{m_2 - m_3}{m_1} \times 100\% \quad (2)$$

Where, m_1 is mass before immersion, g; m_2 is mass after immersion, g; m_3 is mass after drying, g; S is re-dissolution rate, %; w_m is water penetration rate, %.

Strength properties were measured on a universal testing machine with the same shell, the fracture load and deformation were read by sensors, and the size was determined by caliper measurements. Three-point flexural strength M and fracture index $FI^{[7]}$ can be calculated by Eq.(3) and (4):

$$M = \frac{3Ls}{2wT^2} \quad (3)$$

$$FI = \frac{M^2 T w s}{18 E} = \frac{L \gamma}{2} \quad (4)$$

Where, L is fracture load, N; s is span, 30 mm; W is shell width, mm; T is shell thickness, mm; E is modulus, MPa; γ is the deflection, mm.

The distribution of the surface precipitates was observed by optical microscope, then sampled by tape and tested using SEM combined with EDS after gilding to study the morphology and the composition. The composition of the ZA-Y shell was measured by XRF.

2 Results and Discussion

2.1 Re-dissolution of the ZA-Y shell

The re-dissolution under hot water and steam conditions was studied to learn the case in autoclave dewaxing. The re-dissolution degree of the two layers of direct contact with hot water would be more serious while the re-dissolution degree would be less but deeper under steam condition.

2.1.1 Re-dissolution in hot water

The re-dissolution and water penetration rate of the shell in hot water are shown in Fig.3. The penetration rate is comparable to that of the water-insoluble porous media, such as concrete and rock^[8,9]. The penetration rate presents a nonlinear increase with time: it is high at beginning (10 min), but gradually slows down. The dissolution rate also owns similar nonlinear increase character. Within 20 min, the total water penetration rate is 2.5%, and the re-dissolution rate is 0.8%.

The re-dissolution of the shell is caused by the hydroxide ions which are absorbed onto the binder particle surface, resulting in the decomposition of polymeric zirconium diacetate. Not until the moisture penetrating to a certain depth, the re-dissolution of this depth occurs.

The penetration of porous media relates to solid content, porosity and pore size^[9]. For the ZA-Y shell, the high content of yttria powder makes the surface density high. So its moisture penetration resistance is high, and the penetration rate is limited. Decomposition of zirconium diacetate will weaken the bonding between materials, but also form a high viscous fluid. This fluid will clog pores in the adjacent layer, further reducing the penetration rate. So the dissolution rate is confined, and the shell would not collapse immediately.

2.1.2 Re-dissolution in steam

The water penetration rate under atmospheric steam condition is shown in Fig.4. The penetration rate is 1.6%

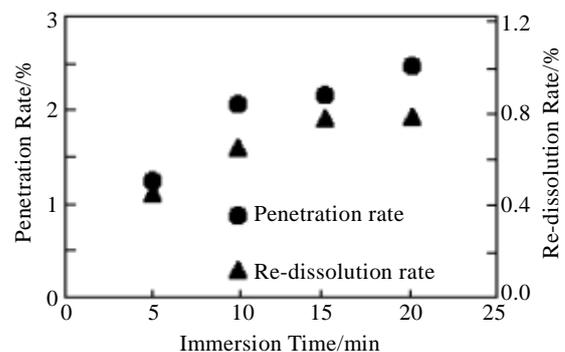


Fig.3 Re-dissolution and penetration rate vs immersion time

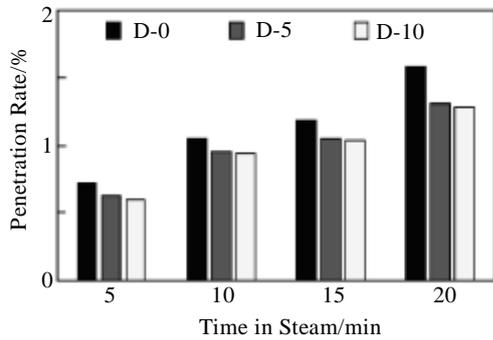


Fig.4 Penetration and drying rate under steam condition (D-0: tested without drying; D-5: dried for 5 min; D-10: dried for 10 min)

within 20 min, lower than that in hot water. After removing from dewaxing device, the water content decreases by over 10% within 5 min, suggesting that a part of the absorbed moisture is still in vapor state which could run out of the shell more quickly than normal water evaporation.

According to J. D. Snow^[10], the moisture penetration can be divided into three stages under steam condition:

(1) Penetration of water

At first, the steam would release latent heat to the low-temperature shell and turn into water. Most water flows away, but some may penetrate into the shell.

(2) Penetration of steam

When the shell temperature reaches the steam temperature, it turns to the second stage, i.e. the steam penetrates the shell directly. Under steady-state condition, the water-vapor transmission intensity ω can be estimated by formula (5)^[11]. It is proportional to the partial pressure difference and inversely proportional to the permeation resistance. So the penetration will gradually slow down. The autoclave is under 0.6 MPa to 0.8 MPa, and the steam penetration should be greater than that of normal pressure.

$$\omega = \frac{1}{H} (e_o - e_i) \tag{5}$$

Where, ω is vapor permeation rate, $g/(m^2s)$; H is vapor permeation resistance, $(m^2 s Pa)/g$; e_i is vapor partial pressure in the shell, Pa; e_o is vapor partial pressure in the environment, Pa.

(3) Overflow of moisture

In the pressure relief and removing process, as e_o decreases quickly, most steam penetrates out of the shell, while only a little turn into water and stay. The vapor partial pressure difference and temperature changes drastically, so the pressure release speed should be restricted to prevent the moisture in the porosity violently boiling. Since vapor partial pressure changes more intensely in autoclave

dewaxing, the water content running out of the shell is higher as well.

Meanwhile, the wax will inevitably seep into the shell in a real dewaxing process^[12], greatly hindering the penetration. So the re-dissolution degree in a real dewaxing would be lower.

2.2 Influence on the strength properties

The green strength is mainly attributed to the polymerization of the binder^[13]. Dissolution of zirconium diacetate would affect the strength properties. The strength property of the shell immersed in hot water was investigated, as it should be a more serious evaluation. As the layers of the sample and the real shell used in the factory are different, absolute numbers in this case are not important; the relative numbers tell the story.

2.2.1 Wet and dry strength

Fig.5 shows the wet and dry strengths of ZA-Y shell and Y-Al shell. In the first 5 min, the wet strength reduces little; but after 10 min, the strength of ZA-Y shell reduces by 26%, the strength of the Y-Al shell reduces by 30%.

The gelled binder network is deliquescent, both for the colloidal silica^[14] and the zirconium diacetate, as the hydroxide ions would be absorbed back onto the binder particle surface. So although the re-dissolution degree is different, the strengths of the shells would both be affected by the moisture penetration. And as the permeation resistance increases with the penetration, the weakening effect slows down with time. The two shells own similar re-dissolution degree, and the penetration of aluminum-silicon layer would be higher due to its high permeability, so its strength decrease is a little more serious.

The weakening effect is transient as the bonding condition basically restores after drying. So the dry strength restores over 90% of the original strength.

2.2.2 Fracture Index

FI represents rupture energy required for shell cracking. The higher the index, the stronger the shell resistance to cracking. As shown in Fig.6, within 20 min the ZA-Y shell

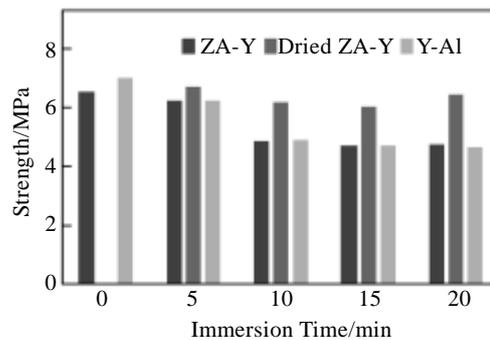


Fig.5 Wet and dry strength of the shells with immersion time

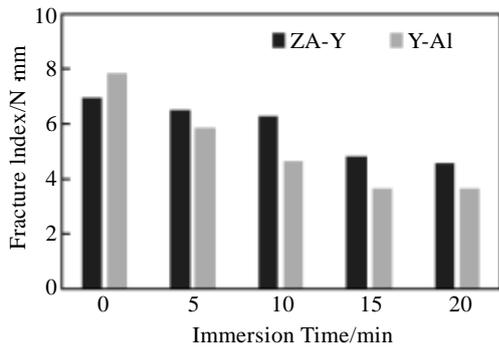


Fig.6 Fracture index of the shells vs immersion time

FI reduces to 66% and the Y-Al shell FI decreases to 54%.

FI is determined by fracture load and deflection. The bending ability decreases with dissolution, leading the decline of fracture load and deflection. So the FI declines with the increase of penetration (time). The parallel decline suggests the similar impact of re-dissolution on the ZA-Y layer and aluminum-silicon layer again. And the wetting of the surface may even help heal the microcracks, but it needs further research.

2.3 Influence on surface quality

The shell dewaxed in autoclave generally owns good quality, but sometimes the surface precipitates (tiny white particles) occur. The precipitates on the shell surface may be washed down by the titanium liquid during pouring, resulting in casting defects.

2.3.1 Surface precipitates

The wax seeping into the shell makes the measurement difficult, so the precipitates after calcination were studied. Mostly, the precipitates are distributed in an aggregated state as shown in Fig.7. But for some dewaxing batches, the morphology of the precipitates is similar to the crater after volcano eruption, as shown in Fig.8. The morphology difference should be related to the precipitation process.

According to SEM study, the precipitates I and II are same in microstructure and both could be divided into two kinds: mostly the precipitates are in microns with regular form (Fig.9) but some are in irregular form (Fig.10).

The composition of the ZA-Y shell and the two precipitates are given in Table 1 and Table 2. The content of W element in the precipitates is greater than that of the matrix, but no Zr element is detected. The Al, Si and Ca contents of precipitate B is higher than that of the matrix. Considering about the matrix being inevitably introduced in the sample during taping process, the main composition of the precipitates is W element. And the major precipitate in the dewaxing and drying stages is AMT, and little zirconium diacetate precipitate. In the calcination stage, the AMT

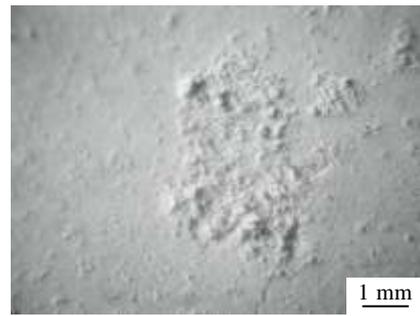


Fig.7 Morphology of the surface precipitates I: aggregated state

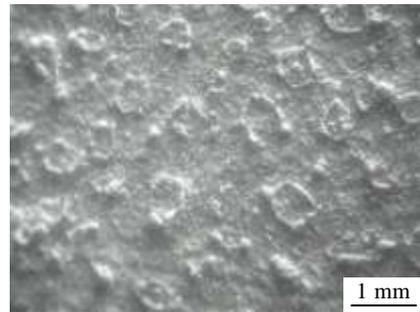


Fig.8 Morphology of the surface precipitates II: crater state

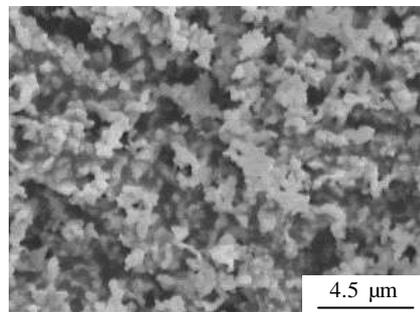


Fig.9 Microstructure of surface precipitate A: regular form

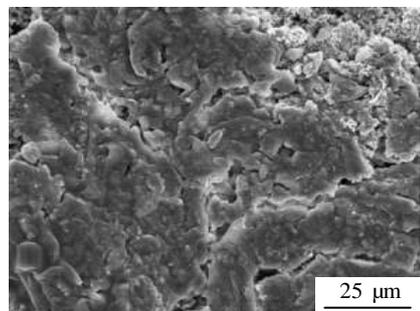


Fig.10 Microstructure of surface precipitate B: irregular form

would decompose into tungsten oxide, which reacts with yttria into yttrium tungsten oxide, and thus the precipitates are still white after calcination^[15]. The remelting state of

Table 1 Composition of the shell (wt%)

O	Y	W	Zr	Al	Si	Ca
22.18	64.58	8.09	4.48	0.36	0.19	0.11

Table 2 Composition of precipitate A, B (wt%)

	O	Y	W	Au	Al	Si	Ca
A	12.62	26.52	35.76	25.10	-	-	-
B	15.22	21.48	27.06	32.59	1.28	1.47	0.89

precipitate B is attributed to aggregation of low-melting compounds of Al, Si and Ca elements in the calcination process.

2.3.2 Analysis of precipitation

Only for a little batch, the precipitates were found on the shell right after removing from the device. Most precipitates appear during the subsequent drying stage. So the precipitates must be related to the moisture migration and temperature change.

The moisture penetrates into the shell throughout the dewaxing process. The content of AMT in the slurry is about 20%^[1], which is higher than that of the polymerized zirconium diacetate in a shell. The solubility of AMT at 25 °C is 300 g/100 mL H₂O^[16], which increases with the increase of temperature. Therefore, the re-dissolution rate of AMT should be significantly greater than that of the polymerized zirconium diacetate. In the pressure relief stage, the moisture which migrates outward rapidly^[17] would take a lot of AMT to the near surface.

If the pressure relief is drastic, the aqueous solution will overflow from the shell violently, resulting in the annular precipitates as showed in Fig.8.

In the drying process, the water evaporates gradually. With the decreasing of temperature, the AMT is supersaturated and precipitates continuously along the migration way. Whether the surface precipitate occurs is determined by the drying and cooling rate. If the shell is dried fast and cooled slowly, little precipitation occurs in the middle way, the amount of AMT brought to the near surface is large, and it is likely to cause surface precipitates. But when the shell is dried slowly and cooled fast, the AMT will precipitate during the migration, the surface precipitates may not occur. The large amounts of microcracks in the shell surface are important channels for the moisture to overflow, and the uneven distribution of microcracks results in uneven drying. Eventually the high concentration zone of AMT would be formed, so the precipitates would be in an aggregation state.

3 Conclusions

1) Re-dissolution of ZA-Y shell is limited for a period of time of 20 min, the maximum water penetration rate is

2.5% and the dissolution rate is 0.8% in moisture condition.

2) The shell strength decreases by 26% and F.I. reduces to 66% within 20 min when the shell is immersed in water. The moisture has a similar impact on the strength properties reduction of the ZA-Y shell and aluminum-silicone based shell.

3) The surface precipitates are attributed to dissolution of AMT and there are two reasons: drastic pressure release or fast drying condition with slow heat dissipation rate.

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钛合金熔模铸造二醋酸锆-氧化钇型壳的回溶及影响

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摘要: 研究了二醋酸锆-氧化钇型壳(ZA-Y型壳)的回溶及其影响。使用重量法测定了型壳热水、蒸汽条件下的回溶率;使用电子万能试验机测定了型壳抗弯强度,并计算了裂纹指数随润湿时间的变化规律;利用光学显微镜(OM)观察了表面析出物的分布情况,用扫描电镜(SEM)结合能谱分析(EDS)研究了其形貌与成分,使用X射线荧光分析(XRF)方法测定了ZA-Y型壳的成分,并分析了表面析出物产生的原因。结果表明,型壳20 min内的回溶程度有限,最大吸水率为2.5%,回溶率为0.8%;强度下降26%,但裂纹指数下降至66%;表面析出物主要是由于偏钨酸铵的回溶,包含2种原因:泄压速度过快或后续干燥快而散热慢。

关键词: 钛合金; 熔模铸造; 回溶; 强度; 析出物

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