A MOLD MATERIAL USED FOR TITANIUM-ALUMINUM ALLOY —CALCIA[①]

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ABSTRACT The effects of binder, additive and sintering temperature on the properties of calcia as a mold material used for titanium-aluminum alloys have been studied. The results showed that the solution of $CaCl_2$-C_2H_5OH is the best binder for calcia, the additive of CaF_2 not only increases the strength but also the anti-watering property of calcia; sintering at 900~ 1 000 ℃ is adaptable. The contamination of calcia on titanium-aluminum alloy castings has been studied, and the experimental results showed that the thickness of contamination is less than 15 μm.

Key words titanium-aluminum alloy mold material calcia casting

1 INTRODUCTION

The intermetallic compound containing titanium has developed quickly in the last twenty years[1-4]. Due to the difficulty of machining of this kind of material, casting is more competitive[5-7]. The molten titanium alloy has very high reactivity and it can react with almost all refractory materials. To date, no materials appear completely stable to the molten titanium alloy[8]. The aim of the study on mold materials used for titanium alloys in recent years is to decrease the cost and reduce the pollution[9, 10]. Among the oxides, CaO has a high melting point and is more stable than TiO_2 below 1 700 ℃. CaO has not been used as mold material yet because it absorbs moisture easily and breaks up in a short interval. The anti-watering property of CaO has been improved through theoretical and experimental studies. This paper aims to develop CaO as a mold material for titanium-aluminum casting.

2 EXPERIMENTAL

2.1 Materials and methods of experiment

The calcia sample was made with semi-dry compressive forming method in order to study the effects of binder, additive and sintering temperature on its properties. CaO, $CaCl_2$ and CaF_2 are chemical triple. The anti-watering time and compression strength of calcia sample were tested. During testing the anti-watering time the calcia sample was sunk in water and the time was recorded until a crack appeared on the sample. The compression strength was measured with high temperature strength testing unit for mold material.

2.2 Results and discussion

2.2.1 Effect of binder on properties of calcia sample

Like all other mold materials, making calcia mold needs binder. The water-base binder can not be used for producing calcia sample because it absorbs moisture easily. Four kinds of binder were referred in Refs. [11- 14] and had different effects on the properties of calcia controversially. We selected three binders and investigated their effects. Table 1 lists the experimental results about the effects of the three binders on the properties of the calcia sample.

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Table 1 Effects of binder on properties of calcia sample

Binder	Compression strength/ MPa	Anti-watering time/ min
Solution of $CaCl_2$-C_2H_5OH	48	56
Solution of organic glass-acetone	43	38
Solution of rubber-gasoline	41	36

The results showed that the solution of $CaCl_2$-C_2H_5OH has the best contribution. The later two kinds of binder are organic binders, they only have the function of binding and lubrication at lower temperatures. When the sample was sintered at high temperatures, the binder was oxided and/or vaporized and there is no trace in the sample finally. The strength of calcia sample mainly depends on the lap joint between calcia particles.

C_2H_5OH in $CaCl_2$-C_2H_5OH solution has lubricating effect during shaping stage but vaporizes quickly. The binding effect depends on $CaCl_2 \cdot C_2H_5OH$ complex compound[15], which decomposes bit by bit with increasing temperature and releases the active $CaCl_2$ covering the calcia particles. As the temperature is up to the melting point of $CaCl_2$, the solution of CaO-$CaCl_2$ will be generated. Under high temperatures and oxidizing atmosphere, $CaCl_2$ may be oxidized to form CaO. No $CaCl_2$ can be detected after high temperature sintering, as shown in Fig. 1. So the combination of calcia particles is accelerated by the solution of CaO-$CaCl_2$. Under this condition, not only is the strength raised but also the surface defect of calcia particles is minimized. As a result, the anti-watering time is lengthened.

2.2.2 Effect of additive on properties of calcia sample

The completed sintering of CaO is difficult because of its high melting point (2 570 ℃). Even it is sintered completely, the properties

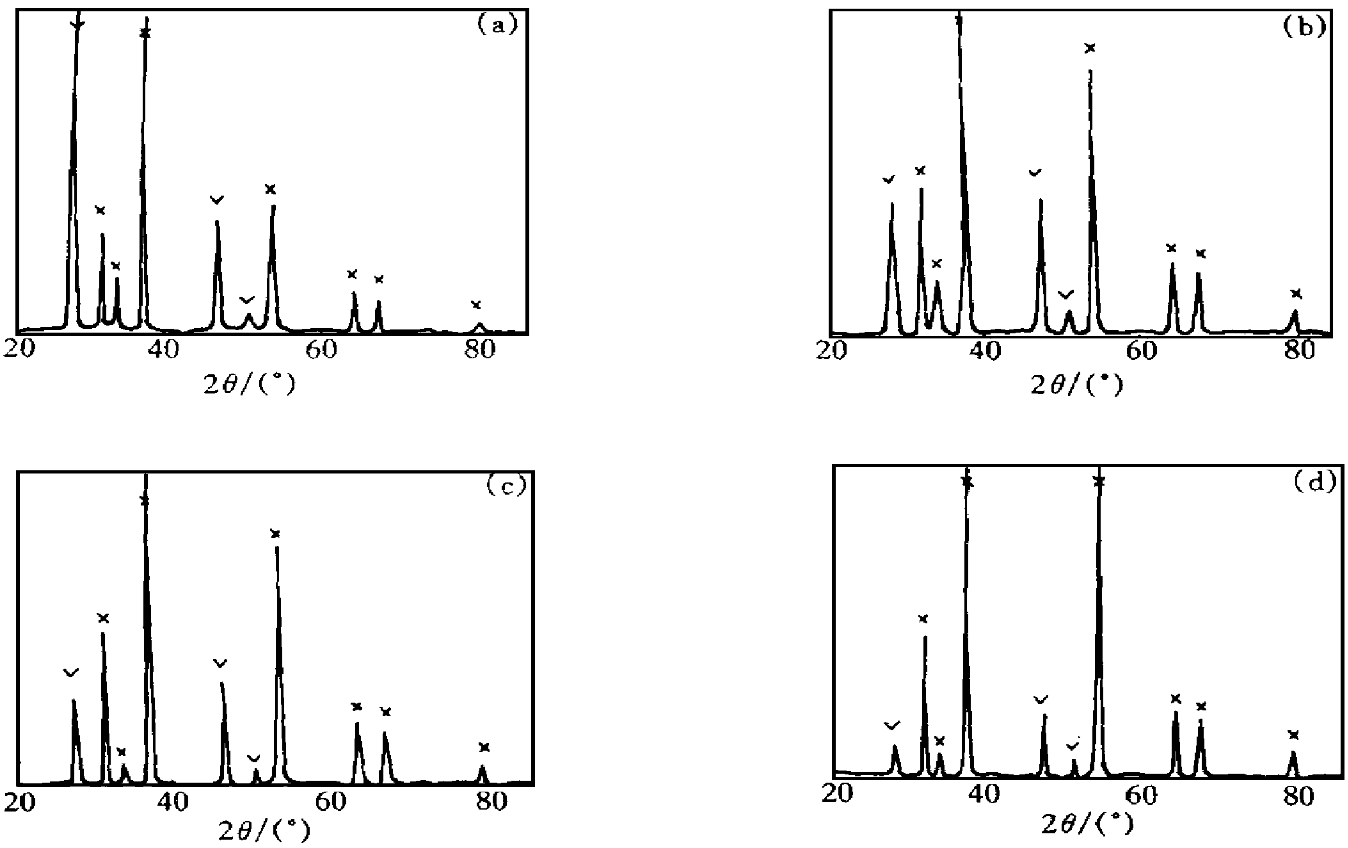

Fig. 1 XRD spectra of calcia sample sintered at different temperatures
(a) —200 ℃ sintering; (b) —950 ℃sintering; (c) —1 100 ℃sintering; (d) —1 500 ℃sintering
× —CaO; √—CaF_2

such as strength and anti-watering time are not good enough. So some additives should be selected to improve the properties of calcia.

The additive must have the following properties when it mixes with calcia used as mold material for titanium alloys:

(1) The additive must be thermodynamically stable with molten titanium;

(2) The additive must have lower melting point than calcia;

(3) The additive is not hydrometric.

CaF_2 is the best candidate for this usage. First, it is stable to titanium. CaF_2 has been used as slag material in slag induction melting in America and does not pollute titanium[16]. Second, the melting point of CaF_2 is only 1 419 ℃ and a low melting point compound, $CaO\cdot CaF_2$ can be produced at 1 360 ℃[17]. Third, CaF_2 is not hydrometric, even it reacts with moisture at high temperature, the product is CaO and there is no any other material polluting calcia.

The effect of CaF_2 content on calcia properties was studied. As shown in Fig. 2, in the range of 0~ 25% CaF_2, anti-watering time increases with increasing CaF_2 content. Compression strength increases with increasing CaF_2 below 20% and then decreases.

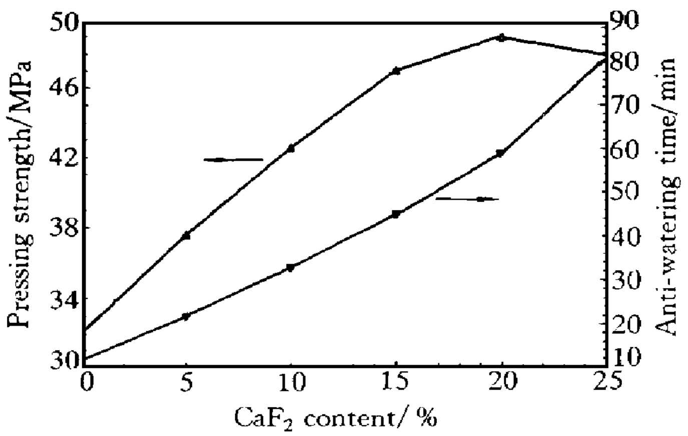

Fig. 2 Effect of CaF_2 content on CaO sample properties

As mentioned above, the melting point of the lower melting point compound is about 1 360 ℃, but the sintering temperature is only 950 ℃, so the sintering is difficult. Because active $CaCl_2$ covers CaO particles, the $CaO\cdot CaF_2$ solution will form easily. In other words, CaO and CaF_2 will react at 950 ℃ under the condition of the existence of active $CaCl_2$. With increasing CaF_2 content, the amount of $CaO\cdot CaF_2$ solution increases and the sintered neck is enlarged, and the clip joint is strengthened. So, compression strength increases. Over that composition, more CaF_2 will remain in the sample and result in the decrease of compression strength.

In Fig. 2, the anti-watering time increases with increasing CaF_2. This is just due to the fact that CaF_2 is not hydrometric and the product of $CaO\cdot CaF_2$ covering around the particles prevents the calcia from absorbing moisture.

2.2.3 Effect of sintering temperature on properties of calcia sample

Sintering at high temperature is a method to improve strength and anti-watering time. The requirement for the properties of mold material used in foundry is not as high as in other field because the mold only endures short time under low tension level. To select an optimal sintering temperature which can satisfy the need of practical production and meanwhile reduce the cost is significant.

Three temperatures, 950 ℃, 1 100 ℃ and 1 500 ℃ were selected to investigate the effect of sintering temperature on the properties of calcia sample. As shown in Fig. 3, the properties are improved with increasing sintering temperature and the anti-watering time increases significantly. As certified by Figs. 1 and 4, these result from the increasing of dissolving degree of CaF_2

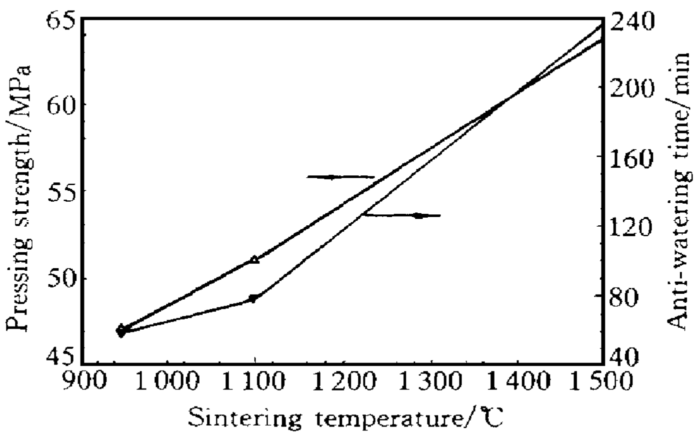

Fig. 3 Effect of sintering temperature on CaO sample properties

Fig. 4 Morphologies of CaO particles after sintering
(a) —950 ℃; (b) —1 100 ℃; (c) —1 500 ℃

in CaO with increasing sintering temperature. In XRD spectra, the CaF_2 strength decreases with increasing sintering temperature and the calcia particles are protected by a surface film of CaF_2-CaO and/or CaF_2 as shown in Fig. 4. At 1 500 ℃, CaO particles are driven into more closely by the surface tension force because CaF_2 is melted at this temperature. So the properties are improved significantly, but the sample shrinks noticeably at the same time. This is harmful to the accuracy of mold dimension. From the above analyses, it follows the conclusion that the sintering temperature should not be too high.

3 POLLUTION OF CALCIA ON TiAl CASTINGS

The calcia sample was inserted in an emery mold and the Ti-34% Al (mass fraction) melted with ISM (Induction Skull Melting) was poured into this mold. The sample was vertically machined to the surface of calcia sample with electric discharge machine. The depth of pollution coat was analyzed by Microhardness-Meter and EMPA (Electronic Micro-Probe Analyzer) and the results are shown in Fig. 5 and Fig. 6.

In Fig. 5, only titanium and calcium were analyzed to discover the pollution of calcia on the TiAl castings. The curves vary abruptly from

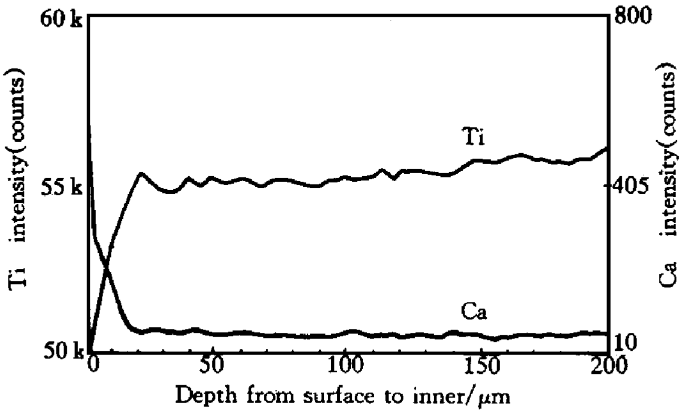

Fig. 5 Distribution of Ti and Ca from surface to inner

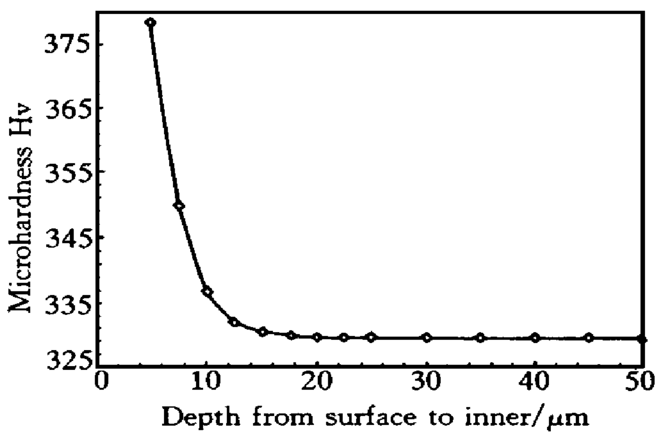

Fig. 6 Distribution of micro-hardness from surface to inner

surface to inner in a range of 18 μm. Apart from the first 6~ 10 μm formed due to the tessera, the calcium diffuses into 12 μm approximately. The curve of microhardness from the surface to the inner decreases abruptly before 15 μm and then stabilizes near 329 MPa as shown in Fig. 6. The difference of coat thickness between the two results caused by the faster diffusion of oxygen than that of calcium in TiAl alloy.

4 CONCLUSIONS

(1) Among the three binders, the solution of $CaCl_2$-C_2H_5OH has the best contribution to calcia properties. The latter two organic binders only have the function of binder and lubricant at lower temperatures.

(2) CaF_2 is the best additive for calcia. In the range of 0~ 25% CaF_2, the anti-watering time increases with increasing CaF_2 content. The compression strength increases with increasing CaF_2 below 20% and then decreases.

(3) The sintering temperature should not be too high. An optimal sintering temperature is between 950~ 1 000 ℃.

(4) The thickness of the pollution coat of calcia on TiAl casting is less than 15 μm.

REFERENCES

1 Kim Y- W. Mater Sci Technol, 1992, 8(3): 299.
2 Froes F H. J Mater Sci, 1992, 27: 5113.
3 Ashley S. Mechanical Engineering, 1991, 113(12): 49.
4 Dimiduk D M. in: Kim Y- W *et al* eds, Gamma Titanium Aluminides, TMS, 1995: 3.
5 Austin C M *et al*. in: Kim Y- W *et al* eds, Gamma Titanium Aluminides, TMS, 1995: 21.
6 Pettersson B *et al*. in: Kim Y- W *et al* eds, Gamma Titanium Aluminides, TMS, 1995: 33.
7 Choudhury A *et al*. IVC- 13/ICSS- 9, Abstract No. VM2- 004, Program No. VM3- TU.
8 Frueh C *et al*. Int J Cast Metals Res, 1996, (9): 233.
9 Shaha R L *et al*. AFS Trans, 1990, 98: 253.
10 Saha R L *et al*. J Mater Sci Lett, 1991, 10: 1318.
11 Sato T *et al*. Castings, (in Chinese), 1990, 62 (9): 732.
12 Xiang C X *et al*. Refractory, (in Chinese), 1982, 16(3): 32.
13 Ni R M *et al*. Refractory, (in Chinese), 1989, 23 (2): 13.
14 Li F L *et al*. Refractory, (in Chinese), 1993, 27 (5): 275.
15 Tianjin Institute of Chemistry Industry. The Production of Non-Organism, (in Chinese). Beijing: Chemical Industry Press, 1993.
16 Sears J W. JOM, 1990, 42(3): 17.
17 Li Z B *et al*. Slag Melting and Casting, (in Chinese). Beijing: National Defense Industry Press, 1981.

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