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Microstructure and strength of needle coke modified ceramic casting molds

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Abstract

Properties of an investment casting mold using needle coke additions have been investigated in this work. The use of needle coke increases the mold thickness by a factor of 30% on flat section and 60% at sharp edges over that of a comparable full fused silica system. The extra mold thickness in the needle coke modified system, especially at edges, gives a higher load bear capacity. Ceramic molds modified with needle coke exhibit higher “green, dry” strength, and show less reduction in “green, wet” strength. The extra volume of cavity left after needle coke combustion is not acting as a significant defect which would reduce the hot strength of the mold.

Keywords: Investment casting; Ceramic molds; Needle coke; Microstructure; Mold properties

1. Introduction

Investment casting allows dimensionally accurate components to be produced and is a cheaper alternative than forging or machining, since waste material is kept to a minimum [1]. The production of the investment casting ceramic mold is a crucial part of the whole process [2]. Ceramic molds are used preferentially to achieve high dimensional accuracy and perfect surface smoothness, as well as high quality and freedom from impurities in the microstructure of the cast product [3]. With the rapid development of industry technology, it demands that the castings have higher manufacture precision and more complex shape. This puts out higher requirement of mold properties.

Ceramic mold materials should be selected with care if optimum mold properties are to be achieved. Different combinations of refractory and binder have been used to produce ceramic mold. Most investment foundries use a silica based binder system which can be either water or alcohol based. Problems associated with ceramic mold materials have been exacerbated, as the degree of environmental emissions allowed from industrial processes have been limited. This has led to the increasing use of water-based binders which can greatly decrease volatile organic compound (VOC) emissions. Unlike alcohol-based binders, water-based colloids are not chemically set and require gelation by moisture removal. Colloidal binders produce ceramic molds with very low green strengths which are prone to cracking during wax removal and handling [4].

The strength distribution all over the mold can vary considerably. The structure in corners of the shell can be different from flat regions due to the placement of the stucco. Variation of the structure can cause these regions of the shell to break under smaller loads [5]. Many new pattern materials, such as polymeric foams, have greater coefficients of thermal expansion than wax which can increase the chance of shell cracking during pattern removal [6]. Due to the majority of these cracks forming along the edges and in the corners of the shell, the properties of these areas are of interest [7].

Liquid polymer is normally added to the ceramic slurry to increase the green strength of the ceramic mold [8,9]. However, previous work has shown that the green strength of liquid polymer modified mold is reduced significantly when placed in a steam bath for a relatively short period of time [10]. And liquid polymer has little contribution to the better coverage at sharp edges. These have implications with regard to crack resistance during the de-wax process.

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The molds using organic fiber to replace liquid polymer additions have been intensively investigated by Yuan and Jones [11,12]. It was found that the fiber additions could greatly increase mold thickness especially at edges. However, the fiber modified mold had relatively low green strength, which is most likely a result of the very smooth nature of the nylon fiber surface, and there is little resistance and little force required to pull the fibers from the matrix. It was found by Doles and Viers that the fiber-containing slurries could not always reproduce small holes, slots, grooves and other fine details to the desired degree, although these materials worked well in many commercial uses [13].

Needle cokes are special grade of petroleum cokes prepared from petroleum residues or coal tar through a delayed coking process, and now they are mainly used as the filler materials of the graphite electrodes for electric arc furnaces because of their high graphitizability, abundance and low cast [14,15]. Meanwhile, the needle cokes also have the advantages of high strength, low expansion coefficient and good resistance to thermal shock. In the present work, a silica sol mold system using needle coke additions is investigated. It is designed to improve the green strengths of the mold, and to optimize mold building for thick and uniform coverage at both flat section and edges. Properties such as modulus of the rupture (MOR) and adjusted fracture load (AFL) are studied.

2. Experimental work

Slurries were prepared by conventional mixing of the raw materials according to the recipes shown in Table 1. The primary slurry consisted of colloidal silica binder (Nalco, LATRIX6002) and alumina filler (Shanghai Zhenjiang Chemical Co., Ltd, 325 mesh). Two different backup slurries were prepared, full fused silica slurry and needle coke modified slurry. The full fused silica slurry consisted of colloidal silica binder (Nalco, DVSTU006) and fused silica filler (Minco, Min-Sil 120F). The needle cokes (Nalco), as shown in Fig. 1, were added into the modified backup slurry with a ratio of 2 wt% of refractory filler. The chemical compositions of the needle coke are listed in Table 2. When preparing the needle coke modified slurry, the fused silica filler was first mixed into the binder. When the mixture was uniform with low viscosity, turned down the stirring rate of the slurry mixer and slowly whisked in the needle cokes to the slurry until the slurry was mixed well. Predetermined amount of wetting agent (Remet, Victawet 12) and anti-foam (Remet, Burst RSD-10) were added to both primary and backup slurries before filler additions.

The shells were built by first investing the wax pattern into the primary slurry. A zircon stucco (Minco, zirosol 80/120 mesh) was applied by the rainfall sanding method. The assembly was rotated during this process in order to obtain a uniform coat of stucco material adhering to the slurry coat. The primary coat was dried at a temperature of 22 °C, 50% relative humidity and 0.5 m/s air speed for 24 h. Four backup coats were then applied sequentially in the same manner. A coarse Min-Sil stucco (Minco, Min-Sil 30/50 mesh) was used as a backup stucco.

Fig. 1. Photograph of the needle cokes.

Table 2
Chemical compositions (wt%) of needle coke.

Carbon	95.38
Hydrogen	3.85
Sulfur	0.12
Nitrogen	0.23
Ash	0.28

Table 1
Slurry compositions and properties for ceramic mold samples.

Slurry	Primary	Secondary1	Secondary2
Binder	LATRIX6002	DVSTU006	DVSTU006
Binder silica (wt%)	28	28	28
Polymer (wt%)	4.8	7.7	7.7
Filler	Alumina 325M	Min-Sil 120F	Min-Sil 120F
Needle coke	n/a	n/a	2 wt% of filler
Wetting agent (wt%)	0.3	0.3	0.3
Antifoam (wt%)	0.3	0.3	0.3
Filler loading (kg/kg binder)	3.2	1.9	1.9
pH value	9.8–10.2	9.8–10.2	9.8–10.2
Viscosity (s) Zahn cup #5	25–30	12–15	12–15
Density (g/cm^3)	2.45	1.73	1.71

Table 3
Mold build for ceramic mold samples.

Mold system	Coat	Slurry type	Stucco	Dip time (s)	Drain time (s)	Air speed (m/s)	Dry time (h)
Full fused silica mold	1	Primary	Zircosil 80/120	30	60	0.5	24
	2–5	Secondary1	Min-Sil 30/50	30	60	3	2
	6	Secondary1	n/a	30	60	3	24
Needle coke modified mold	1	Primary	Zircosil 80/120	30	60	0.5	24
	2–5	Secondary2	Min-Sil 30/50	30	60	3	2
	6	Secondary2	n/a	30	60	3	24

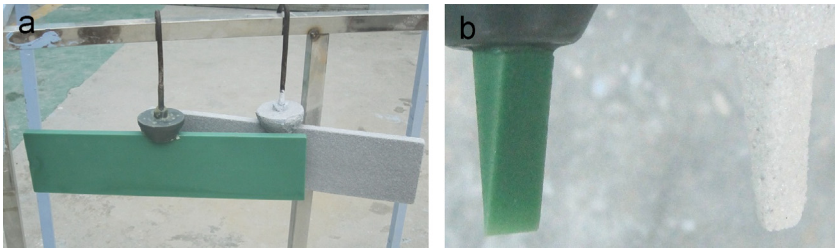

Fig. 2. Photographs of the patterns and dipped molds: (a) MOR plates and (b) wedge pieces.

Each secondary coat was dried at a temperature of 22 °C, 50% relative humidity and 3 m/s air speed for 2 h. Finally, a seal coat of secondary slurry which has the function of bonding the outermost stucco was applied and dried at a temperature of 22 °C, 50% relative humidity and 3 m/s air speed for 24 h. Details of shell build are listed in Table 3. The wax inside the ceramic mold was then removed by steam autoclaving at 7.5 bar pressure for 5 min using an autoclave dewaxing.

For flat bar mechanical testing, the mold samples were prepared upon a wax pattern with dimensions approximately 400 mm × 100 mm × 10 mm. The molds were cut into MOR bars after dewax. For the measurement of mold thickness, the 12° Vee-shaped pieces were taken from molds produced using a triangular prism wax pattern, which produces symmetric trailing edge sections. The triangular prism pattern is 20 mm tall, 10 mm wide with a 12° included angle. The photographs of the patterns and the examples of molds produced can be seen in Fig. 2.

Flexural strength tests were made in three-point bending over a span of 70 mm using test pieces of 90 mm in length and 10 mm in width cut by diamond wheel sawing. Samples were loaded in an Instron-5500R tensile testing machine at a constant load rate of 1 mm/min until failure. Tests were conducted on: 1. “green, dry” test-pieces (24 h at room temperature after autoclaving); 2. “green, wet” test-pieces (placed over a steam bath for 15 min before testing); 3. “hot” test-pieces. The MOR, σ_{Max}, was calculated using Eq. (1) [12]

$$\sigma_{Max} = \frac{3P_{Max}L}{2WH^2} \tag{1}$$

where P_{Max} is the fracture load, L is the test span, W is the test-piece width and H is the test-piece height.

The 'adjusted fracture load' in flexure (AFL_B) is defined as the force required to break a 10 mm wide test-piece of shell across a 70 mm span, and is a method of normalizing the load bearing capacity of the shell. It can be expressed as Eq. (2) [16]

$$AFL_B = f_B \sigma_{Max} H^2 \tag{2}$$

where f_B is a constant equal to 0.1.

The AFL takes the mold thickness into account and therefore represents the actual shell performance when the mold is subjected to an external load [17].

Microstructure of the needle coke and the ceramic molds were investigated using a NOVA NanoSEM 230 field emission scanning electron microscopy.

3. Results and discussion

3.1. Microstructure of needle coke and mold

The microstructure of the needle coke is illustrated in Fig. 3. The average length of the needle coke is approximately 0.5–2.0 mm, with a width of 0.2–0.5 mm. The surface of the needle coke is quite rough, having well developed needle-like micro-domains and many small tapered heaves.

In the cross section of the needle coke, it shows mixed domains that are composed of needle-like micro-domains and mosaic-like domains. The needle-like domains (width = 3–8 μm), having many tiny heaves, are aligned with the needle-like micro-cracks. However, the mosaic-like domains are the main structure of the needle coke section, having a smaller anisotropic structural unit than that of the needle-like ones. The mosaic-like domains are porous, which come in a variety of pore sizes from tens of nanometers to tens of microns.

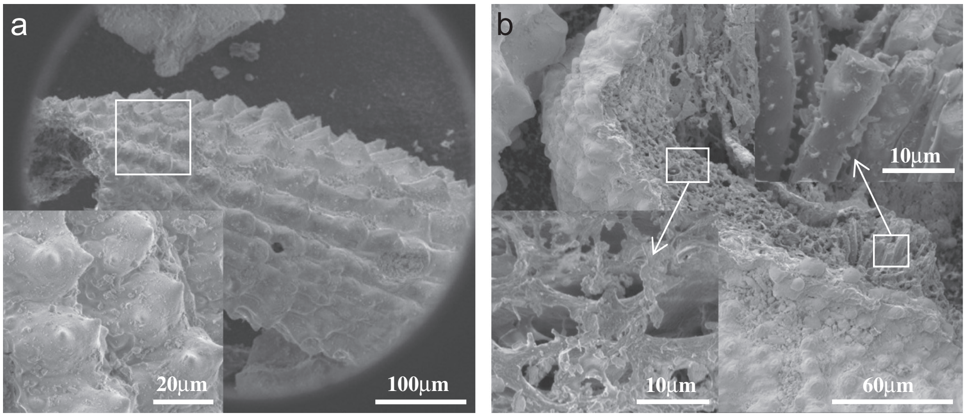

Fig. 3. Microstructure of needle coke: (a) surface and (b) cross-section.

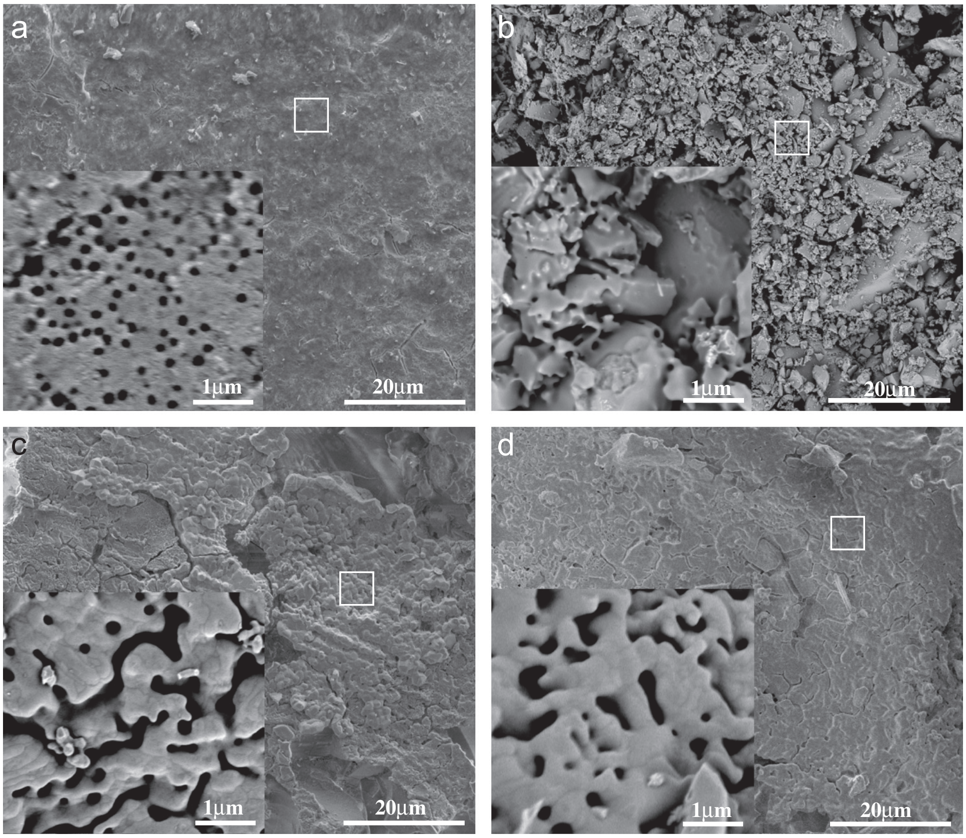

Fig. 4. Microstructure of the needle coke modified molds: (a) green sample; (b) fired at 800 °C for 1 h; (c) fired at 1000 °C for 1 h and (d) fired at 1400 °C for 1 h.

The green sample of the needle coke modified mold has uniform structure with many tens to hundreds nanometers pores which come from the cross-section of needle coke, as seen in Fig. 4(a). After sintered at 800 °C, as all the moisture and the polymer in the mold have been burned off, the mold has higher porosity compared to the green mold, as illustrated in Fig. 4(b). Besides, about 60 wt% of the needle cokes added to the mold are burned off at the sintering temperature of 800 °C, as shown in Fig. 5(a), which is also one of the reasons to increase the porosity of the mold. When the sintering temperature rise to 1000 °C, the ignition loss of the needle coke additions exceeds 95 wt%. The density of the mold increases as the sintering temperature continued to increase, as seen in Fig. 4(c) and (d).

The molds contain significant quantities of silica. When exposed to temperatures above 1000 °C, amorphous silica crystallizes, forming beta cristobalite [18]. Fig. 5(b) depicts the X-ray diffraction (XRD) patterns of needle coke modified molds sintered at different temperatures. It can be seen that the crystallization of cristobalite is very obvious when the sintering temperature is higher than 1000 °C. The crystallized cristobalite phase can be clearly found in Fig. 4(c) and (d). Cristobalite phase transition reduces the fired strength of silica that constitutes investment casting shells.

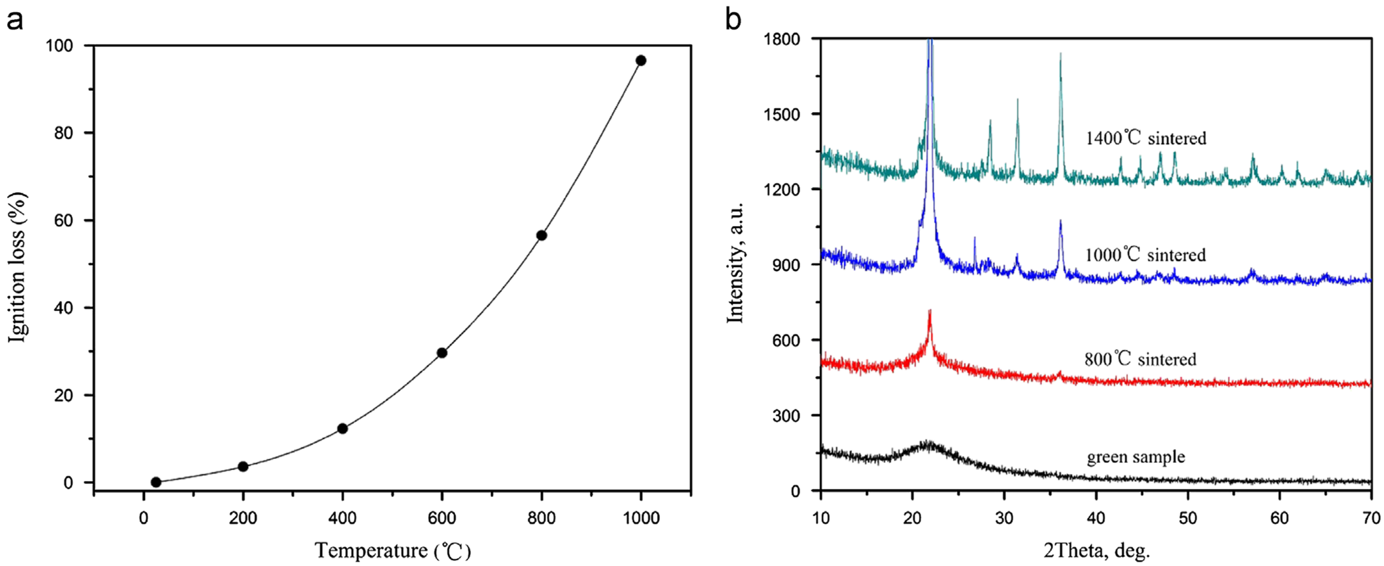

Fig. 5. (a) Ignition loss vs. calcination temperature of needle coke. (b) XRD patterns of needle coke modified molds sintered at different temperatures.

3.2. Mold build

In order to determine the thickness of the slurry coat and the stucco coat, the plate weight test was carried out using a metal plate (150 mm × 150 mm × 3 mm) which was dipped in slurry and recording the weight of slurry and stucco adhering to the plate against time, as shown in Fig. 6(a). With the slurry viscosity listed in Table 1, the needle coke modified slurry has a much higher ceramic retention rate after dipping, which leads to a thicker coat compared to that produced with full fused silica slurry, as shown in Fig. 6(b). Sagging occurred after dipping because of gravity. This results in continuous decrease of the slurry retention on the plate. The slurry retained on the standard metal pattern can be viewed as a total, consisted of many very thin layers. The addition of the needle coke increases the bonding strength between layers, and leads to a high ceramic retention. A stucco (Minco, Min-Sil 30/50 mesh) was applied by the rainfall sanding method with different drain times of the metal plate. The needle coke modified mold has a higher stucco retention rate after stuccoing compared to the full fused silica mold, as shown in Fig. 6(c). It seems that the needle coke improves the adhesion of the slurry. This could lead to a thicker stucco coat. The effect of needle coke on the moisture evaporation rate of the mold was also studied. The loss of moisture in mold at different dry times was recorded, as shown in Fig. 6(d). The needle coke modified mold has an increased drying rate compared to the full fused silica mold. The existence of the needle coke is favorable for the evaporation of the moisture from the inside to the outside of the mold. Further study will be carried on to research the mechanism.

The 12° Vee-shaped pieces were taken from molds produced using a Vee-shaped wax pattern to determine the mold thickness at both flat section and edges, as illustrated in Fig. 7(a). The thicknesses of two different mold systems are shown in Fig. 7(b). Thinner mold walls at edges are found in both systems, showing reduced coverage and shell build at the point. With the mold build condition listed in Table 3, at flat section, the needle coke modified molds are 30% thicker than full fused silica molds over a six-coat system, and at the trailing edge, the needle coke modified molds are 60% thicker than full fused silica molds. Most mold cracking and damage during dewax and casting occurs at the sharp radii and corners, such as trailing edges of turbine blades and sharp corners, where reduced mold build and high stress results in ceramic failure [19,20]. The addition of needle coke in the mold optimizes mold building for thicker and uniform coverage at both flat section and edges. This can minimize mold cracking.

For this reason, to produce an equivalent mold thickness at the flat section, the secondary coats number can be reduced by using needle coke modified slurry. The needle coke modified molds would still have greater wall thickness at the sharp corners, comparing to the full fused silica mold system. This could provide sufficient mechanical properties at both flat section and edges to reduce mold failure, whilst significantly reducing production time and material costs for investment shells.

3.3. Mold strength

The results of the strength and load capacity achieved for the green mold samples are depicted in Fig. 8. For the green mold samples under dry condition, needle coke modified mold exhibits higher green strength than that of the full fused silica mold, being 9.32 MPa as compared to 7.10 MPa. After normalizing for the mold thickness, the same trend is also found in the adjusted fracture load bearing capacity (AFL) measurement, giving a fracture load of 32.44 N for the needle coke modified mold and 14.57 N for the full fused silica mold. The rough surface of the needle coke has implication for the relatively larger friction between needle coke and matrix, increasing the green strength of the mold. Furthermore, silica colloidal particles from the slurry can enter into the pore

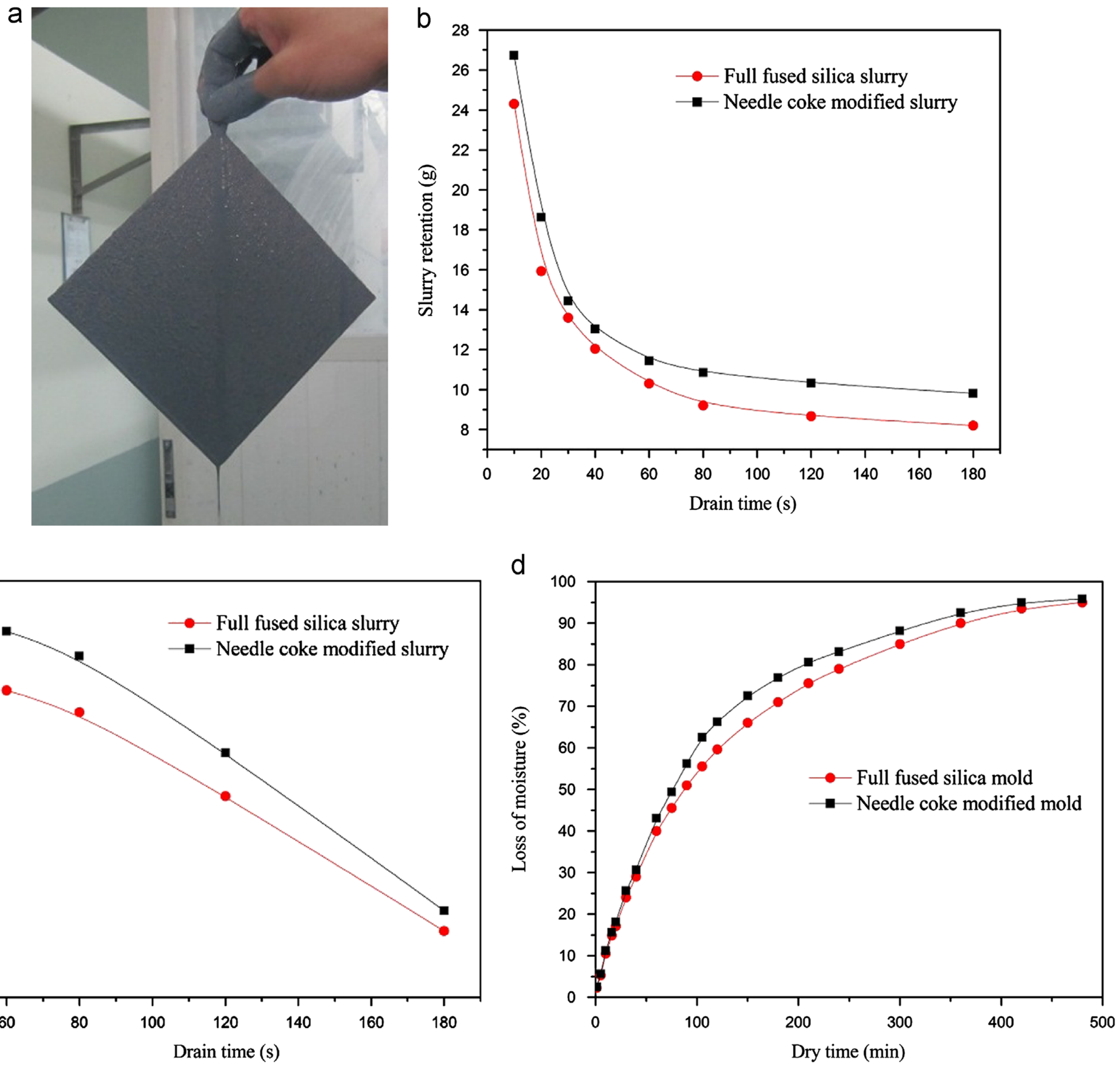

Fig. 6. (a) Schematic diagram of the measurement of plate weight. (b) Drain time vs. retention of different slurries. (c) Drain time vs. stucco retention of different molds. (d) Dry time vs. loss of moisture in two mold systems.

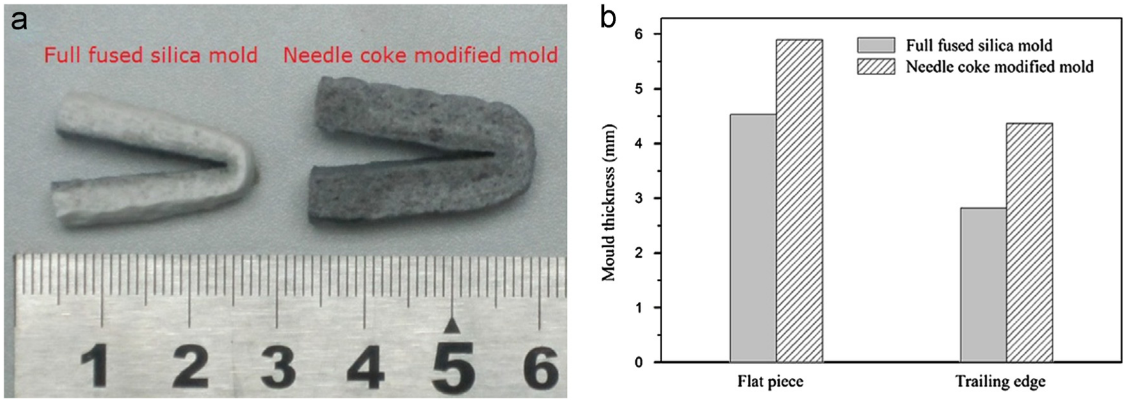

Fig. 7. Photograph and thickness comparison of two mold samples: (a) photograph and (b) thickness comparison.

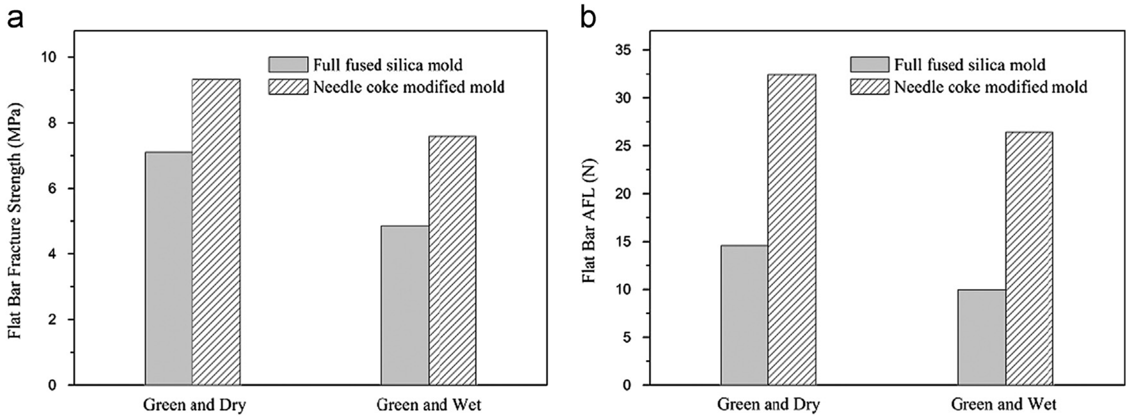

Fig. 8. Comparison of strength and load capacity of green mold samples: (a) MOR and (b) AFL.

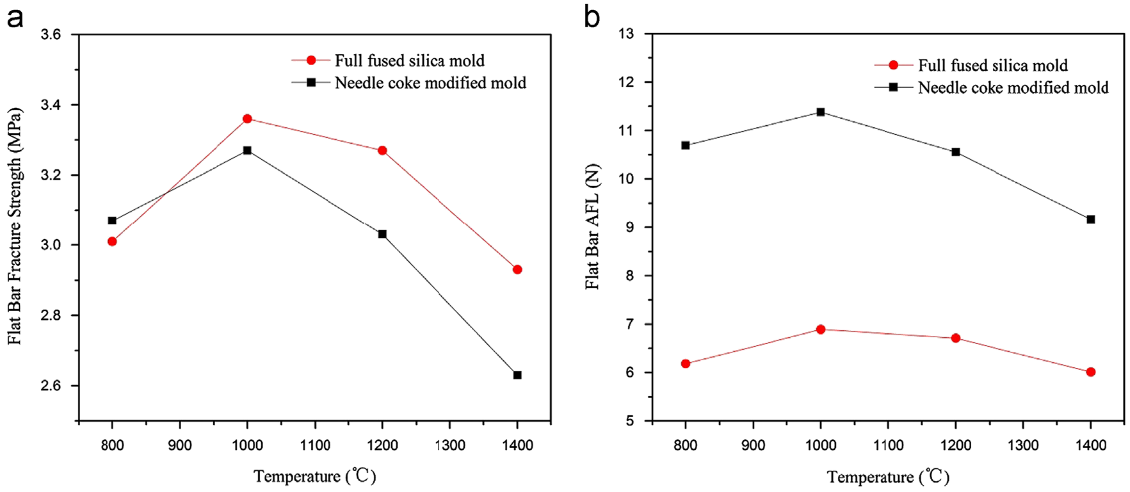

Fig. 9. Comparison of strength and load capacity of hot mold samples: (a) MOR and (b) AFL.

spaces of the needle coke interior, which can reinforce the interface combination between the needle coke and the mold, and increase the mold strength.

It has been suggested that the "green, dry" strength should not be an accurate measure of the shell crack resistant during hydrothermal dewax procedures [21]. The atmosphere (temperature and moisture) has a great influence on mold properties and has to be taken into account. Therefore, in this work a comparison of strength and load bearing capacity under wet condition was also carried out. It is found that the strength of full fused silica mold dropped significantly from 7.10 MPa to 4.86 MPa when it was tested "green, wet". This could be related to the softening of the polymer when in direct contact with steam during autoclaving. The steam reduces the adherence between the polymer and the surrounding colloidal network. Meanwhile, the colloidal network itself also reabsorbs moisture. When it reaches a certain level, the colloidal network will weaken and the mold strength will decrease. However, the needle coke modified molds are less susceptible to autoclave cracking, the "green, wet" strength drops slightly from 9.32 MPa to 7.59 MPa.

The results of both AFL and MOR tests on hot samples are shown in Fig. 9. At the test temperature of 800 °C, as all the moisture and the polymer in the mold have been burned off, the strengths of two mold systems decrease greatly, being 3.07 MPa for the full fused silica mold and 3.01 MPa for the needle coke modified mold. Since about 60 wt% of the needle cokes added to the mold are burned off at the sintering temperature of 800 °C, it leads to a faster decrease in strength of the needle coke modified mold. When the test temperature reached 1000 °C, the strengths of both mold systems increase slightly, being 3.27 MPa for the full fused silica mold and 3.36 MPa for the needle coke modified mold. As most of the needle cokes in the mold have been burned off, the full fused silica mold shows higher strength than the needle coke modified mold. The strengths of both molds decrease obviously with the further increase of test temperature. While at 1400 °C, the needle coke modified mold exhibits lower strength than that of the full fused silica mold, being 2.63 MPa and 2.93 MPa, respectively. The minor differences between the hot strengths of two mold systems suggest that the extra volume of cavity left after needle coke combustion is not acting as a significant defect which would reduce the hot strength of the mold. Due to the thicker coverage at edges, higher AFL of the needle coke modified system is found compared to that of the full fused silica mold, being 6.01–6.89 N and 9.16–11.38 N, respectively. This gives the needle coke modified mold a 52–73% increase in load bearing capacity and potentially a better resistant to the mold wall bulge and related defects of the casting components.

4. Conclusions

Properties of an investment casting mold prepared using needle coke additions have been investigated in this work. Needle cokes (width = 0.2–0.5 mm, length = 0.5–2.0 mm), with rough surface and porous cross section are added into slurry to improve the green strength especially the "green, wet" strength of the mold, and to optimize mold build for thick and uniform coverage at both flat section and sharp corners. The conclusions can be drawn as follows:

(1) The use of needle coke increases the mold thickness by a factor of 30% on flat section and 60% at edges over that of a comparable full fused silica system. This equates to the ability to reduce the number of coats applied to the wax, which has significant reduce on production time and material cost implications for foundries.

(2) The needle coke modified mold exhibits higher green strength than that of the full fused silica system. It is found that the strength of the full fused silica shell drops significantly when it is subjected to simulated autoclave conditions, while the needle coke modified system shows less reduction in strength when it was tested in the same conditions. Adjusting for variance in mold build thickness, the adjusted fracture load bearing capacity (AFL) of the needle coke modified system is much higher than that of the full fused silica mold when the samples are "green, wet", showing a 165% increase for test specimens.

(3) The hot strength of the needle coke modified mold decreases evidently compared to the green strength due to the burn off of the needle coke. The minor differences between the hot strengths of two mold systems suggest that the extra volume of cavity left after needle coke combustion is not acting as a significant defect which would reduce the hot strength of the mold.

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