ELSEVIER

Ceramics International 31 (2005) 873–878

CERAMICS
INTERNATIONAL

www.elsevier.com/locate/ceramint

Properties of ceramic casting molds produced with two different binders

H. Saridikmen*, N. Kuskonmaz

Department of Metallurgy and Materials Engineering, Yildiz Technical University, 80750 Yildiz, Istanbul, Turkey

Received 5 April 2004; received in revised form 10 August 2004; accepted 4 October 2004

Abstract

In this study, a method for preventing the reaction between ceramic mold and stainless steel that occurs during the metal casting process has been introduced. The ceramic molds are produced using zircon ceramic powder with binders which are prepared with two different compositions, ethyl silicate [$C_8H_{20}O_4Si$] and ethyl silicate/aluminum tri-*sec*-butoxide [$Al(OCH(CH_3)C_2H_5)_3$] solution. Hardness, porosity, sintering shrinkage, bulk density, surface morphology and chemical composition of the phases are examined. Stainless steel is poured into the ceramic mold and the mold–metal reaction behavior was examined in the cast product. Accordingly, burn-on casting defects encountered in stainless steel casting have exclusively been eliminated.

Keywords: Ceramic mold; Ethyl silicate; Aluminum tri-*sec*-butoxide

1. Introduction

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. Ceramic mold materials should be selected with care if optimum mold properties are to be achieved. The refractory and the binder materials being used for the production of ceramic molds are the most important parameters for controlling the reactions between the mold and the metal during ceramic mold casting processes. The term ‘‘ceramic mold’’ is a general expression for the types of molds used in the Shaw, Unicast and investment casting methods. In all of these methods, similar refractory and binder materials are being used as the ceramic mold material. The types and melting temperatures of refractory materials, which can be used for producing ceramic molds are given in Table 1 [1]. As it can be seen in Table 1, there are a wide range of materials for ceramic mold production. Selection of the most suitable refractory material depends on various characteristics, such as the melting point, thermal expansion and conductivity, particle purity, particle size distribution, and economical aspects related to the casting process.

The primary and the most widely used refractory in the ceramic molding processes are: alumina, fused silica, alumino-silicates, zircon, mullite and zirconia. Generally, binders can be produced by using colloidal silica and hydrolyzed ethyl silicate as a source of silica. Colloidal silica can be used only in the investment casting method whereas the ethyl silicate can be used in the Shaw, Unicast and investment casting methods without any restriction.

The ceramic mold casting process has been the preferred casting procedure because it gives a perfect surface quality with intricate details and dimensional stability. A surface smoothness of around 2 μm is highly probable using the ceramic mold casting method compared to the surface smoothness varying within the range of 10–50 μm obtained by using the sand mold casting methods [2].

The cooling rate of the liquid metal in the ceramic mold casting, however, is slower than that realized in other casting processes, which can result in surface oxidation and decarburization during steel castings. Also a slower cooling

---

* Corresponding author.
E-mail address: kkonmaz@yildiz.edu.tr (H. Saridikmen).

0272-8842/$30.00 © 2004 Elsevier Ltd and Techna Group S.r.l. All rights reserved.
doi:10.1016/j.ceramint.2004.10.004

Table 1
Refractory materials and their melting points suitable for the ceramic mold casting processes [1]

Material	Chemical notation	Melting temperature (°C)
Magnesia	MgO	2800
Zirconia	ZrO_2	2677
Calcia	CaO	2600
Zircon	$ZrO_2 \cdot SiO_2$	2420
Calcium zirconite	$CaO \cdot ZrO_2$	2345
Magnesia spinel	$MgO \cdot Al_2O_3$	2135
Alumina	Al_2O_3	2050
Mullite	$3Al_2O_3 \cdot 2SiO_2$	1810
Fused silica	SiO_2	1710

rate can cause a coarse grain structure in the microstructure that may be unacceptable in a casting. This problem can be eliminated by using grain refining methods [1]. A cast surface may be further affected by pitting, especially in stainless steels that contain chromium [3]. The most common defect in high Cr steels is known as the ‘‘pitting defect’’, which is formed by the reaction of carbon in the metal with either oxygen in the air or silica in the ceramic mold that provides the ceramic mold bond. This leads to decarburization and carbon monoxide bubbles, which can be produced as a consequence of these reactions. Decarburization and CO bubbles have negative effects on the quality of casting products, and can deform the casting surface. It may not be possible to eliminate decarburization completely since oxygen is always present in silica, which provides the bond [1–3].

In practice, many methods have been developed for solving casting defects, which can occur during metal casting in ceramic molds. One successful method is to insert hexamethylene tetramine (HTM) into the gating system in the ratio of 110 g HTM to 100 kg of liquid metal during metal casting process. HTM decomposes above 260 °C, forming decomposition products, which can stop the decarburization effect occurring in the interface between ceramic mold and metal. There are several other methods used to prevent decarburization of the cast metal products and to hinder the metal–mold reactions. These include inserting graphite powder in the mold facing material, applying a vacuum treatment to remove air from the mold, and filling the mold, cavities with an inert gas [3].

However, the methods used for preventing decarburization and surface oxidation problems are not very effective since the binder materials being used in the ceramic molds contain SiO_2, the main source of oxygen [1]. Another type of defect can occur during the sand metal casting processes, when FeO reacts with SiO_2 that comes from sand, producing fayalite ($2FeOSiO_2$), a phase that has a low melting temperature of 1205 °C. It causes the sand grains to fuse and collapse as they melt into each other. The reacted sand grains adhere to the surface of the casting because of the presence of this low-melting-point liquid ‘‘glue’’. This defect is, known as burn-on and fayalite is recognized as the basic source of this defect [4]. It is well known that SiO_2 is the basic element in the ceramic mold that produces the bond. For this reason, in ceramic mold binders, the amount of SiO_2 concentration must be decreased to a level lower than 2%, in order to reduce the chemical activity in the interface between the ceramic mold and the liquid metal [5]. However, decreasing the SiO_2 concentration in the binder leads to a sharp fall in the mechanical properties of the molds. Owing to this problem, specific methods must be developed for producing ceramic molds which do not have a decrease in the mechanical properties and which have a high resistance to mold–metal reactions.

Therefore, in the present work, the effects of the binder composition on the structural and physical properties of the zircon ceramic mold were examined using two different binder compositions, i.e., ethyl silicate [$C_8H_{20}O_4Si$], will be named (ES) hereafter and ethyl silicate mixed with aluminum tri-*sec*-butoxide [$Al(OCH(CH_3)C_2H_5)_3$], will be named (ES/ATB) hereafter. It was found that the ES/ATB binder system developed was very effective to produce a ceramic mold with homogeneously distributed pores that help to remove gases formed during casting. It was also found that the ceramic mold obtained using the ES/ATB does not react with the liquid metal as the active free silica presents in the ceramic mold reacts with Al_2O_3, which comes from aluminum tri-*sec*-butoxide in the binder instead of liquid metal to form mullite.

2. Experimental procedures

Two binder systems Ethyl silicate ($C_8H_{20}O_4Si$) and ethyl silicate with aluminum tri-*sec*-butoxide [$Al(OCH(CH_3)$-$C_2H_5)_3$] with butoxide ethanol ($C_4H_9C_2H_4OH$) as solvent are combined with acetic acid ($C_2H_4O_2$) as a gelling-agent and used for the binder solutions in the ceramic mold production. During ceramic mold sample production, zircon powder (particle size less than 74 μm) was used. The slurry containing 24 wt.% binder solution was mixed using a mechanical mixer for 5 min at 400 rpm speed and cast into silicone rubber mold, then vibrated for 2 min. Setting time for the ceramic mold samples was approximately 20 min. The ceramic molds were than removed after an additional set of 30 min. The outlines of the ceramic mold sample production process are shown in Fig. 1. After releasing from the silicone rubber mold, the ceramic mold samples are dried at room temperature for 24 h and placed in an oven at 80 °C for 12 h. The ceramic mold samples are then sintered in a slightly oxidizing atmosphere in three groups at 1450 °C, 1500 °C and 1600 °C, for 1, 2 and 4 h at each temperature. The heating rate of the sintering furnace was 3 °C/min.

Porosity, sintering shrinkage, density and hardness of the sintered samples have been determined. For the porosity and density measurements, the samples were dried at 110 °C in a furnace and weighed (m_1), after which, they were immersed in pure water for 24 h and weighed (m_2). After taking the

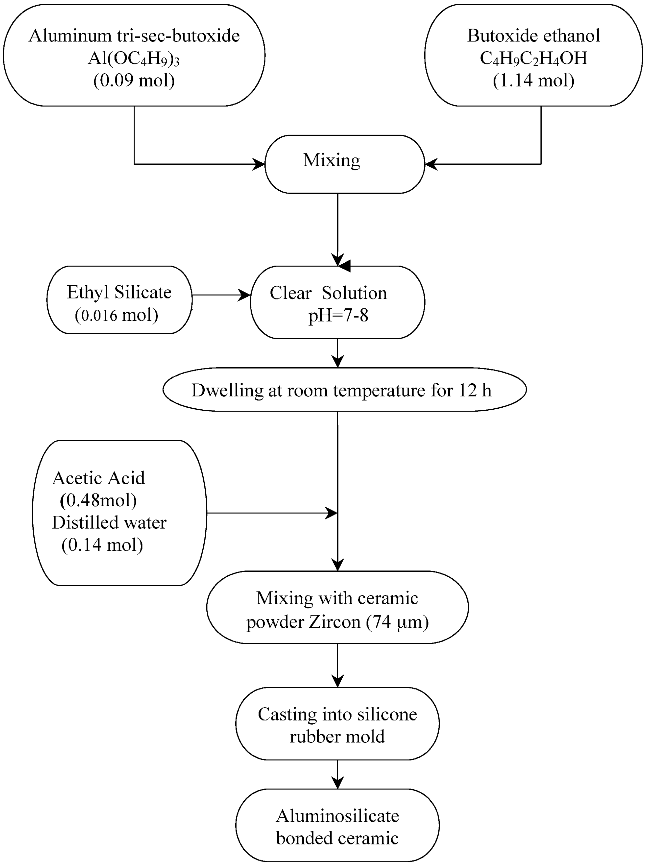

Fig. 1. The outline of ceramic mold production.

samples out of the water, they were wiped with a damp cloth to remove the free water on the surface of the samples and weighed once again (m_3). Thereafter, porosity and density values are calculated as follows;

$$\text{Apparent porosity} = \frac{m_3 - m_1}{m_3 - m_2} \qquad (1)$$

$$\text{Density} = \frac{m_1}{m_3 - m_2} \qquad (2)$$

Sintering shrinkage measurements were performed on three samples for each sintering temperature and averaged. At least three measurements were taken on each sample before (L_1) and after sintering (L_2), and the sintering shrinkage percent was calculated as follows:

$$\text{Sintering shrinkage}\,(\%) = \frac{L_1 - L_2}{L_1} \times 100 \qquad (3)$$

The surface morphology of the ceramic molds was investigated by scanning electron microscopy (SEM) and the different phases that occurred in the samples were examined using EDAX spectrometer. The hardness values of the ceramic mold samples after the sintering process were determined via Vickers hardness method at a 10 kg load. The load was applied for 20 s, and no less than three measurements on each sample was taken and averaged.

Table 2
Chemical composition (wt.%) of the stainless steel ingots

C	0.121
Si	0.35
W	0.11
Mn	0.49
P	0.03
S	0.02
Cr	16.8
Mo	0.11
Ni	0.89
Co	0.02
Cu	0.133
Ti	0.01
V	0.04

For the investigation of the mold–metal reaction behavior, the stainless steel (SS) specimen was cast into the aluminosilicate bound ceramic mold, which had been sintered at 1600 °C for 2 h. The composition of the stainless steel is given in Table 2. The samples are prepared by melting stainless steel ingots in a high frequency induction furnace of 35 kg capacity. The 25 kg SS ingots were melted for 45 min. The melt was grain refined at 1650 °C with 75 g Ca–Si addition, whose chemical composition is given in Table 3. After the grain refining process, the melt was brought to a temperature of 1670 °C. The liquid metal was then poured into the pre-heated ladle and deoxidized with 20 g of aluminum. After removing the slag, the melt was cast into the ceramic molds at 1610 °C. The chemical composition of Al is also given in Table 3. The cast sample is examined afterward in order to determine the surface quality.

3. Results and discussion

Sintering shrinkage, porosity, hardness and bulk density values of ceramic mold samples that are produced using an ethyl silicate and an ethyl silicate/aluminum tri-*sec*-butoxide binder are listed in Table 4. It can be seen from Table 4 that increasing the sintering temperature and time bring about a decrease in the porosity and an increase in shrinkage of the molds, and accordingly, an increase in the bulk density for both binders. For example, for the working temperature of

Table 3
Chemical compositions of the grain refiner and the deoxidizer, which are used during stainless steel casting

Chemical composition of Ca–Si grain refiner (wt.%)		Chemical composition of Al deoxidizer (wt.%)	
Ca	30.17	Al	95
Si	61.03	Si	1
Fe	6.80	Fe	1
C	0.49	Ti	0.2
Al	0.50	Cu	0.2
		Zn	1
		Mn	1

Table 4
Hardness, sintering shrinkage, porosity and bulk density values for ES and ES/ATB binder systems obtained for the samples sintered at selected temperatures and duration

Sintering temperature (°C)	Sintering time (h)	Sintering shrinkage (%)		Porosity (%)		Bulk density (g/cm^3)		Hardness (HV 10)	
		ES	ES/ATB	ES	ES/ATB	ES	ES/ATB	ES	ES/ATB
1450	1	–	4.30	–	37.45	–	2.79	–	–
1450	2	2.86	4.59	39.65	38.29	2.56	2.87	–	–
1450	4	–	4.67	–	36.60	–	2.94	–	52.10
1500	1	–	4.33	–	36.70	–	2.94	–	–
1500	2	–	4.49	–	35.60	–	2.98	–	–
1500	4	–	6.30	–	33.70	–	3.02	–	81.30
1600	1	–	6.68	–	33.68	–	3.08	–	–
1600	2	6.20	7.36	34.10	31.90	2.91	3.16	–	–
1600	4	–	7.55	–	31.30		3.18	165.60	107.80

1600 °C for 2 h, ceramic molds prepared with ES and ES/ATB binders exhibited shrinkage (%) values of 6.20 and 7.36, respectively, porosity (%) values of 34.10 and 31.90 and bulk density values of 2.91 and 3.16, respectively. It is clear from the data presented in Table 4 that ES/ATB binders resulted in the formation of ceramic molds with low porosity and high bulk density that all contribute to a better surface quality (it is attributed that the reaction sintering process between the free silica within the mold and alumina promotes densification behavior of the ceramic mold, and therefore, higher bulk densities could be obtained as shown in Table 4). Ceramic molds, produced using ethyl silicate binder (15 wt.% SiO_2), exhibited a 6.20% sintering shrinkage when these samples were sintered at 1600 °C for 2 h. As shown in Table 4, the ceramic molds that are produced using ethyl silicate/aluminum tri-*sec*-butoxide binder solution and sintered at the same temperature and time (1600 °C for 2 h), demonstrate a 7.36% sintering shrinkage. According to Table 4, with the increase in sintering temperature, there is a remarkable increase in the hardness values of the ceramic molds. For example, the ceramic mold prepared using ES/ATB binder indicates hardness values of 52.10 and 81.30 (HV 10) after sintering at 1450 °C and 1500 °C for 4 h, respectively, (see Table 4). The ceramic molds that have been prepared using an ethyl silicate binder had a hardness of 165.60 (HV 10) when fired at 1600 °C for 4 h. This is in contrast with the ceramic molds that are produced by using ethyl silicate/aluminum tri-*sec*-butoxide binder, whose hardness was only 107.80 HV under the same sintering conditions. The reason for this considerable variation in the hardness values can be attributed to the breaking of the SiO_2 bonds and secondly, to the formation of mullite ($3Al_2O_3{\cdot}2SiO_2$) formation in the texture of ceramic molds in the present investigation.

X-ray analyses have been performed on the ceramic mold samples having ethyl silicate and aluminum-tri-*sec*-butoxide solution as binders in their structures (Fig. 2). The results indicated that a mullite phase had already been formed in ceramic molds when sintered at 1300 °C for 4 h. Scanning electron microscopy studies and EDAX analyses have been performed on the ceramic molds produced using two different binders and which were sintered at 1400 °C for 2 h. The results of EDX analyses are given in Table 5. As can be seen from EDAX results shown in Table 5, there was no Al near the zircon grain boundaries on the ceramic molds that have been produced using an ethyl silicate binder, and only 32.05% Si was detected. The EDAX analysis that has been conducted on the ceramic mold which has an ethyl silicate/aluminum tri-*sec*-butoxide solution binder that formed a mullite phase in the structure has 24.23% Si and 3.79% Al located at the grain boundaries. These EDAX results clearly show that the second binder system i.e., ES/ATB is very effective to form mullite as a result of reaction between alumina and silica within the binder.

The SEM micrographs in Fig. 3(a) and (b) show the surface structure of the ceramic molds produced using ES and ES/ATB binders, respectively (after sintering at 1600 °C for 2 h). Although the both binders provide very porous microstructure, which is desirable for the removal of the gases formed during casting, their interactions with casting material, and therefore, the surface quality of the products are very different from each other as explained in the latter sections.

The photographs shown in Fig. 4(a) and (b) indicates the typical surface structures of the ceramic molds formed using ES and ES/ATB binders, respectively, stating that all fine

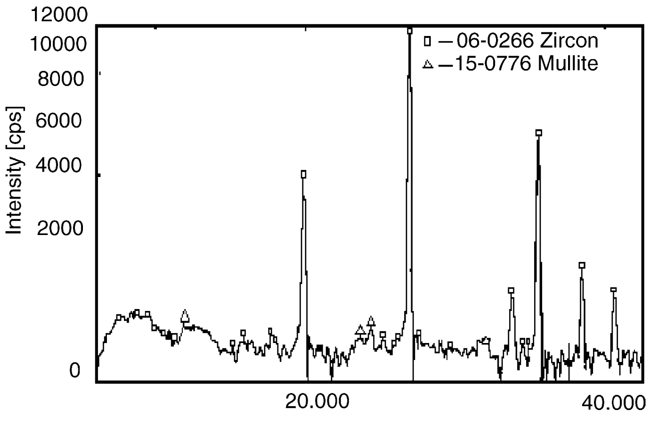

Fig. 2. X-ray analysis of ceramic mold using ethylsilicate–aluminum tri-*sec*-butoxide binder, and sintered at 1300 °C for 2 h.

Table 5
EDAX analysis results of ceramic molds produced by using two different binders and sintered at 1400 °C for 2 h

Element (wt.%)	$ZrOSiO_2$ + ethyl silicate binder		$ZrOSiO_2$ + ethyl silicate + aluminum tri-*sec*-butoxide binder	
	Grain	Grain boundary	Grain	Grain boundary
Si	20.23	32.05	20.47	24.13
Zr	79.77	67.95	79.53	72.08
Al	00.00	00.00	00.00	3.79

details are obtained on the ceramic mold surface. However, it is also clear from the Fig. 4 that the shrinkage values of the two ceramic molds are different from each other as previously mentioned in Table 4.

The stainless steel cast product is inspected for its metal–mold inter-surface quality and for defect control for two different ceramic molds produced using ES and ES/ATB binders, as shown in Fig. 5(a) and (b), respectively. As can be seen from Fig. 5(a) the fine details on the ceramic mold shown in Fig. 4(a) are not visible on the metal cast specimen as a result of the reactions between the ceramic mold and the cast material. On the other hand, when using the ES/ATB binder system in the ceramic mold no ‘‘pitting’’ and ‘‘burn-on’’ type defects are observed on the surface of the cast specimen leading very good quality surface structure as the surface of the cast sample demonstrates every fine detail on the pattern surface as shown in Fig. 5(b).

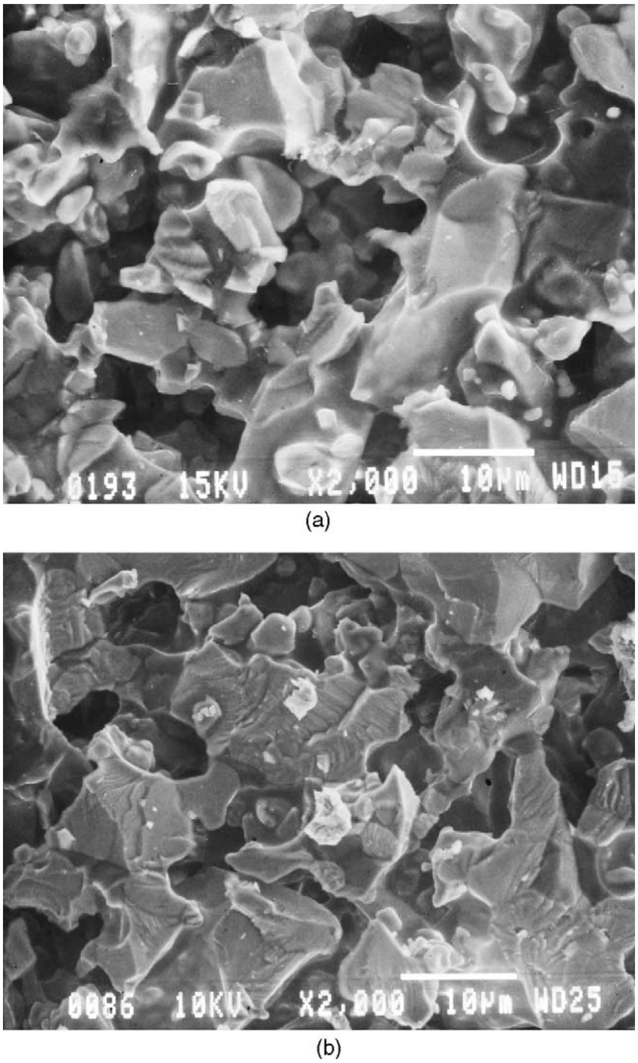

Fig. 3. SEM micrographs of porous surface microstructure of the ceramic molds produced using: (a) ES and (b) ES/ATB binders after sintering at 1600 °C for 2 h.

Fig. 4. The surface structure of the molds used in the SS casting using: (a) ES and (b) ES/ATB binder systems (sintered at 1600 °C for 2 h).

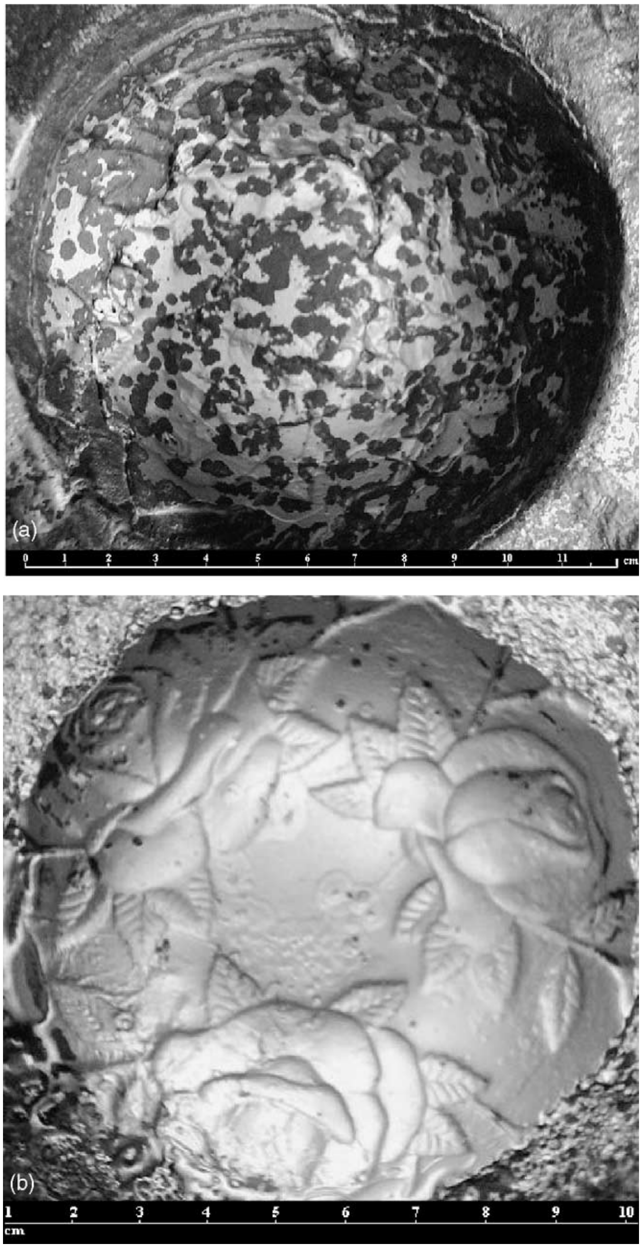

Fig. 5. Surface details obtained on the stainless steel cast products using: (a) ES and (b) ES/ATB binder systems. Note that all the fine details are visible on the micrograph shown in (b).

Overall, it can be concluded from the results presented in Figs. 4 and 5 and Table 4 that the binder system selected for ceramic molds has a detrimental effect on the properties of the ceramic mold as well as surface quality of the cast specimen (stainless steel in the present work). A new binder system (ES/ATB) was developed and effectively used in this investigation to improve the surface quality of the cast stainless steel without compromising the properties of the ceramic mold.

4. Conclusions

The fundamental feature of this study is to present a method for preventing the reaction between the ceramic mold and metal that occurs during metal casting processes. An effective binder system containing ethyl silicate [$C_8H_{20}O_4Si$] combined with aluminum tri-*sec*-butoxide [$Al(OCH(CH_3)C_2H_5)_3$] is developed and used to solve the above problem. SiO_2, which is present in the binder, is eliminated using aluminum tri-*sec*-butoxide with ethylsilicate in the binder solution as silica reacts with alumina within the binder system prepared. After reaction sintering process between silica and alumina, a mullite phase can be formed and as a result, burn-on casting defects encountered in stainless steel casting have been exclusively eliminated. Furthermore, the decarburization and pitting defects can be completely eradicated, since there is no oxygen coming from silica.

Acknowledgments

The authors wish to acknowledge The State Planning Organization Prime Ministry of T.R., Yildiz Technical University Research Fund and BCACT—Balkan Advanced Casting Centre for their financial supports.

References

[1] A.J. Clegg, Precision Casting Processes, Pergamon Press, Great Britain, 1991, pp. 123–144.
[2] A.J. Clegg, The Shaw Process—a Review, Foundry Trade J. (1980) 429–438.
[3] G.E. Doremus, C.R. Loper, A study of decarburization accompanying the casting of steel in ceramic molds, AFS Trans. 78 (1970) 338–342.
[4] J. Campbell, Casting, Butterworth-Heinemann Ltd, Great Britain, 1995, pp. 118–119.
[5] V.M. Aleksandrov, B.A. Kulakov, A.A. Solodyankin, Increasing the strength and reducing the chemical activity of ceramic moulds, Sov. Cast. Technol. 4 (1988) 41–45.