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ZIRCON-BASED COATING FOR THE APPLICATIONS IN LOST FOAM CASTING PROCESS

In this work, a possibility to develop a new zircon-based refractory coating for casting applications was investigated. Optimization of the coating composition with controlled rheological properties was attained by application of different coating components, particularly by application of a new suspension agent and by alteration of coating production procedure. Zircon powder with particle size of 25×10^{-6} m was used as filler. The zircon sample was investigated by means of X-ray diffraction analysis, diffraction thermal analysis and polarized microscopy. The shape and grain size were analyzed using OZARIA 2.5 software. It was shown that application of this type of water-alcohol-based coating had a positive influence on surface quality, structural and mechanical properties of the castings of cast iron obtained by pouring into sand molds by means of the expandable patterns method (Lost Foam casting process).

Keywords: sand casting; Lost Foam casting process; refractory coating; zircon.

Ceramic coatings are usually based on raw materials of composition and properties that are set in advance. Certain properties of these materials, like refractoriness for example, should prevent reactions on the mold-metal contact surface. This provides a smooth and clean surface of castings, with no adhered sand or defects occurring due to the metal penetration into the mold. In casting practice, the sand casting technology is widely applied for molding production (scheme given in Figure 1). Quartz sand, which is often used as component in the composition of the mold and core blends, has a number of flaws: low refractoriness, high thermal expansion coefficient, etc. In addition, this causes molding surface defects, especially when metals and alloys with high melting temperatures are applied. Higher quality mold blends based on zircon, olivine, chromite or sintermagnesite, which show much better thermal and physical properties than quartz sand, are relatively less applied because they are significantly more expensive. A more frequently used solution is the application of different additions for the mold blend, as well as the application of ceramic coatings on the molds and cores. Application of higher quality ceramic coatings significantly influences either reduction or elimination of expensive cast house cleaning and machining operations for the moldings, thus directly reducing production costs of a cast house [1-7].

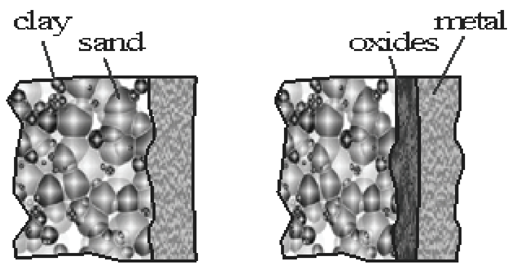

Figure 1. Sand casting: interaction between metal oxides and mold sand.

Unlike sand mold or metal mold casting, where liquid metal flows into the mold cavity, in case of expandable polymer pattern casting (Lost Foam casting process scheme given in Figure 2) patterns and inflow systems made of polymers are retained in the

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mold until liquid metal flows in ("full mold" casting). In contact with liquid metal, polymer pattern degradation and expansion process is carried out rapidly, during a relatively short time. This process is followed by molding crystallization [8-10]. In order to properly understand the role of ceramic coatings for polymer patterns in this process, it is necessary to point out that the polymer pattern degradation is an endothermic process commencing during liquid metal inflow. During "full mold" casting, expandable pattern degradation products formed in contact with liquid metal disappear through the refractory coating layer into unbound sand which the mold is made of. This can only occur if the permeability of the mold is satisfactory. It is primarily attained by choosing the suitable coating type, coating preparation procedure, coating suspension density and the coating dry film thickness on the pattern [11-15].

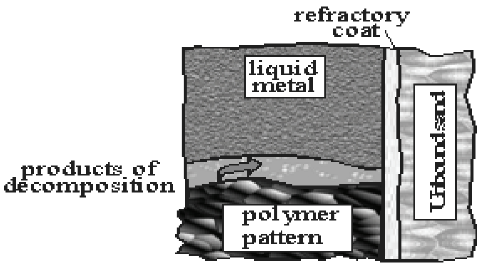


Figure 2. Lost Foam casting process: liquid metal-ceramic coat-polymer pattern-sand.

The investigation of synthesis, characterization and application of refractory coatings showed that sediment stability of the coating suspension was a crucial quality parameter. Different kinds and quantities of additives were examined, as well as their activation procedures, with an aim to enable easy additive absorption into the refractory filler particles, maintenance of the filler in a dispersed state and prevention of the filler building up. A bonding agent for the coating was chosen with regard to the size and shapes of the refractory filler particles and in order to enable connection of the particles and to secure good adhesion of refractory particles to the observed surface of either the sandy mold or polymer pattern. Alcohol was used as a liquid solvent, as well as water. It was proventhat the optimal density of refractory coating was 2000 kg/m^3, which is consistent with our previous study [16].

EXPERIMENTAL

Zircon was chosen as refractory coating filler due to the following properties:

- high melting temperature/high refractoriness;
- low coefficient of thermal expansion;
- not readily wetted by liquid metal;
- minimal gas production when in contact with liquid metal.

For characterization of the zircon sample, X-ray diffraction analysis was applied by means of a Philips PW-1710X-ray diffractometer. Typical temperatures at which solid state reactions in the zircon sample are taking place were determined by means of the differential-thermal analysis (DTA) using a Shimadzu DTA-50 apparatus, with a heating rate of 10 °C within the temperature interval from 20 to 1200 °C. The reference sample was alumina, Al_2O_3. The analysis was carried out in the nitrogen atmosphere, N_2, at the flow rate of 2×10^{-5} m^3/min. Distribution of the refractory filler and bonding agent in the coating suspension was observed and recorded by means of a Jenapol polarized microscope with passing light (Carl Zeiss, Jena) using Microphoto system Studio PCTV (Pinnacle System).

Analysis of the particle size and shape factor was conducted using OZARIA 2.5 software. The results ranges were within 0-1 scale, shape factor 0 corresponding to the needle shape and shape factor 1 corresponding to the circle. Grain size is given in micro-meters (10^{-6} m). Properties of the coatings were investigated on the test-samples made of mold sand mixture and polystyrene. The prepared coatings were applied on the surface of the samples. Investigation of the sediment stability of refractory coatings was carried out by holding the samples prepared in a 2.8×10^{-1} m high cylinder-like vessel, with a volume of 1×10^{-4} m^3 and plugged with a cork, for 24 h. The result of the investigation was expressed in percent, *i.e.*, the number of recorded 1×10^{-6} m^3 of transparent layer was equal to the build up percentage. Determination of the penetration into sand mold was tested by using the test-tubes made of mold mixture. After application and drying of the coating, these test-tubes were broken and the coating penetration depth was measured at the breaking point. The penetration depth was expressed in 1×10^{-3} m.

As far as the influence of the ceramic coatings on the quality of the moldings is concerned, it is necessary to discuss preparation of the coating components, coating production and its application rheology which is tightly bound to a proper choice and use of a suitable stabilizer. Generally, application might be defined as follows:

- immersion,
- spraying,
- pouring and
- brush application.

When using a coating, it is necessary to maintain constant stirring, at the rate of 1 rev/min, in order to obtain a homogenous suspension which, after being applied, creates even and uniform coating layer on the surface of mold, core or pattern.

Zircon sample was used as refractory filler in three types of coatings based on organic solvents (isopropyl alcohol) or water. Compositions of zircon-based refractory coatings are given in Table 1.

Table 1. Composition of zircon-based refractory coatings

Type of coating	Composition
I	Refractory filler: zircon with grain size of 26.65 $\times 10^{-6}$ m, 93-95%; bonding agent: colophonium ($C_{20}H_{30}O_2$), 2-2.5%; additive: an organic compound of clay with the commercial name Bentone 25, 0.8-1%; solvent: isopropyl alcohol
II	Refractory filler: zircon with grain size of 26.65 $\times 10^{-6}$ m, 93-95 %; bonding agent: colophonium ($C_{20}H_{30}O_2$), 1.2-1.5%; dextrin 0.5-1 %; additive: Bentone SD-3, 1.2-1.5%; phenolphormalde hidration resins, 1.2-1.7%; solvent: isopropyl alcohol
III	Refractory filler: zircon with grain size 26.65 $\times 10^{-6}$ m, 92-94%; bonding agent: bentonite 1.5-2.5%; bindal H, 0.5-1%, suspension maintanance agent: $Na_3P_3O_3$ 1-3%, carboxymethylcellulose (CMC), 0.5-1%; solvent: water

Refractory coatings were applied on sandy molds by brushing and pouring. The coatings were applied on polystyrene models by submerging into a tank containing suspension and by pouring. The method to eliminate the suspension excess from the model after being taken out from the cladding tank was as follows: models were squeezed after being placed in vertical position for 5-10 s and afterwards they were inclined under an angle of 45° for 5 s in order for the suspension layers to get even on the model surface. Constructions of polystyrene models were the step probes with different wall thickness ($\times 10^3$ m): 10, 20, 30, 40 and 50.

Cast iron was used for pouring. A skimming agent was used for cast preparation, as well as disoxidation of aluminum granules. Casting temperature was in the range 1250-1350 °C. A mold mixture based on quartz sand was used for the production of sand molds. The mean grain size of sand quartz was 1.7×10^{-4} m. The mold mixture contained a 3% bentonite addition and a 0.5% dextrin addition. Dry quartz sand with mean grain size of 2.6×10^{-4} m was used for the production of Lost Foam casting process molds. Expandable plate-shaped patterns sizing 0.2 m$\times$0.05 m$\times$0.02 m were made of polystyrene with the density of 18 kg/m^3. The patterns were clustered for casting purposes; four models each, on the common central conductor with the size of 0.02 m$\times$0.02 m$\times$0.4 m.

RESULTS AND DISCUSSION

The zircon-based filler contained 99.99% of $ZrSiO_4$ in the chemical coposition. The X-ray diffractogram of the investigated zircon sample showed a prevailing presence of zircon (Figure 3).

Figure 4 shows the DTA curve of zircon sample with typical hold-up points.

Zircon is a refractory material and apart from its high melting temperature, which is about 2200 °C, it is not readily wetted by liquid metal. It has a significantly

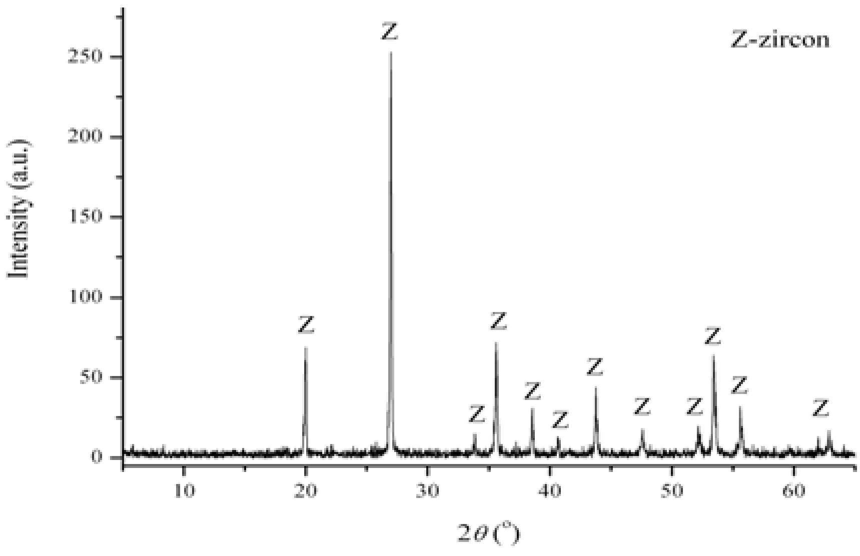


Figure 3. Diffractogram of powder of zircon sample.

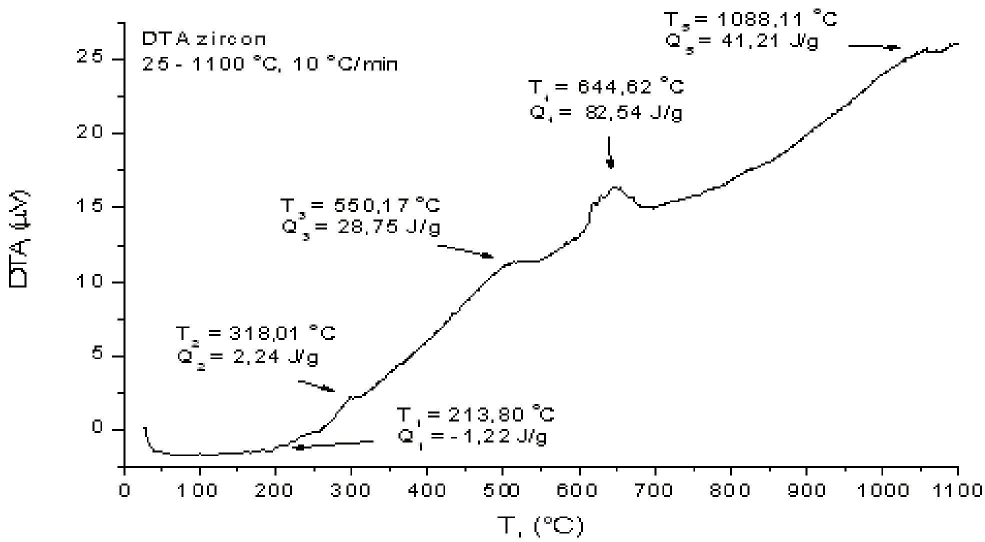


Figure 4. DTA Curve of zircon sample.

lower coefficient of thermal expansion (0.003×10^{-2} m/m) than quartz (0.018×10^{-2} m/m). Regarding these properties, zircon is suitable for application as filler in a refractory coating for molds and cores produced out of a quartz-based blend, as well as for polymer patterns for the Lost Foam process. This coating is particularly suitable for casting of moldings made of cast iron, where an exceptionally clean surface is required or when quick heat removal from metal is required in order to speed up the crystallization process and to attain good structural and mechanical properties of the material.

Figures 5 and 6 show histograms of grain size and grain shape factor for the zircon samples. Table 2 shows the test results of shape and grain size of zircon sample.

In order to achieve the sediment stability of coating suspension, grain sizes of zircon sample of up to 25×10^{-6} m were used. It was expected that tiny grains would slowly create debris and that suspension might get homogenized easier and faster. Tiny grains also cover the mold and model surfaces on which the coating is applied more evenly and more thoroughly. Microstructure analysis of the zircon samples showed that grains mostly had a uniform size and morphology and that the grains were more irregularly shaped (grain shape factor from 0.4 to 0.8, Figure 7).

It was concluded that there were differences in grain sizes. The mean grain size was35×10^{-6} m. It was estimated that the irregularly shaped grains of various grain size would contribute to forming a uniform and constant coating layer on the mold and mo-

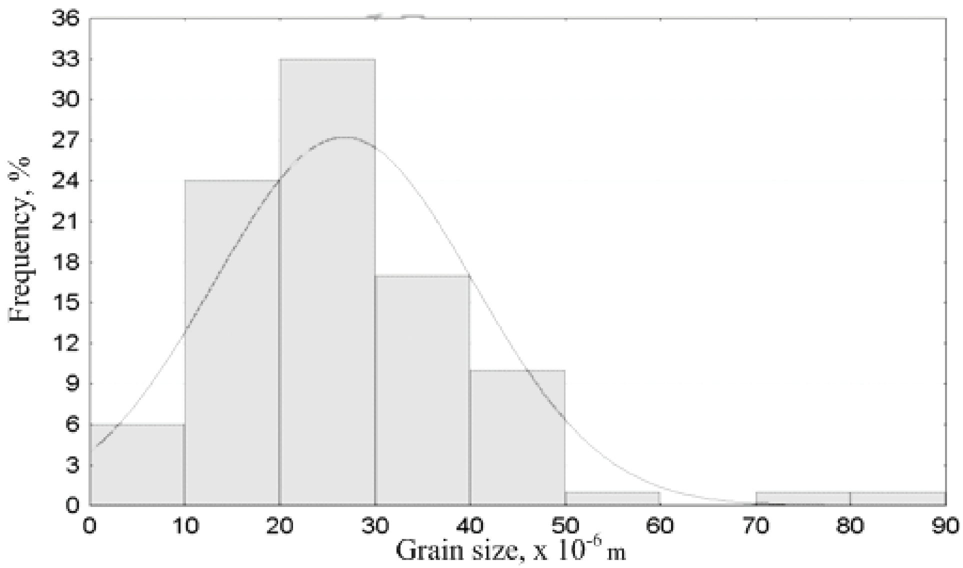


Figure 5. Histogram of grain size of zircon sample.

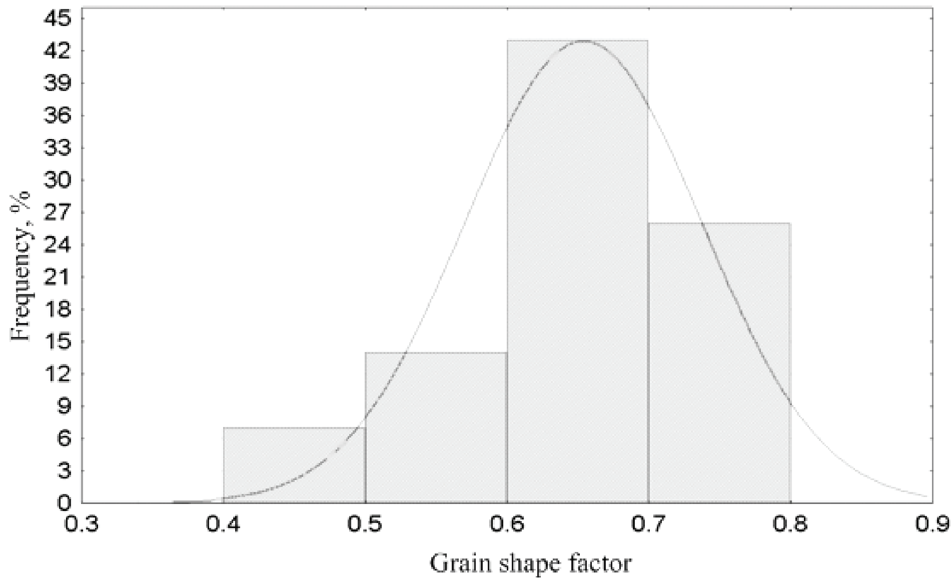


Figure 6. Histogram of grain shape factor of zircon sample.

Table 2. The test results of shape and grain size of zircon sample

Grain size, $x10^{-6}$m			Standard deviation, σ	Grain shape factor			Standard deviation, σ
Mean	Min	Max		Mean	Min	Max	
26.65	9.00	86.21	13.56	0.65	0.41	0.80	0.84

del surfaces due to better interrelations of grains, which was shown by the results of coating properties tests.

The tests of the sediment stability of all three types of refractory coatings showed that the coating with composition I had debris matters in amount of 10%, while solid matters build up with the coatings of II and III compositions was smaller, amounting to 5-7%, which met the coating quality requirements.

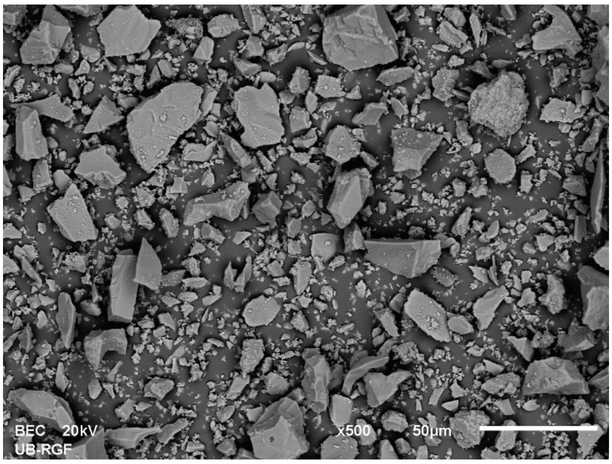


Figure 7. Microphotograph of zircon sample.

Homogeneity of refractory grains distribution also depends on suspension preparation technology and application technology. The grains concentration and adhesion have an important influence on the suspension rheological properties. Adhesion forces between zircon grains were increasing with the increase of the grain concentration in the suspension. Furthermore, constant and uniform coating layers are being formed on surfaces, due to the influence of rheological additives and bonding agents. The coating easily adheres to the surfaces and does not get cracked or wiped out after drying (Figure 8).

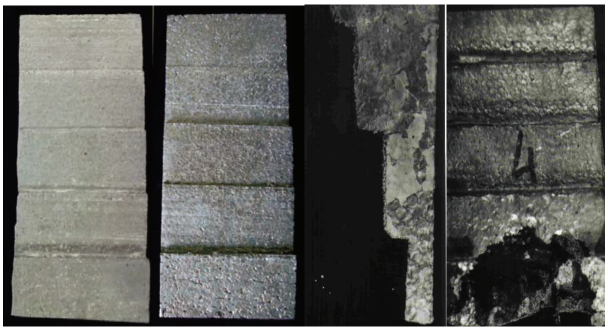
(a) (b) (c)

Figure 8. Errors on coated patterns (from left to right): a) quickly dried coat layers of high thickness; b) bubbles on coated pattern surface; c) quickly dried coat layers cracking.

The optimal coating density was 2000 kg/m^3. The coating mixtures were carefully stirred during application at a rate of 1 rpm in order to achieve homogenous filler distribution in the suspension. This is consistent with our earlier work [16].

Surfaces of castings (the step probes) obtained by application of the coatings with thin layer thickness

(5×10^{-4} m) were bright and clean (Figure 9a). When these coatings were applied in thicker layers (with thickness above 1×10^{-3} m), rugged casting surfaces were obtained (Figure 9b). The gas permeability of thicker coating layer is smaller and often causes the appearance of porosity in the casting. When diluted coatings were applied and the coatings were not homogenized by careful stirring before application, the following defects were obtained: bad surface adhesion, non-uniform dried coating layers, and cracks on the coating layer after drying. Also, there were errors on the coatings, like presence of the sintered sand on the castings surface (Figure 9c). Use of diluted coating applied in thinner layers may cause penetration of liquid metal into the mold, especially in case of casting thicker walls-cross sections at a step probes sizing above 40×10^{-3} m (Figure 9d).



(a) (b) (c) (d)

Figure 9. The surfaces of the step probes (from left to right): a) clean surface, thinner coating layer 5x10^{-4} m; b) a rugged surfaces, a thicker coating ayers above 1×10^{-3} m, less permeability to gases; c) sintered sand on the castings surface; d) metal penetration into sand.

Alcohol coatings are well suitable for application in sand molds and cores. The test of coating penetration into the sand test-tube showed that the measured penetration depth was satisfactory, being 5×10^{-4}-9×10^{-4} m. Both alcohol-based and water-based coatings did not penetrate the test-tube surfaces made of polystyrene. Water-based coatings are much more economical in comparison with alcohol-based coatings; therefore, further tests would be carried out using the coatings with the composition III.

Application of the three types of coatings in the processes of casting into sand molds and according to Lost Foam casting process enables obtaining the castings with advance quality settings. Prepared coatings, with a 2000 kg/m^3 density, were applied in two layers and, after drying, it was noted that constant, thin coating layers were formed on the molds and polymer models. It provided good gas permeability of the coating layers and enabled faster liquid metal cooling in the mold and forming a tiny-grained casted part structure. This was confirmed by the results of the investigation of the structural and mechanical properties of the castings.

The investigation showed that refractory coatings have an insulating effect which does not allow the fluctuation of the temperature of the liquid metal during molds filling phase. After the mold is filled with the liquid metal, *i.e.*, when the polymer model has evaporated, the insulation effect decreases the rate of cooling and solidification of the molding. At the same time, under cooling, which was created in the liquid metal, as a result of endothermic decomposition of polymer model in contact with the liquid metal, has a significant influence on the formation of structures of drip molding. If the under-cooling is higher, formation of a fine grain structure drip molding is enabled. It all points to the complexity of drip molding solidification by Lost Foam process and the necessity of determining of the correlation parameters of casting process, structure and properties of castings. The aim of this work is the optimization of Lost Foam casting process and production of drip molding with advanced quality and default properties.

CONCLUSION

The investigation showed that zircon-based coatings with water as solvent met all the casting application requirements. The coatings with the investigated composition are easily applied on the sand molds and polymer models, they evenly flow down during pouring and submerging, they are easily applied by brush, with no brush traces, leakage or formation of coating drops or lumps. After drying, coating surfaces are smooth, coating layers have got an even thickness all over the surfaces of the molds and patterns, with no bubbling, cracks, peeling or taking off. It was concluded that the coatings had a positive influence on the surface quality of the moldings, that the surfaces were smooth and shiny without cracks or adhered sand. Application of the coatings with thinner layers, below 1×10^{-3} m, due to improved permeability, showed that the cast part quality was higher, with no flaws in terms of porosity, wrinkles or cracks. Further research to improve this type of refractory coating shall be continued in terms of improving the properties of the zircon-based filler by using a mechanical activation process, which would influence the improvement of the coating rheological properties and coating suspension stability. It would also be favorable to test new additives and bonding agents in order to improve the sediment stability of the coating and to reduce the building up below 5% during 24 h.

This would provide good quality of the refractory coating during storage, transport and application.

Acknowledgements

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REFERENCES

[1] A. Svarika, Pokritia litejnih form, Mašinostroenije, Moskva, 1977, p. 224

[2] N.Cibrik, Fizičko-hemičeskije procesi v kontaktnoj zone metal-forma, Nauka Dumka, Kiev, 1977, p. 154

[3] J. Brome, Brit. Foundry **80**(4) (1988) 342-350

[4] R.W. Davies, Brit. Foundry **89**(9) (1996) 287-290

[5] Z.Aćimović-Pavlović, Lj. Andrić, V. Milošević, S. Milićević Ceram. Int. **37** (2011) 99-104

[6] Ž.Josipović, S.Marković, Z.Aćimović, S. Tomović J. Found. **194** (1994) 17-20

[7] Z. Gorny, J. Marcinkowski Trans. AFS **59** (1977) 893-910

[8] S. Kumar, P. Kumar, H.S. Shan, J. Mater. Processing Technol. **209** (2009) 2699-2706

[9] S. Kumar, P. Kumar, H.S. Shan, J. Mater.Processing Technol. **182** (2007) 615-623

[10] S. Shivukumar, L. Wang, B. Steenhoft, Trans. AFS **95** (1987) 791-800

[11] M.Burdit, Mod. Cast. **8** (1988) 20-24

[12] A.Clegg, Trade. J. **8** (1978) 383-398

[13] Z. Aćimović-Pavlović, A. Prstić, Lj. Andrić, Chem Ind. Che. Eng. Q. **13**(1) (2007) 1451-9372

[14] Z. Aćimović-Pavlović, M. Đuričić, S. Drmanić, R. Đuričić, Hem. Ind. **64**(2) (2010) 121-127

[15] Z. Aćimović, Lj. Pavlović, Lj. Trumbulović, Lj. Andrić, M. Stamatović, Mater. Lett. **57** (2003) 2651-2656

[16] Lj. Trumbulović, Z. Aćimović, Z. Gulišija, Lj. Andrić, Mater. Lett. **58** (2004) 1726-1731.

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NAUČNI RAD

PREMAZI NA BAZI CIRKONA SA PRIMENOM U *LOST FOAM* PROCESU LIVENJA

U ovom radu je istraživana mogućnost dobijanja novih vatrostalnih premaza na bazi cirkona koji bi imali primenu u livarstvu. Optimizacija sastava premaza kontrolisana reološkim svojstvima postignuta je primenom različitih komponenata premaza, naročito primenom novog veziva na bazi suspenzije i variranjem načina spravljanja premaza. Čestice cirkonskoh praha veličine 25×10^{-6} m su korišćene kao ispuna. Uzorak cirkona ispitivan je pomoću sledećih metoda: difrakcija X-zraka, diferencijalna termalna analiza i mikroskopija. Oblik i veličina zrna su analizirani pomoću računarskog programa za analizu slike OZARIA 2.5. Pokazano je da primena ovih premaza na bazi vode i alkohola ima pozitivan uticaj na kvalitet površine, tj. na strukturne i mehaničke karak-teristike odlivaka livenog gvožđa koji su dobijeni metodom livenja u peščane kalupe i pomoću isparljivih modela (Lost Foam metoda livenja).

Ključne reči: livenje u peščanim kalupima, Lost Foam metoda livenja, vatrostalni premazi, cirkon.