

Effect of different additives on the properties of alumina-spinel castables

(Efeito de diferentes aditivos nas propriedades de concretos de alumina-espinélio)

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Abstract

Physical properties of low cement castable containing 22 wt.% Al₂O₃-rich MgO-Al₂O₃ spinel and 1.7 wt.% CaO with addition of polyacrylates, castament FS20, TPP and citric acid were investigated. Results showed castables including castament FS20 have higher flow values and better final properties comparing with castables including Darvan 7S and TPP. Also in this study we investigated the effect of addition of microsilica up to 4 wt.% on the properties of alumina-spinel castables. Microsilica is the finest particles in the system and due to suitable distribution of microsilica among other particle the open porosity reduced and mechanical strength increased. Slag penetrations resistance increased with increasing microsilica addition by forming a densification layer right behind the hot face of castables in service.

Keywords: refractory castables, microsilica, alumina-spinel.

Resumo

As propriedades físicas de concretos de baixo cimento contendo 22 peso% Al₂O₃ em espinélio MgO-Al₂O₃ e 1,7 peso% CaO com adição de poliácridatos, concrtagem FS20, TPP e ácido cítrico foram estudadas. Os resultados mostram que os concretos contendo FS20 tem maiores valores de fluência e melhores propriedades finais comparando com concretos como Darvan 7S e TPP. Foi também estudado o efeito da adição de microsilica até 4 peso% nas propriedades de concretos de espinélio-alumina. Microsilica é a partícula mais fina no sistema e, devido à distribuição adequada de microsilica entre as outras partículas, a porosidade aberta foi reduzida e a resistência mecânica aumentou. A resistência à penetração de escória aumentou com o aumento da adição de microsilica formando uma camada de densificação logo atrás da face quente dos concretos em uso.

Palavras-chave: concretos refratários, microsilica, espinélio-alumina.

INTRODUCTION

In recent years, monolithic refractories are replacing traditional refractory bricks in many steel making applications such as the EAF (electric arc furnace) roof [1]. Castables should be used in the electric arc furnace roof which cover various requirements such as cyclic thermal treatment, high temperature, and corrosion by slag and smoke respectively. The alumina-spinel castables show good properties such as high modulus of rupture, low porosity, high density, good resistance to thermal shock, high refractoriness and good resistance to slag penetration and corrosion. Another most important factor of castables is flowability that affects casting properties of the system and makes them suitable to fill complex molds and give good final properties. The production of highly fluid castables depends on the particle size distribution and dispersent of particles in the matrix [2-5].

The purpose of present work is to investigate the influence of three types of dispersants such as castament FS20, Darvan 7S (polyacrylates), TPP (tripolyphosphate) and microsilica addition on the properties of castables for use in EAF (electric arc furnace) such as flowability, bulk density and cold modulus of rupture and cold crushing strength and slag penetration resistance.

EXPERIMENTAL PROCEDURE

Tabular alumina, calcined alumina, microsilica, alumina calcium cement contained 17 wt.% CaO were used as raw materials. The chemical analyses of the raw materials are listed in Table I. Different batches, with three types of additives were prepared (Tables II, III). Water content was about 5 wt.%. Flowability of castables was measured by using a vibrating flow table immediately after mixing based on JIS [6]. Castables were cured in air at ambient

Table I - Chemical analysis of the raw materials.

[Tabela I - Análise química da matéria-prima.]

Type	Composition (wt.%)							
	Al ₂ O ₃	SiO ₂	Fe ₂ O ₃	TiO ₂	K ₂ O	Na ₂ O	MgO	CaO
Tabular alumina	99.4	0.09	0.02	-	-	0.4	-	-
Calcined alumina	99.5	0.03	0.05	-	-	0.3	-	-
Spinel (MAS76)	75.3	0.3	0.28	-	-	-	23.1	0.5
MgO powders	-	-	-	-	-	-	>99	-
Cement	80	0.35	0.2	0.3	0.3	0.4	0.5	17.20
Microsilica	0.7	97.5	0.3	-	0.6	0.3	0.5	0.3

Table II - Additive combination for alumina–spinel castables (wt.%).

[Tabela II - Combinação de aditivos nos concretos alumina-espínélio (peso%).]

Additive	A ₁	A ₂	A ₃	A ₄	A ₅	A ₆	A ₇	A ₈	A ₉
Darvan 7S	0.05	0.1	0.15	-	-	-	-	-	-
TPP	-	-	-	0.05	0.1	0.15	-	-	-
Castament FS20	-	-	-	-	-	-	0.05	0.1	0.15

Table III - Additive combination for alumina–spinel castables (wt.%).

[Tabela III - Combinação de aditivos para concretos alumina-espínélio (peso%).]

Additive	B ₁	B ₂	B ₃	B ₄	B ₅	B ₆	B ₇	B ₈	B ₉
Darvan 7S	0.1	0.1	0.1	-	-	-	-	-	-
TPP	-	-	-	0.1	0.1	0.1	-	-	-
Castament FS20	-	-	-	-	-	-	0.05	0.05	0.05

temperature for 24 h and then dried at 110 °C for at least 16 h before firing. Specimens 160 by 40 by 40 mm were cast for measuring the physical properties.

Castable properties are strongly affected by even a little variation in particle size distribution. Castable particle–size distribution (PSD) was calculated from the Andreasen's equation, as follows:

$$[\text{CPFT}/100] = (d/D)^q$$

CPFT: cumulative percentage of particles finer than the diameter d ; d : particle size; D : maximum particle size; q : distribution coefficient. For this work a constant value of $q = 0.29$ was used. The D value was 6.35 mm.

RESULTS AND DISCUSSION

Fig 1. shows the effect of three types of dispersant on flow values in Al₂O₃-spinel castables. Formulation of low-cement castables consists of calcium-aluminate cement, microsilica, finely milled calcined alumina. Cement will release Ca²⁺ ions in suspension, these ions will be absorbed by silica surface and cause coagulation defloculant will place on the surface particles and these particles will get negative charge on the

surface and the agglomerate of the system will be broken up. Fig. 1 shows that Al₂O₃-spinel castables including castament FS20 have high flow values comparing with castables including Darvan 7S and TPP. Results also show the optimum castament FS20 is 0.05 wt.%. Increase of amount of dispersant by increase of concentration of ions in solution might cause compress of the electric double layer around particles, induce coagulation, and decreases flow values [7].

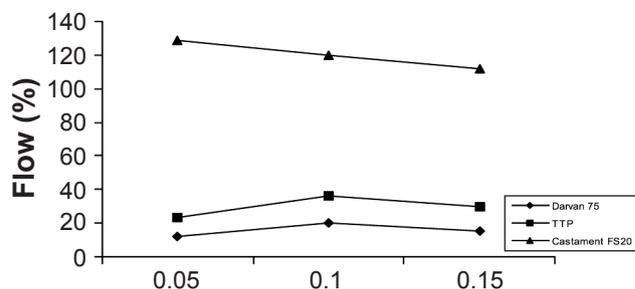


Figure 1: Flow decay curves for the alumina-spinel castables.

[Figura 1: Curvas de decaimento da fluidez de concretos alumina-espínélio.]

Castament FS20 belong to polycarboxy late eter (PCE) group which operates on the basic principle of electrosteric

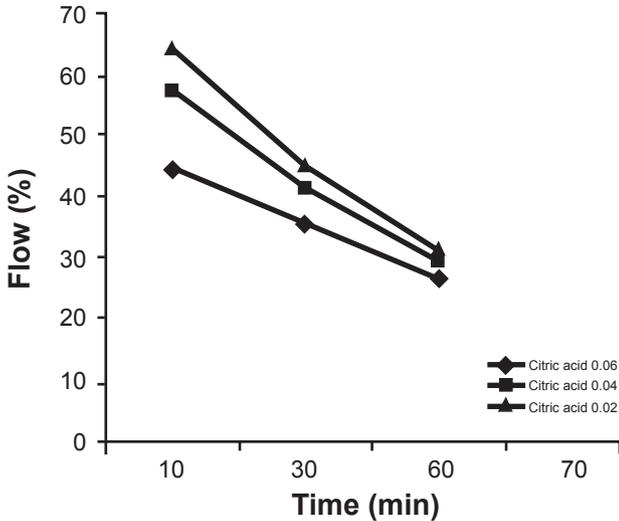


Figure 2: Effect of citric acid on flowability of alumina-spinel castables containing 0.1 wt.% Tpp.
 [Figura 2: Efeito do ácido cítrico na fluidez de concreto espinélio-alumina contendo 0,1% peso Tpp.]

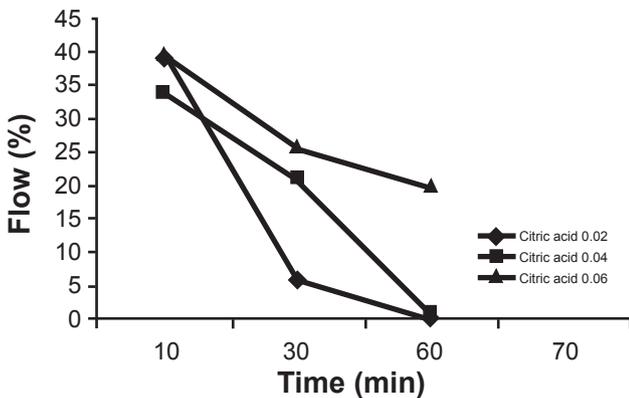


Figure 3: Effect of citric acid on flowability of alumina-spinel castables containing 0.1 wt.% Darvan 7S.
 [Figura 3: Efeito do ácido cítrico na fluidez de concreto espinélio-alumina contendo 0,1% peso Darvan.]

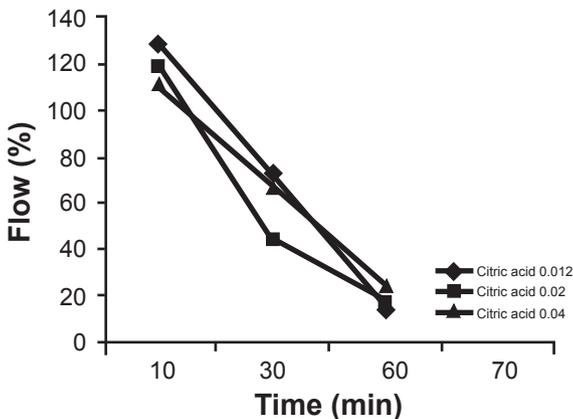


Figure 4: Effect of citric acid on flowability of alumina-spinel castables containing 0.05 wt.% castament FS20.
 [Figura 4: Efeito do ácido cítrico na fluidez de concretos de alumina-espinélio contendo 0,05 peso% FS20.]

stabilization. Electrosteric stabilization is a combination of electrostatic and steric stabilization. Due to these strong electrosteric repulsive forces, the agglomerates of the mineral particles will be thoroughly broken up and the enclosed water in the agglomerates will release. Therefore friction between the mineral particles will be neutralized. These dispersant are very suitable for dispersion and also for deflocculation of Al₂O₃-Spinel castables. Another important parameter in designing refractory castables is the control of setting time. Samples without retarders will have shorter working times. Retarders influence on kinetics of hydration by slowing down the dissolution of the anhydrous cement particles. Its mechanism is of inhibiting dissolution by absorption on cement grain and/or combination with calcium ions [8]. Acid citric will be used as a retarder in this work. This additive possesses carboxylate group (COO⁻). Citrate ions react with the calcium ions and will form calcium citrate which will limit solubility. The activity of Ca²⁺ suspension and hydrate precipitation will be decreased in suspension [8].

Figs. 2, 3 and 4 show the effect of citric acid on flowability of Al₂O₃-spinel castables. Results show that by adding citric acid in castable formulation, flow values will be increased in all of the samples including the three types of dispersants. Results reveal that castable formulation including castament FS20 and acid citric will have good flow properties.

Figs. 5, 6 and 7 show variation cold crushing strength (at 110 °C and 1500 °C) and cold modulus of rupture alumina-spinel castable including Darvan 7S, TPP, castament FS20. Results show the samples including optimum dispersant content have higher cold crushing strength comparing with another samples.

The optimum dispersant will cause the agglomerates of the particles broken up and enclosed water in the agglomerates release and cause increase of flow values and this mode of action cause the best possible rheology of the castables and filling of porosities so the strength of samples will increase.

Tests showed that chemical reaction at elevated

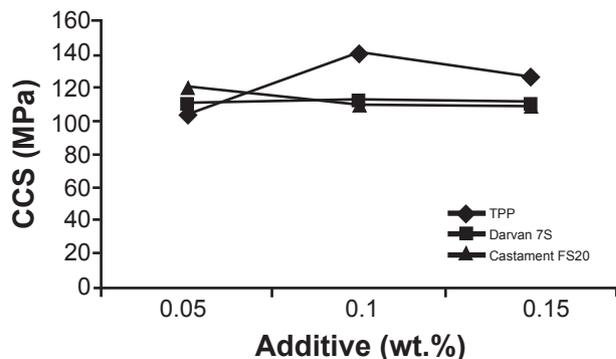


Figure 5: Cold crushing strength alumina- spinel castables at 110 °C.
 [Figura 5: Resistência de esmagamento a frio de concreto alumina-espinélio a 110 °C.]

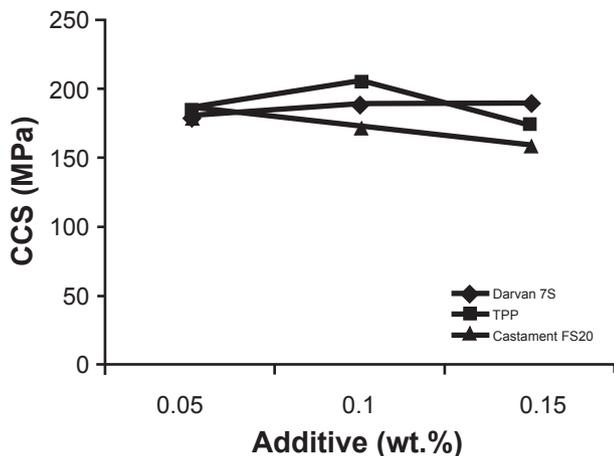


Figure 6: Cold crushing strength alumina-spinel castables after firing at 1500 °C for 3 h.

[Figura 6: Resistência de esmagamento a frio de concreto alumina-espinió após tratamento térmico a 1500 °C durante 3 h.]

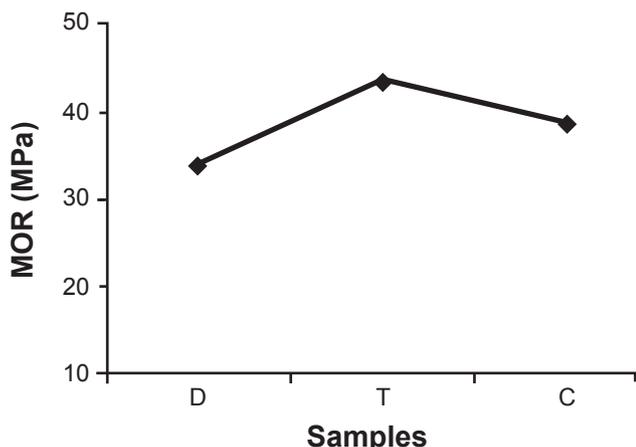


Figure 7: Cold modulus of rupture of alumina-spinel castables after firing at 1500 °C for 3 h.

(T: 0.1 TPP, D: 0.1 Darvan 7S, C: 0.05 castament FS20).

[Figura 7: Módulo de ruptura a frio de concretos alumina-espinió após tratamento térmico a 1500 °C durante 3 h. T: 0,1 TPP, D: 0,1 Darvan 7S, C: 0,05 FS20.]

temperatures plays an important role in changes of physical properties of fired castables with microsilica addition.

Figs. 8 and 9 show that both bulk density and cold crushing strength after drying at 110 °C increased with addition of microsilica. Because microsilica is the finest particle in the system, then with increasing microsilica addition open porosity decreased. The addition of fine-grained powders, such as reactive alumina and microsilica can decrease the mixing water content in the castables. These powders also influence on the better filling of the spaces between the large grains [6]. Then porosity decreased and mechanical strength increased [9].

Fig. 10 shows bulk density increase after firing at 1500 °C for 3 h. Figs. 11 and 12 show that both cold crushing strength and cold modulus of rupture of the castable after firing at 1500 °C for 3h increased with increasing of microsilica

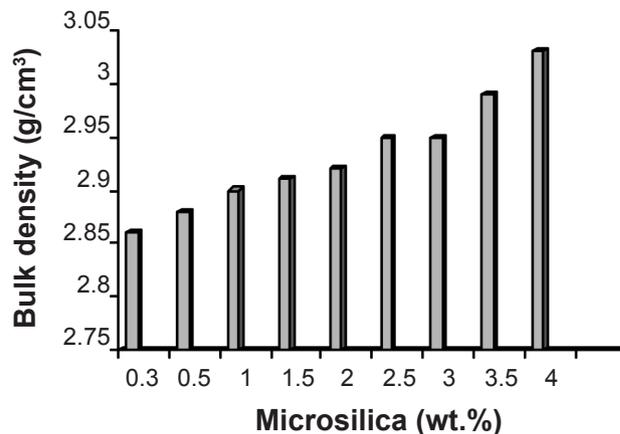


Figure 8: Bulk density alumina-spinel castables at 110 °C.

[Figura 8: Densidade do volume de concretos alumina-espinió a 110 °C.]

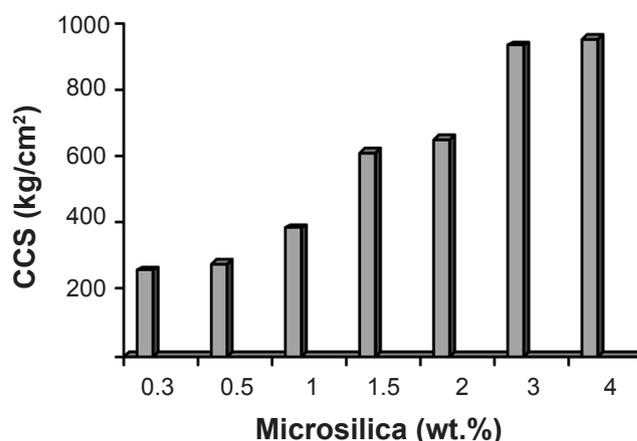


Figure 9: Cold crushing strength alumina-spinel castables at 110 °C.

[Figura 9: Resistência ao esmagamento a frio de concretos alumina-espinió a 110 °C.]

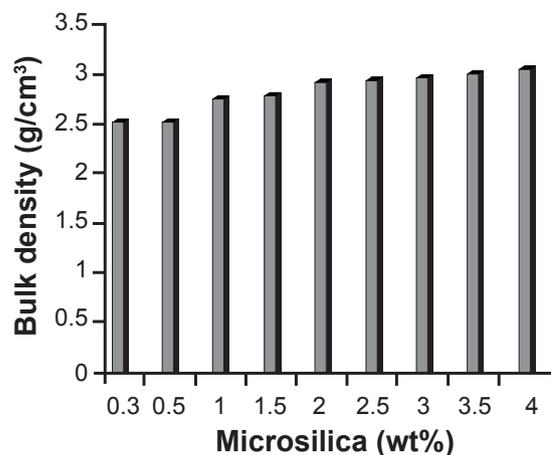


Figure 10: Bulk density alumina-spinel castables at 1500 °C/3 h.

[Figura 10: Densidade de concretos alumina-espinió a 1500 °C/3 h.]

content.

Ko Yung-chao [6] found that the bond linkage between the CA₆ and spinel grains in the bonding matrix of alumina-spinel castables is responsible for the increased hot modulus

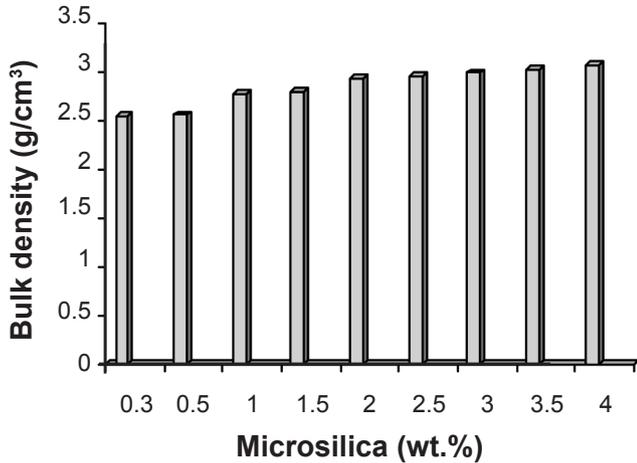


Figure 11: Cold crushing strength alumina-spinel castables after firing at 1500 °C for 3 h.

[Figura 11: Resistência ao esmagamento a frio de concretos alumina-espínélio após tratamento térmico a 1500 °C durante 3 h.]

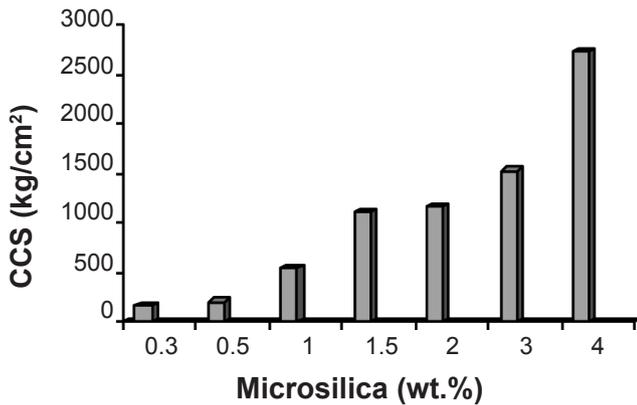


Figure 12: Cold modulus of rupture alumina-spinel castables after firing at 1500 °C for 3 h.

[Figura 12: Módulo de ruptura a frio de concretos alumina-espínélio após tratamento térmico a 1500 °C durante 3 h.]

of rupture with both increased CaO content and temperature from 1300 °C to 1500 °C. The results show that, porosity decreased with increasing microsilica addition. The trends is also due to increasing liquid phase sintering with increasing microsilica addition. Simonin et al.[10] found that vitreous calsium magnesium aluminosilicate (CMAS) phases exist at (1000 °C-1300 °C) and ternary calcium aluminosilicate (CAS) phases exist at low temperatures. These compounds will reduce the temperature of primary liquid phase formation to 1170 °C, which corresponds to the eutetic point of the Al_2O_3 -CaO-SiO₂ ternary diagram.

Microsilica reacts with alumina, thus mullite phase has been produced. Mullite, which is formed as a result of silica and alumina reaction, causes the increase of cold resistance (CCS and CMOR).

Figs. 13, 14, 15 show slag penetration resistance increased with increasing microsilica content to 4wt%. Based on the SEM observations fine particles of CaO particles transported by the fuel-gas aspiration system and these particles reacted with the alumina and formed



Figure 13: Slag penetration test alumina-spinel castable including (A= 2.5, B=3 %wt. microsilica).

[Figura 13: Teste de penetração de escória no concreto alumina-espínélio incluindo (A=2,5, B=3 peso% de microsilica).]

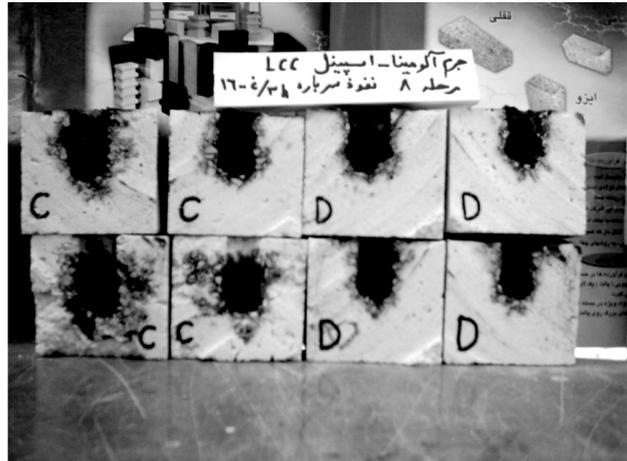


Figure 14: Slag penetration test alumina-spinel castable including (C= 3.5, D= 4 %wt. microsilica).

[Figura 14: Teste de penetração de escória no concreto alumina-espínélio incluindo (C= 3,5, D= 4 peso% de microsilica).]



Figure 15: Slag penetration test alumina-spinel castable including (E= 4.5, F= 5 %wt. microsilica).

[Figura 15: Teste de penetração de escória no concreto alumina-espínélio incluindo (E= 4,5, F= 5 peso% microsilica).]

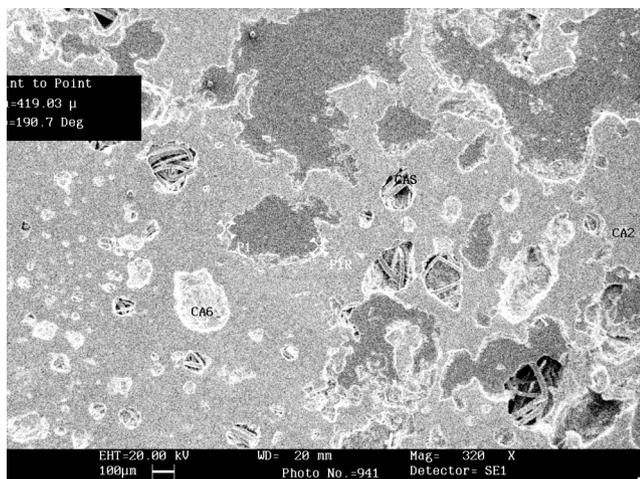


Figure 16: SEM micrograph of the Al_2O_3 -Spinel castable.
 [Figura 16: Micrografia MEV do concreto alumina-espinélio.]

low melting point phases, such as CA_2 and CA_6 in the hot side of the castable (Fig. 16). In the deeper area of the slag penetration layer, crystal growth of $\text{CaO} \cdot 6\text{Al}_2\text{O}_3$ proceeded well, and its crystal growth led to the densification of the castable texture and restrained the slag penetration.

Slag penetration resistance decreased with increasing microsilica addition more than 4wt%, which can be perhaps attributed to forming cristobalite. Microsilica converted in to cristobalite with a volume expansion and porosity in fired bodies increased. With increasing porosity slag penetration resistance decreased.

CONCLUSIONS

Alumina-spinel including castment FS20 have higher flow values than castable including Darvan 7S and TPP. Bulk density and cold crushing strength after drying at 110 °C increased with increasing microsilica. Cold modulus of rupture and cold crushing strength of castables after firing at 1500 °C for 3h, increased with increase of microsilica content. Slag penetration resistance increased with increasing microsilica content to 4 wt.% when the content of microsilica is more than 4 wt.% slag penetration resistance decrease.

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