

Magnesium removal from aluminum molten alloys using silica based minerals and waste from coal-fired power (cenospheres)

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ABSTRACT

In this work cenospheres, zeolite, silica or mixtures of them were injected into a molten aluminum alloy using argon as a carrier gas in order to measure their efficiency as Mg removers. The Mg content of the molten alloy was measured during the injection period and the produced dross was weighted for each experiment. The physicochemical characterization and the use of the thermodynamic software FactSage version 6.2, allowed the determination of the reaction mechanism between the powders and the molten aluminum. Cenospheres demonstrated their capacity as Mg removers with an efficiency similar to silica but lower than that corresponding to zeolite and zeolite:silica mixtures. The use of a zeolite:silica mixture (65:35wt%) produced the best results, removing the magnesium of the alloy from an initial content of 1wt% to a final content of 0.0072wt%.

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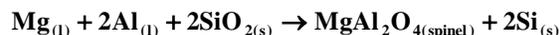
KEYWORDS

Molten aluminum;
Injection;
Cenospheres;
Zeolite;
Dross.

INTRODUCTION

Various techniques are used for the Mg removal from the Al-Si A380alloy for automotive use (which requires a maximum of 0.1wt% of Mg). Some of these techniques are chlorination, electrochemical methods and the incorporation of powder reagents (fluorides)^[1-4]. However, these methods have some disadvantages. The Mg removal from aluminum alloy melts performed by chlorine injection is the most common method used industrially. Although the kinetics of the magnesium removal as MgCl₂ is rapid^[1], the un-reacted chlorine and the co-product gaseous AlCl₃ limit the environmental acceptability of the process. Despite no these kinds of products are formed by electrochemical methods, this

process is not used due to the high electricity costs. Taking into account the mentioned above, the secondary aluminum industry has been focused on the development of processes that overcome the mentioned limitations. One option is represented by the use of purified silica-based powders because of the generated products in the treatment are not pollutants. Reports on literature establish the effect of SiO₂ on the Mg removal^[5-7], which is performed according to the following reaction (1)^[8]:



$$\Delta G^\circ = -377.09\text{kJ} \quad (1)$$

However, silica requires supplementary processes for its concentration resulting in additional costs. Addition-

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ally, the kinetics of the Mg removal using silica is relatively slow.

Recent studies^[5,8] have demonstrated the feasibility of Mg removal from aluminum molten alloys by injecting zeolite (containing more than 50wt% of SiO₂) and silica using an inert carrier gas. The relative abundance of zeolite ores and silica sand deposits makes their use feasible to remove Mg from this type of alloys at a very attractive cost of treatment.

In order to search for new materials that potentially combine higher productivity with environmental acceptability, cenospheres from landfill of coal-fired power were tested. The main characteristics of the cenospheres are their morphology (spherical hollow particles of an average diameter of 45 μm) and high content of SiO₂ (55-61 wt%)^[9]. The considerably high reaction surface and the acceptable SiO₂ content make the cenospheres an attractive candidate for the Mg removal from molten aluminum alloys.

The aim of this work is the study of the capacity of cenospheres as Mg removers from aluminum alloy melts. This capacity will be evaluated by comparison with that of zeolite, silica, zeolite:silica mixtures and zeolite:cenospheres mixtures.

EXPERIMENTAL PROCEDURE

Raw materials characterization

The mineral zeolite and silica were separately crushed in a ball mill and classified obtaining, in both cases, powders with an average particle size smaller than 150 μm. The cenospheres were sieved using a -325 ASTM mesh. Samples of the minerals and cenospheres were analyzed by X-ray diffraction (XRD), energy dispersive spectroscopy (EDS) and scanning electron microscopy (SEM). In addition, the chemical composition of the minerals was determined by atomic absorption spectroscopy, inductively coupled plasma atomic emission spectroscopy and gravimetric method. The selected alloy was the A332 aluminum base alloy (Al-11.64Si-0.338Fe-2.05Cu-1.00Mg-1.54Ni). Ultra high purity argon was used as a carrier gas.

Mg removal by injection

An induction electric furnace, equipped with a silicon carbide crucible of 12kg of capacity and tempera-

ture control, was used to treat the alloy. An injection equipment with devices to measure and control the gas and powder flows was used. The injection lance was made of graphite and covered externally with refractory material. The internal diameter of the lance was 6.98mm. The selected parameters used for the submerged powder injection experiments were: argon flow of 4.4L/min, powder flow of 16.2g/min, mass of aluminum alloy of 8kg and aluminum alloy treatment temperature of 750°C. The lance was submerged at the 85% of the depth of the melt. The variable in the experiments was the composition of the powders to be injected. The following powders were tested: Pure mineral zeolite, pure cenospheres, pure silica, two mixtures of zeolite:cenospheres (70:30 and 50:50wt%) and two mixtures of zeolite:silica (20:80 and 65:35wt%). The mass of the powders to be injected was calculated considering the SiO₂ as the solid reagent and spinel and silicon as products according to the chemical reaction (1). For each experiment, samples of the melt were obtained every 10min and the produced dross was collected at the end of the experiment. The solidified samples were analyzed by spark atomic emission spectrometry to determine their chemical compositions and a sample of the dross was analyzed by XRD.

RESULTS AND DISCUSSION

Raw materials

Figure 1 shows the XRD patterns of mineral zeolite, cenospheres and silica. As it can be seen in Figure 1(a), the selected zeolite was identified as Na_{0.78}Ca_{3.54}(Al_{6.52}Si_{29.48}O₇₂)(H₂O)_{21.4}(heulandite). According to Figure 1(b), cenospheres are composed mainly of SiO₂(quartz) and Al_{4.52}Si_{1.48}O_{9.74}(mullite), but CaCO₃(calcite) is also present. It is noticeable that the XRD pattern shows an amorphous halo between 20 and 30° due to the presence of amorphous material. The XRD pattern of silica, Figure 1(c), shows only the presence of SiO₂(quartz).

Figure 2 shows SEM images of cenospheres, zeolite and silica and their corresponding EDS spectra. As shown in Figure 2(a), cenospheres are spherical particles and their chemical nature, analyzed by EDS, approaches to that of the aluminum-silicate compound with traces of impurities Al_{1.8}Si₂O_{4.9}(Na_{0.1}Mg_{0.15}S_{0.03}

$K_{0.1}Ca_{0.2}Ti_{0.09}Fe_{0.2}$). On the other hand, zeolite particles show a variety of irregular morphologies and sizes. These particles have a very high surface area^[7] (Figure 2(b)). The chemical nature of these particles, determined

by EDS, corresponds to a typical complex stoichiometry of zeolitic minerals ($(Fe_{0.1}Ca_{0.1})K_{0.3}Al_{0.5}Si_{2.7}O_4(Na_{0.065}Mg_{0.07}Ti_{0.01})$). As observed in Figure 2(c), silica particles show irregular morphology.

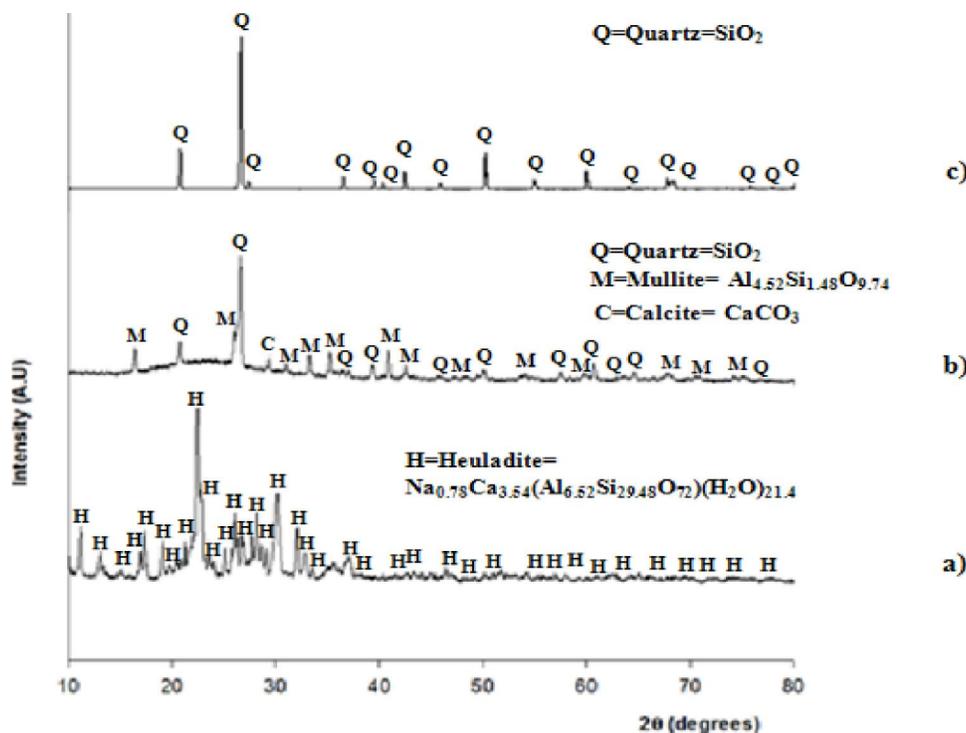


Figure 1 : XRD patterns of the powders used to remove Mg. a) Zeolite, b) Cenospheres and c) Silica.

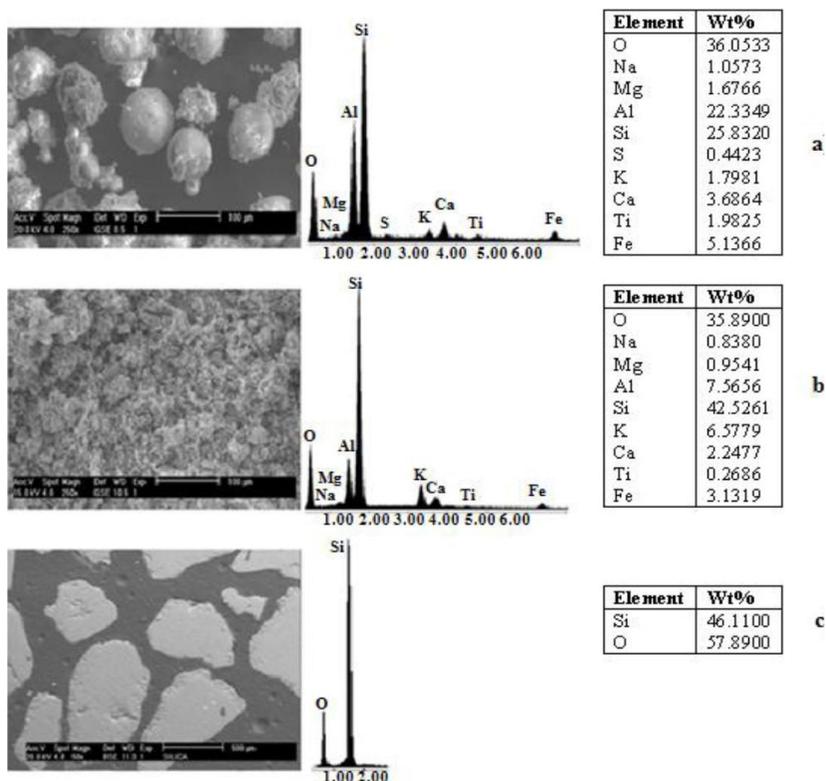


Figure 2 : SEM images of materials before injection into the molten alloy: a) Cenospheres, b) Zeolite and c) Silica.

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Mg removal

Mg removal tests were performed, as outlined earlier, using zeolite, cenospheres, silica, silica:zeolite mixtures (35:65wt% and 80:20wt%), and cenospheres:zeolite mixtures (30:70wt% and 50:50wt%). Figure 3 shows the variation of the Mg content in the aluminum alloy as a function of the injection time for the different experiments.

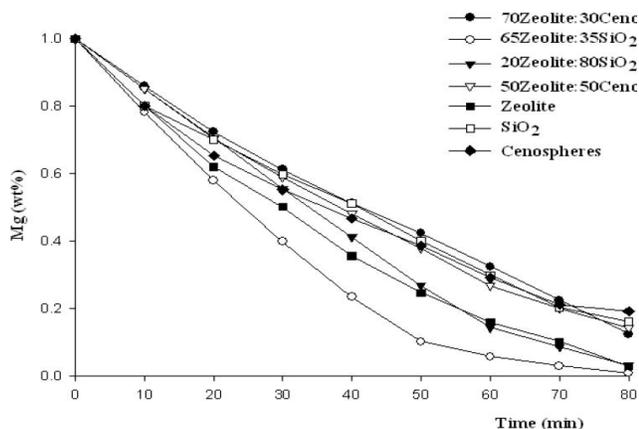


Figure 3 : Mg content in the alloy as a function of the injection time for the performed experiments.

TABLE 1 : Efficiency of Mg removal and metal losses for each experiment (Mg_f is the final Mg content of the alloy, η is the Mg removal efficiency and m are the metal losses).

Sample	Mg _f (wt%)	η(%)	m(%)wt
Zeolite	0.028	97.2	16.25
Silica	0.208	79.2	16.78
Cenospheres	0.220	78	18.81
70Zeolite:30Cenospheres	0.140	86	15.52
50Zeolite:50Cenospheres	0.190	81	18.36
65Zeolite:35Silica	0.007	99.3	10.93
20Zeolite:80Silica	0.031	97	11.75

As it can be observed in Figure 3, the best results were obtained using the mixture 65Zeolite:35SiO₂ (final Mg content of 0.0072wt%), zeolite (final Mg content of 0.028wt%) and the mixture 20Zeolite:80SiO₂ (final Mg content of 0.0300wt%). TABLE 1 shows the efficiency of Mg removal (η) and metal losses (m) for each experiment. It was further observed that by using mixtures of silica and zeolite, a smaller amount of slag was generated, forming highly stable oxides such as MgAl₂O₄ (spinel), MgO (periclase), Al₂O₃ (corundum) and Mg₂SiO₄ (forsterite) in addition to SiO₂ (quartz) and CaAl₂Si₇O_{18.6}H₂O (heulandite). The main reaction products, identified in the slag using XRD analysis, can be observed in TABLE 2.

TABLE 2 : Reaction products detected in the slag by using XRD analysis (Z is zeolite, S is silica and C are cenospheres).

Reaction product	Composición of the injected powder						
	Z	S	C	70:30 Z:C	50:50 Z:C	65:35 Z:S	20:80 Z:S
Al	X	X	X	X	X	X	X
Si	X	X	X	X	X	X	X
SiO ₂ quartz		X	X	X	X	X	X
AlN	X						
MgO periclase		X	X	X	X	X	X
MgAl ₂ O ₄ spinel	X	X		X	X	X	X
KCl silvite	X						
Mg ₂ (SiO ₄) forsterite	X					X	X
Ca _{8.16} Si ₃₆ O ₇₂ (H ₂ O) _{21.8}	X					X	X
Clinoptilolite							
CaAl ₂ Si ₇ O _{18.6} H ₂ O heulandite			X	X	X		

As observed in Figure 3, the use of zeolite, alone or in mixtures, leads to improve the Mg removal processes. This behavior can be explained considering the following three zeolite characteristics: i) zeolite is a hydrated compound (the percentage of water in the zeolite used was 12 wt%) and, on the effect of the molten alloy temperature, water in the zeolite is evaporated and the particle is fragmented by the water vaporexpansion inside the zeolite channels, increasing the reaction surface^[8,11], ii) water is a strong oxidizing agent that contributes to the elimination of Mg^[8] and, iii) the stirring conditions into the molten alloy created by the magnetic induction forces of the furnace and the carrier gas flow, contribute to the comminution of the particles due to the presence of Carlsbad twins in the zeolite. The Carlsbad twins have a tabular habit parallel to the (010) plane, typically present in brittle materials^[9,11]. These zeolite characteristics produce its fragmentation inside the molten bath resulting in final zeolite sizes smaller than 80μm. Figure 4 (a) shows an SEM image of a zeolite particle before injection (approximate size of 130μm) and Figure 4 (b) shows an SEM image of a semi-reacted zeolite particle obtained after 10 min of injection (approximate size of 50μm).

Figure 5 (a) shows an SEM image of a silica particle before its injection into the molten alloy (approximate size of 140μm) and Figure 5 (b) shows an SEM image of semi-reacted silica particles obtained after 80 min of injection (sizes ranging from 5 to 300μm). In each particle it is possible to observe (Figure 5 (b), a layer of

reaction products surrounding an unreacted silica nucleus. The formation of this layer around the silica explains the relatively low rate of Mg removal when silica is used.

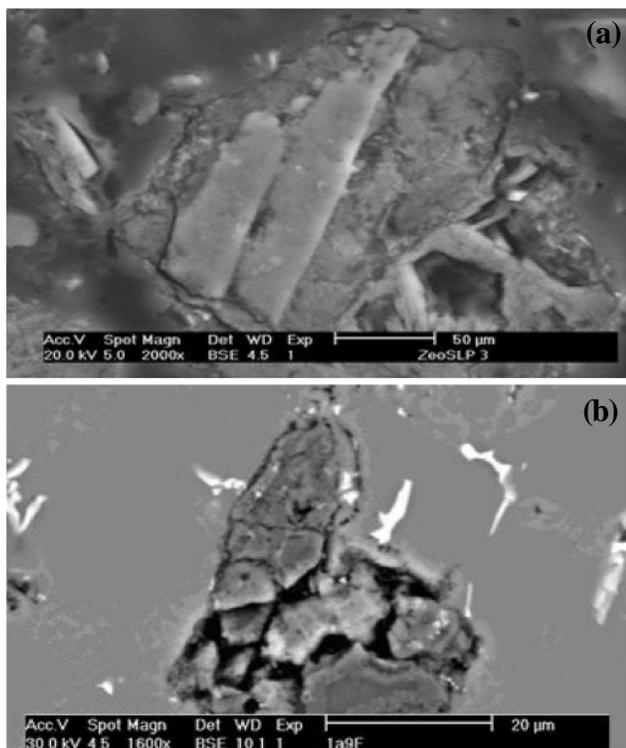


Figure 4 : a) SEM image of a zeolite particle before injection, b) SEM image of a semi-reacted zeolite particle.

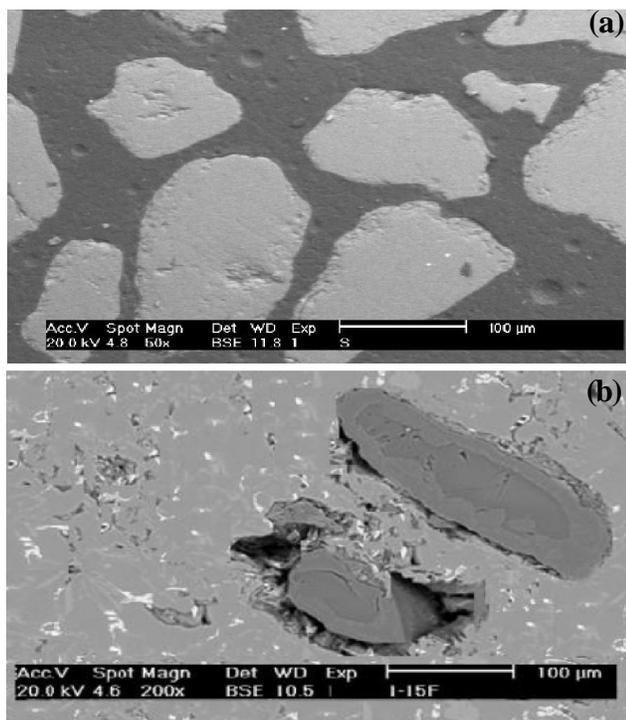


Figure 5 : a) SEM image of a silica particle before injection, b) SEM image of a semi-reacted silica particle.

Figure 6 (a) shows an SEM image of a group of cenospheres before their injection into the molten alloy (sizes ranging from 5 to 100 μm) and Figure 6 (b) shows an SEM image of the cross-section of a semi-reacted cenosphere obtained after 20min of injection. It is possible to observe, inside of this semi-reacted cenosphere, reaction products and a smaller cenosphere. Cenospheres present a similar behavior than silica, forming a layer of reaction products around them. As it can be observed in Figure 3, the cenospheres and the cenospheres:zeolite mixtures (30:70wt% and 50:50wt%) present the lower efficiency as Mg removers. This unexpected result could be explained taking into account two factors: i) cenospheres are hollow spheres and their density ranges from 0.4 to 0.8 g/cm³, which gives them a high buoyancy. This characteristic reduces the time that the cenospheres remain in the zone of permanent contact (inside of the molten alloy), where the reaction occurs more efficiently, ii) due to their very small sizes, cenospheres have the tendency to attract themselves and to form agglomerates, reducing significantly the reaction surface.

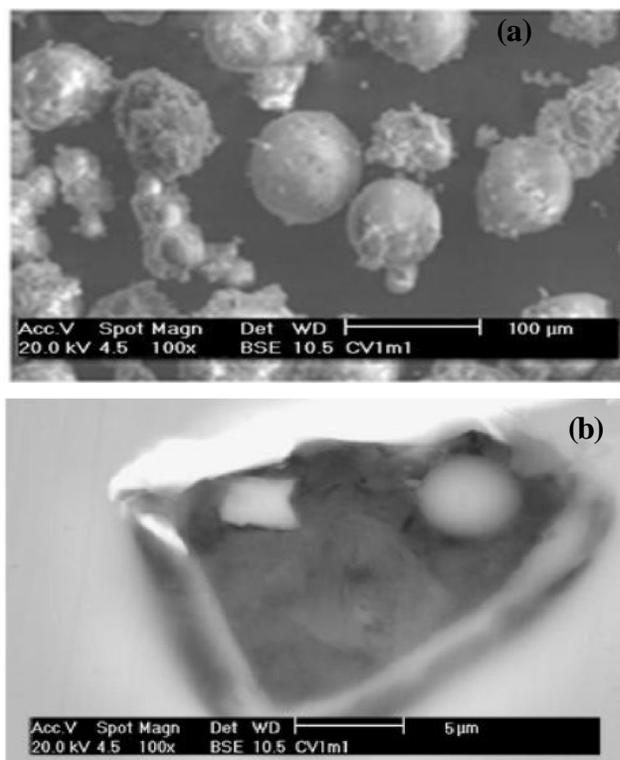


Figure 6 : a) SEM image of cenospheres before injection, b) SEM image of a semi-reacted cenosphere.

According to the results presented in Figure 3, the

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behavior of pure cenospheres as Mg remover is very similar to that of pure mineral silica, despite its lower SiO₂ content and its lower density (0.4 -0.8 vs. 2.65 g/cm³). However, the behavior of the mixtures of cenospheres:zeolita and silica:zeolite is quite different because silica enhances the performance of zeolite as Mg remover while cenospheres worsen it. This negative effect of cenospheres when they are mixed with zeolite may be explained by the fact that cenospheres partially coat the zeolite surface into the molten alloy. Cenospheres are light and insulative, dragging quickly the zeolite particles to the bath surface which leads to the decrease of the reaction time and prevents their effective heating.

CONCLUSIONS

Cenospheres demonstrated their capacity as Mg removers with an efficiency similar to silica but lower than those corresponding to zeolite and zeolite:silica mixtures. The use of a mixture of zeolite:silica (65:35wt%) produced the best results, removing the magnesium of the alloy from an initial content of 1wt% to a final content of 0.0072wt%. Furthermore, the use of this mixture reduces the amount of generated slag, decreasing the metal losses by oxidation.

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