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Compatibility study between aluminium alloys and alternative recycled ceramics for Thermal Energy Storage applications

Haoxin Xu^a, Fabio Dal Magro^a, Najim Sadiki^b, Jean-Marie Mancaux^b, Xavier Py^b, Alessandro Romagnoli^{a*}

^a Nanyang Technological University, 50 Nanyang Ave, Singapore 639798

^bPROMES CNRS laboratory UPR 8521, University of Perpignan Via Domitia, Rambla de la Thermodynamique Tecnosud, 66100 Perpignan France.

Corresponding author, e-mail: a.romagnoli@ntu.edu.sg - tel: +65 8389 9657

Highlights

- Conducted high temperature corrosion tests at 1000 °C for 100 hours
- Performed ESEM and XRD characterization for reliable post-corrosion analysis
- First time to report the compatibility between molten al-based alloys and three recycled ceramics
- Concluded possible encapsulation materials from wastes for molten aluminium alloys

Abstract

Recycled ceramics from industrial wastes, compared with traditional high-purity ceramics, present high market potential as refractory materials due to their low cost production process with very low environmental impacts. However, there still exists a research gap of how recycled ceramics behave while in contact with liquid metal. In order to study the feasibility of using recycled ceramics as the encapsulation material in the application of high temperature Latent Heat Thermal Energy Storage system, this paper investigates the compatibility of recycled ceramics with three kinds of aluminium-based alloys at high temperature, with a comparison to the corrosion resistant behaviour of alumina. The recycled ceramics explored include Cofalit from asbestos containing waste, blast furnace slags from steel production, and coal fly ashes sintered ceramics from incineration plants. The study consists of a steady state thermal treatment of ceramic samples in contact with the three different alloys at 1000°C for 100 hours, and a post instrumental characterization of ceramic samples by Environmental Scanning Electron Microscopy, Energy Dispersive Spectrometry and X-ray diffractometer, to understand the chemical and structural transformation of the ceramics. Results demonstrate that Cofalit shows chemical stability with Al99% but instability with AlSi5% and AlSi12%. Blast furnace slag presents quite good thermochemical stability towards molten AlSi5% and AlSi12%. Coal fly ashes sintered ceramics are highly interactive towards all three aluminium alloys. In conclusion, besides alumina, Cofalit is recommended as alternative encapsulation material for molten Al99%, while blast furnace slag being recommended for molten AlSi5% and AlSi12%.

Keywords: Latent Heat Thermal Energy Storage; Aluminium alloys; Recycled ceramics; Compatibility, Waste heat recovery, Waste-to-Energy

Nomenclature

Acronyms

CFA	Coal fly ashes
CTE	Coefficient of Thermal Expansion(1/K)
EDS	Energy Dispersive Spectrometry
ESEM	Environmental Scanning Electron Microscopy
LHTES	Latent Heat Thermal Energy Storage systems
PCMs	Phase Change Materials
TES	Thermal Energy Storage

WtE	Waste to Energy
XRD	X-ray diffractometer

Latin letters

C_p	Heat capacity (kJ/kg·K)
k	Thermal conductivity (W/m·K)
T_{mp}	melting point Temperature (°C)
ρ	Density (kg/m ³)

1. Introduction

1.1 Thermal Energy Storage (TES) system in industrial waste heat recovery process

Latent Heat Thermal Energy Storage systems (LHTES) utilize the Phase Change Materials (PCMs) to accommodate excess or intermittent thermal energy sources for a steady and controlled output, by storing and releasing the thermal energy within phase transformation process. Their abilities to store thermal energy at a high density and provide a constant temperature output, make the PCMs an attractive technology in industries for effective and sustainable energy usage [1,2]. Although there have been many applications of LHTES (e.g. domestic hot water supply, space heating/cooling), high temperature LHTES application remains to be a challenge due to its complexity in material selection, configuration design and operation [3] despite its high potential to improve the efficiency of high temperature processes, such as Waste to Energy (WtE) plants [4] and solar industry [5].

A recent study by Dal Magro et al. [6] proposed a new PCMs tile technology to buffer the fluctuation of steam generation in WtE plants. Figure 1 illustrates the new design featuring PCM-based refractory brick. As shown, the design exploits the latent heat of PCMs filled into the holes inside of the refractory brick, thus buffering the fluctuation of heat flux from waste combustion. From the preliminary study and simulation results, this design can not only buffer heat flow, reduce thermal gradient, deliver higher flux to steam flow, it can also avoid steam production fluctuation, increase temperature of superheated steam without using coated super-heaters, and therefore increase overall plant efficiency by over 30%. As a continuation study of the proposed technology, it is critical to choose the best materials to meet the demanding challenge.

Figure 1 Water-wall or radiant superheater protected by PCM-based refractory brick [6]

Table 1 summarizes the main high temperature PCMs (T_{mp} above 500 °C) available for LHTES design. There are numerous studies dedicated to high temperature LHTES using molten salt, including nitrates, chlorides and carbonates [7]. Molten salt presents advantages such as good storage density, low storage cost and a wide melting temperature range to fit into various applications. However, the low thermal conductivity, their corrosive behaviour towards constructional materials and their high volume expansion rate during phase transformation pose great challenge in the design and construction [8]. Another PCMs option for high temperature LHTES is metal alloys, including aluminium series, copper series and iron series. Metal alloys as PCMs, present high storage density, remarkably high thermal conductivity, and low volume expansion rate, which make them an attractive choice for the previously proposed PCM-tile technology [4,7]. Nonetheless, their chemical corrosive behaviour when in contact with metallic encapsulation material restricts their application in many scenarios.

Table 1 A summary of available PCMs properties whose melting temperature is above 500 °C [6]

	Heat capacity	Thermal conductivity	Volume expansion rate during phase change	Corrosion	Examples of materials	Melting temperature (°C)
Molten salts	High	Low	10-30%	Corrosive to metallic shell	Na ₂ CO ₃ -K ₂ CO ₃ (59-41%)	710
					MgCl ₂	714
					NaCl	800
					Na ₂ CO ₃	858
Metal alloys	High	Extremely high	Around 5%	Corrosive to metallic shell	Al-Si (75-25wt%)	557
					Al	660
					Cu-Si (80-20wt%)	802
					Cu	1084

1.2 Compatibility between Al based alloys and ceramics as potential encapsulation materials

In order to facilitate application of metal alloys as high temperature PCMs, it is crucial to find encapsulation material that meets the requirements of adequate thermal properties and mechanical strengths, availability with low price, and compatibility with metal alloys at operational temperature.

Literatures have indicated that ceramics could serve as good candidates for encapsulating molten aluminium alloys. A study by R. Fukahori et al. [8] investigated the corrosion behaviour between Al-Si alloys and commercial ceramics. The alloys and ceramics were placed in tube furnace and underwent thermal treatment at 1000 °C for 100 hours. Then microstructural analysis of the sample surfaces was performed by means of Scanning Electron Microscopy and Energy-Dispersive Spectrometry. The results concluded that Al₂O₃, AlN and Si₃N₄ showed high corrosion resistance to the AlSi25% and Al99.7%. Another study by Yan and Fan [10] reviewed the durability of ceramic materials in molten aluminium alloys. They concluded that besides the aforementioned ceramics, graphite, sialons and aluminosilicate refractories were also characterized as inert in molten aluminium. However, the manufacturing process of commercial high purity ceramics are highly energy intensive and produces a large quantity of wastes since it involves multiple stages in which the product is subject to high temperature treatment [11]. The alumina refineries, according to the International Aluminium Institute, have an average total energy consumption of 11.2 GJ/ton [12].

Unlike the high purity ceramics from commercial sources, the ceramics recycled from industrial waste contribute to a more sustainable environmental pathway if used as refractory materials. These recycled ceramics are made from industrial wastes such as asbestos containing wastes, steel slags or coal-fired power plant fly ash. Due to the nature of the recycled ceramics, they are usually available in most of industrialized areas with a much lower costs. Besides being inexpensive, available in large quantity with potential environmental benefit such as low greenhouse gas emission and low embodied energy, the recycled ceramics also present quite good thermo-physical properties and mechanical strengths [13,14]. A. Gutierrez et al. [15] reviewed several industrial wastes from different sources and reported the origin, the properties and the current research works related. It is noteworthy that the thermal properties of some recycled ceramics are even comparable with the commercial high purity ones. For instance, the recycled ceramics made from asbestos containing wastes, Cofalit, has a density of around 3120 kg/m³, a heat capacity of 0.8-1.03 kJ/kg·K. The Fly ashes coming from municipal wastes has a density of around 2900 kg/m³, the heat capacity ranging from 0.9-1.1 kJ/kg·K. The mechanical strength of Cofalit is reported as very stable even after severe thermal cycling operating conditions.

In summary, recycled ceramics demonstrate great advantages of low environmental cost, low capital cost, and reasonably good thermo-mechanical properties as encapsulation materials for high temperature LHTES systems. A number of corrosion studies have been carried out [13,16,17] to examine the compatibility between molten salts and inorganic industrial waste ceramics, for their application in solar thermal storage systems. However, few studies have reported the compatibility behaviour between liquid

metal alloys and the inorganic industrial waste ceramics. This research gap limits the application of recycled ceramics as the encapsulation material for high temperature LHTES in which metal alloys serve as phase change materials.

With the purpose of further justifying the feasibility of using recycled ceramics as shell material for aluminium based alloys, this study investigates the compatibility of three kinds of Al-Si alloys with three different recycled ceramics (Cofalit from asbestos containing waste, blast furnace slag and coal fly ashes sintered ceramic) regarding their corrosion behaviour under high temperature thermal treatment for a long duration. The study will engage Environmental Scanning Electron Microscopy (ESEM), Energy Dispersive Spectrometry (EDS), and X-ray diffractometer (XRD) for post thermal treatment analysis.

2. Materials

2.1 Aluminium alloys

Metals and metal alloys have greater potential as high temperature PCMs than molten salts since they have higher thermal conductivity, larger latent heat per volume and smaller volume expansion [18]. In particular, aluminium-silicon alloys have been considered as one of the most promising choices for PCM in the high temperature range [19,20] due to their suitable melting temperature, high latent heat of fusion and high thermal conductivity [21]. In this work, the reactivity of three commercial aluminium alloys with different silicon contents (0-12 wt%) have been investigated; Table 2 summarises the composition of the examined alloys. Table 3 reports the main thermo-physical properties of the considered aluminium alloys. A recent study investigated the thermal reliability of AlSi12.2 eutectic alloy and reported that the melting point, latent heat and thermal conductivity of the alloy sample showed outstanding stability even after 1000 thermal cycles [22], which supports its competency as a phase change material for TES applications.

Table 2 Composition of the studied aluminium alloys (weight %)

Name	Standard Code ER	Al	Si	Fe	Cu	Mn	Mg	Zn	Ti	Others
Al99.5	1050	Balance	≤ 0.25	≤ 0.4	≤ 0.05	≤ 0.03	≤ 0.03	≤ 0.07	≤ 0.03	≤ 0.25
AlSi5	4043	Balance	$4.5 \div 6$	≤ 0.8	≤ 0.3	≤ 0.05	≤ 0.05	≤ 0.1	≤ 0.2	≤ 0.15
AlSi12	4047	Balance	$11 \div 13$	≤ 0.8	≤ 0.3	≤ 0.15	≤ 0.1	≤ 0.2	≤ 0.2	≤ 0.15

Table 3 Thermo-physical properties of the studied aluminium alloys (weight %)

Name	Standard Code ER	Melting point (°C)	Latent heat (kJ/kg)	Thermal conductivity (W/m·K)
Al99.5	1050	657	390	227
AlSi5	4043	573-632	412	163
AlSi12	4047	557	498	160

2.2 Recycled ceramics

This study focuses on three kinds of recycled ceramics, namely Asbestos containing waste (Cofalit), blast furnace slags and coal fly ashes sintered ceramics. Table 4 shows their origins and thermo-mechanical properties.

Cofalit is a low-cost recycled ceramics industrially produced by a high temperature plasma treatment or microwave heating of asbestos-containing waste, and then moulded and cooled down at a controlled cooling rate. The specific cooling condition leads to the formation of the ceramic of fine isotropic micro size crystals, which offers high thermochemical properties. The sample used in this compatibility test originates from INERTAM [23]. The composition of Cofalit is mainly calcium magnesium iron aluminosilicate with impurities like Ti, Na etc. Lab testing of the obtained Cofalit proves that this ceramic

demonstrates very stable refractory behaviour under thermal cycling between room temperature and 1000 °C [24]. The annual production of Asbestos containing waste in France is around 250,000 ton, of which 2.4% is industrially inertised while the rest goes to landfill [15]. This results in the low cost of Cofalit, around 8-10 euros/ton as reported by Kere [25].

The steel slags are the high temperature by-products of steelmaking industry, one of the most energy intensive heavy industries in the world. The molten steel slags are removed from the liquid steel by density difference after steel casting. Then the molten slags are solidified into recycled ceramics at a controlled cooling rate. Slags are mainly a mixture of metal oxides, with potentially metal sulphides and heavy metals. The European slag association summarised the main treatment processes for the ferrous slags to give rise to different type of steel slags such as Electrical arc furnace slag, blast furnace slag, and Basic oxygen furnace slag [26]. The slag samples used in this study were blast furnace slags received from industrial company Arcelor Mittal [27]. These slags were re-melted and cooled down into plate shape before being prepared and used in the compatibility test. The global production of steel slag annually is about 250 million ton, out of which 24% is landfilled or stored in the steel-making plants [15]. It is suggested that dumping of steel slags requires long term planning due to its nature of being potentially environmental hazardous [15]. The recycling of steel slags as refractory material can be an alternative solution to dumping, land filling or construction materials for dam, road or other infrastructure. The estimated price of steel slag in 2009 was about 19 euros/ton according to a report released by the U.S. Geological Survey [28].

Coal fly ashes (CFA) come from the gaseous effluents of coal combustion and are collected by electrostatic filters. Their main compounds include SiO_2 , Al_2O_3 , CaO , which make the major contribution to the measured properties of coal fly ashes. The CFA ceramic used in this study was obtained from Eco-Tech-Ceram® [29]. They produced the ceramic samples by lab sintering of the CFA powders received from the EDF company [30]. The main component of the product ceramic is a well-known refractory material mullite. There is an average porosity of 20% exhibiting in the samples. The high worldwide production of CFA globally, 750 Mton per year, presents a huge potential for the valorisation of CFA ceramics. However, the price of CFA sintered ceramic depends highly on the local production and sintering methods. It is noteworthy that all recycled ceramics discussed here in this study present quite stable mechanical properties until the melting point around 1100 °C [31].

Utilization of recycled ceramics contributes to a circular and restorative economy because of:

- Less depletion of natural resources;
- Lower cost and thus higher plant economy compared with commercial high purity ceramics;
- Recycled ceramic can be elaborated into a particular geometry of optimized heat exchanger, which offers an additional value to the materials and a better system efficiency due to less interface for transfer if compared with separated heat exchanger and storage material;
- More energy saving due to the production of slags at the outlet of furnace when slags are still molten; this contributes to fast payback time especially for high temperature applications.

Table 4 Material names, origin of recycled ceramics, and their average values of properties from room temperature to 1000 °C

Material	Material origin	ρ (kg/m ³)	C_p (kJ/kg·K)	k (W/m·K)	CTE (10 ⁻⁶ /°C)	Cost (euros/ton)	Reference
Cofalit	Asbestos containing waste	3120	0.8-1.034	2.1-2.4	8.8	8-10	[5,25]
Blast furnace slags	Metallurgic furnaces	2800	0.7	1-1.5	-	19	[28,32]
Coal fly ashes sintered ceramics	Coal fired power plant	2000	0.735-1.3	1.3-2.1	-	10-1200	[25,29,33]

2.3 Reference Alumina

Several past studies showed that alumina has quite high corrosion resistance to aluminium alloys such as Al99.7% and AlSi25% [8,10]. Thus, it is expected to be inert in molten AlSi5% and AlSi12%. In order to confirm its corrosion resistance, this study included an additional group of alumina, which will undergo same thermal treatment as the recycled ceramic samples. If the alumina group confirms the inert behaviour, its conservation of both surface aspect and element composition will serve as a reference for the results obtained from recycled ceramics. The alumina sample used here is standard 99% Alumina purchased from Latech Scientific Supply Pte.Ltd [34].

3. Methodology

The compatibility study follows the methodology of sample preparation, corrosion test in the tube furnace, and post-corrosion characterization by Environmental Scanning Electron Microscopy, Energy Dispersive Spectrometry and X-ray diffractometer.

3.1 Sample preparation

Figure 3 shows the materials and testing rig employed in the thermal treatment. The ceramic materials were cut into small rectangular samples with the dimensions of 20×20×10 mm. Then the contact surfaces were polished to ensure flatness. The aluminium alloys were initially available in the shape of bars. In order to increase the contact area with ceramic samples, the bars were compressed into thin plates by hydraulic press. After cleaned by ultrasonic device, the samples were held in alumina crucibles with aluminium alloy plates placed on top of their upper surface.

Figure 2 (a) recycled ceramic samples (20×20×10mm); (b) crucible setup

3.2 Corrosion test

The corrosion test involves thermal treatment of ceramic samples in contact with different aluminium alloys at 1000°C for 100 hours in argon environment. The Nabertherm tube furnace in Figure 3(a) provides thermal treatment and argon environment for the crucibles during the treatment. In order to reduce the thermal gradient along the longitudinal direction of the tube, its two sides exposed outside the furnace were covered with high temperature insulation material Superwool 607. The corrosion test was performed in PROMES laboratory in Perpignan France. The ramping and cooling rate of thermal treatment was strictly controlled as 5°C/second to prevent any thermal shock that could happen inside of the furnace. Since thermal treatment itself might possibly result in the change of sample properties besides their contacts with alloys, for each of the three recycled ceramics, there is a control sample, which underwent the same thermal treatment without being in contact with the alloys. This is to better analyse the corrosion effect while excluding the influence of thermal treatment. Post treatment includes separating the alloys from the ceramic samples, and fine polishing of the sample surfaces prior to the characterizations to expose the sample surface.

Figure 3 (a) schematic representation of furnace setup; (b) furnace used in thermal treatment

3.3 Post-corrosion characterization with Environmental Scanning Electron Microscopy (ESEM), Energy Dispersive Spectrometry (EDS) and X-ray diffractometer (XRD)

After the thermal treatment, it was important to adopt the appropriate post-corrosion characterization method for result analysis. Since it was forbidden to open the furnace at high temperature due to safety precaution, the samples could not be separated from the alloy until they were cooled down. However, at room temperature, it was hardly possible to separate the ceramic samples from alloy without tearing each part due to the high wettability of alloys on the ceramic sample surfaces. Therefore, the corrosion rate method could not be executed. Eventually, the post-corrosion characterization was determined following the procedure of fine polishing of ceramic samples' surfaces, Environmental Scanning Electron Microscopy for surface inspection, X-ray energy-dispersive spectrometry to examine element composition of sample surfaces, and X-ray diffractometer to analyse the structural modification.

The Environmental Scanning Electron Microscopy SEM Hitachi 5-4500 was used to examine the surface topology of the upper surfaces of the samples and their cross-section images. For complicated topologies, chemical contrast images were also examined. The SEM apparatus operates at 15 kV in low vacuum mode. A Noran XEDS (X-ray energy-dispersive spectrometry) detector was also adopted to study the composition of the samples, both globally across the surface and locally to analyse the composition of some specific points. The EDS characterization employs a fixed penetration depth of 2 μm for this study. The measurement provides an accuracy of close to 2%.

The X-ray diffractometer analysis was performed at room temperature using a PANalytical XPert Pro diffractometer (CuK α radiation, $\lambda = 0.15418 \text{ nm}$). X-ray diffraction measurements of 2 θ symmetrical scans were made over an angular range of 10 to 80°. The step size and the time per step were fixed at 0.01° and 20 s, respectively. The X-ray diffraction spectra were recorded and studied using the PANalytical software. The instrumental function was determined using a reference material (SRM 660, lanthanum hexaboride, LaB6 polycrystalline sample) and could be expressed by a polynomial function. The crystalline phases were identified by comparison of the obtained spectra with available models of standard references in database provided by International Centre for diffraction data [35].

4. Results and discussions

4.1 Interaction of Alumina with aluminium alloys as a reference group

Previous investigations have reported the inert behaviour of alumina with aluminium alloys such as aluminium and Aluminium-Si25%. However, it is the first time in literature to report alumina's interaction with AlSi5% and AlSi12%. The first visual observation indicates a high wettability of all three alloys on Alumina sample surfaces. Thus, it was necessary to expose the sample surfaces by fine-polishing them before the examination under microscopy. The SEM result, shown in Figure 4, demonstrates almost no surface disturbance on post-contact surfaces. Compared with reference surface, all post-contact surfaces remain intact and preserve surface aspect such as texture, porosity and colour. Table 5 presents the element composition of all sample surfaces with a depth of 2 μm . The dominating elements are oxygen

and aluminium, corresponding to the content of high purity aluminium oxide. The composition varies slightly within the uncertainty range of EDS (2%), thus there is no significant deviation of elements' composition between four sample surfaces. The existence of heavy metal Au on sample surfaces of alumina/AlSi5% and alumina/AlSi12% is due to the necessary pre-conditioning metallization of sample surface prior to the scan to increase the conductivity of the samples. Since alumina presents obvious corrosion resistance to all alloys, the XRD analysis does not report the alumina group.

Figure 4 Surface topology of Alumina samples (a) reference; (b) Al99% post-contact; (c) AlSi5% post-contact; (d) AlSi12% post-contact

Table 5 Chemical compositions of tested Alumina in normalized weight percentage

	Reference alumina	Alumina/Al99%	Alumina/AlSi5%	Alumina/AlSi12%
O	31.86	31.42	32.58	32.05
Al	68.14	68.58	65.99	66.19
Ca	0	0	0	0.53
Fe	0	0	0.74	0
Au	0	0	0.69	1.24

4.2 Interaction of Cofalit with aluminium alloys

The first general visual inspection of sample surfaces after corrosion test reports that all three alloys have very low wettability of the Cofalit surfaces. It was easy to remove the alloy samples from ceramic surfaces by hand, followed by fine polishing to remove the remaining alloys. Figure 5 shows the topology view of Cofalit samples under the microscope. Compared with the reference sample, there are surface disturbances observed in all three post-contact samples. Figure 5(b) illustrates very minor changes on Cofalit/Al99% compared with reference Cofalit, while Figure 5(c) and (d) display that there is a significant increase of surface heterogeneity for Cofalit/AlSi5% and Cofalit/AlSi12%. A number of light

grey spots are observed on sample Cofalit/AlSi5%, corresponding to locations with high iron concentrations, confirmed by point EDS analysis. Major surface depressions, holes and micro cracks also appear in samples Cofalit/AlSi5% and Cofalit/AlSi12%. Cross-section view in Figure 6 illustrates the same trend. The element composition of all tested Cofalit samples from the EDS results are concluded in Table 6. To increase the statistical reliability of data, each composition is a global average of several local measurements. It can be inferred from the results that Cofalit samples contain large amount of silicon and calcium oxides, and other oxides such as aluminium and magnesium oxides. The weight percentage of two main elements, Silicon and Calcium, decreased significantly on Cofalit/AlSi5% and Cofalit/AlSi12%. On the contrary, there is a major increase of iron content in these two groups, corresponding to the light grey spots in the SEM images in Figure 5. This phenomenon indicates possible surface interaction. If compared with alumina group, the result given by the Cofalit/Al99% shows quite decent performance in terms of conservation of both surface aspect and element composition, while Cofalit/AlSi5% and Cofalit/AlSi12% do not.

Figure 5 Surface topology of Cofalit samples (a) reference; (b) Al99% post-contact; (c) AlSi5% post-contact; (d) AlSi12% post-contact

Figure 6 Cross-section topology of Cofalit samples: (a) reference; (b) Al99% post-contact ; (c) AlSi5% post-contact; (d) AlSi12% post-contact

In order to further study the change of micro-structure, the X-ray diffraction patterns for Cofalit group are obtained and presented in Figure 7. The results indicate the augite aluminium as the main phase, diopside ferroan and clinopyroxene as the other phases. All phases belong to the same family of pyroxene. All signal peaks representing the main phases are similar between samples, except for minor differences in the strength of the peaks. The heights of peaks indicate different phase composition, which is summarised in Table 7. In comparison with raw Cofalit, the three post-contact samples have degradations in the diopside phase, resulting a progressively increasing of augite phase. This trend is not obvious for Cofalit/Al99%, but particularly noteworthy for Cofalit/AlSi5% and Cofalit/AlSi12%. A new phase Clinopyroxene appeared in Cofalit/AlSi5%. All the evidence indicates interactions of Al-Si alloys with the sample surface but without modifying the structure.

Taking into consideration the change of surface aspect, element composition, and the evolution of chemical species, it is safe to conclude that Cofalit undergoes insignificant interaction with AlSi99% and thus could be recommended to be used with molten AlSi99% at high temperature. However, there are major interactions of Cofalit with AlSi5% and AlSi12%, and as a result they do not qualify as a potential encapsulation material for these three alloys.

Table 6 Element compositions of tested Cofalit in normalized weight percentage

Atomic elements	Reference Cofalit	Cofalit/Al99%	Cofalit/AlSi5%	Cofalit/AlSi12%
C	2.05	4.17	0	0
O	25.03	25.81	23.31	17.37
Na	0.75	0.60	3.78	7.21
Mg	2.55	2.43	0	0
Al	4.28	3.79	4.05	3.35

Si	21.96	18.74	13.28	10.3
Cl	0	0.25	2.31	3.28
K	0.6	0.51	1.42	0.65
Ca	25.00	23.52	16.83	12.69
Ti	0.38	0.65	1.19	0.83
Fe	17.40	19.52	33.84	44.33

Figure 7 X-ray diffraction patterns of the Cofalit group (Au: Augite; D: Diopside; C: Clynopyroxene)

Table 7 Observed phases in all samples from XRD analysis

Sample	Observed phases
Cofalit reference	Augite aluminium (59%) $\text{Ca}(\text{Mg}, \text{Al}, \text{Fe})\text{Si}_2\text{O}_6$ Diopside ferroan (41%) $\text{Ca}(\text{Mg}_{0.82}\text{Fe}_{0.18})\text{Si}_2\text{O}_6$
Cofalit/Al99%	Augite (58%) $(\text{Mg}, \text{Fe}, \text{Al}, \text{Ti})(\text{Ca}, \text{Fe}, \text{Na}, \text{Mn})(\text{Si}, \text{Al})_2\text{O}_6$ Diopside 42% $(\text{Mg}_{0.6}\text{Fe}_{0.2}\text{Al}_{0.2})\text{Ca}(\text{Si}_{1.5}\text{Al}_{0.5})\text{O}_6$
Cofalit/AlSi5%	Augite (86%), clynopyroxene (or calcium iron silicate) (14%)
Cofalit/AlSi12%	Augite (72%) diopside (28%)
Slag reference	Melilite (53%) $(\text{Ca}, \text{Na})_2(\text{Mg}, \text{Fe}, \text{Al})[(\text{Al}, \text{Si})\text{SiO}_7]$ wollastonite 1A (47%) CaSiO_3
Slag/Al99%	Melilite (70%) , wollastonite 1A (30%)
Slag/AlSi5%	Melilite (57%) , wollastonite 1A (43%)
Slag/AlSi12%	Melilite (48%) , wollastonite 1A (52%)
CFA reference	Mullite $\text{Al}_{4.52}\text{Si}_{1.48}\text{O}_{9.74}$
CFA/Al99%	Mullite (38%), anorthite(19%) $\alpha\text{-Al}_2\text{O}_3$ (43%)
CFA/AlSi5%	Anorthite (89%) $(\text{Ca}_{0.89}\text{Na}_{0.11})(\text{Al}_{1.89}\text{Si}_{0.11})\text{Si}_2\text{O}_8$, iron oxide (11%) $\text{Fe}_{2.133}\text{O}_{3.2}$
CFA/AlSi12%	Mullite(16.8%), $\alpha\text{-Al}_2\text{O}_3$ (40.6%), anorthite($\text{Ca}_{0.8}\text{Na}_{0.2}\text{AlSi}_{2.23}\text{O}_8$) (42.6%)

4.3 Interaction of blast furnace slag with aluminium alloys

First, the general visual inspection reveals that the alloys have medium wettability of slag sample surfaces. Figure 8 presents the surface topology of four slag samples under SEM. As we can see, there is no significant difference between the surface topology of slag/Al99% or slag/AlSi5% compared with the reference sample. However, the sample which had contact with AlSi12% shows more heterogeneity on the surface. In order to check if there was a corroded layer formed at the interface, cross section of

slag/AlSi12% is put under examination with results shown in Figure 9, in chemical contrast. Compared with the reference sample, the slag which had contact with AlSi12% does not reveal any significant difference at the cross-section. There is no corrosion layer visible. The white spots observed in Figure 8(d) could be due to attached alloy residue. Table 8 displays the element composition of all slag samples from EDS analysis. The main elements detected are oxygen, silicon and calcium, indicating a large amount of silicon and calcium oxides. There are also small amounts of aluminium and iron oxides presented. There are slight deviations in elements composition between post-contact samples and reference sample. However, the deviations are not statistically significant in the presence of the uncertainty of EDS method. This result is particularly similar to the result obtained for the alumina group. In both groups, the surfaces did not present noteworthy changes and the element compositions are preserved.

Figure 8 Surface topology of slag (a) reference sample; (b) Al99% post-contact; (c) AlSi5% post-contact; (d) AlSi12% post-contact

Figure 9 Cross-section view of slag sample (a) reference in chemical contrast; (b) AlSi12% post-contact in chemical contrast

From the XRD results, two phases are identified in the slag samples: melilite $(\text{Ca,Na})_2(\text{Mg,Fe,Al})[(\text{Al,Si})\text{SiO}_7]$ which crystallizes in the tetragonal system (space group P-421m) and wollastonite 1A-CaSiO_3 in the anortic system with a space group P-1. Figure 10 presents similar XRD patterns within the slag group, with minor differences in the peaks heights and areas. From Table 7, which concludes the phase composition of each sample identified in XRD, it is observed that there is a major degradation of the wollastonite phase in Slag/Al99% and a corresponding increase of melilite in the same sample, indicating an interaction without change of structure. Slag/AlSi5% and slag/AlSi12% present minor changes of composition compared with reference sample. This diffusion seems to be related to the viscosity of the alloy, the roughness of the contact surface, the pore size and the wettability (contact angles) of the alloy on the contact surface.

In general, blast furnace slag presents good thermochemical stability in contact with AlSi5% and AlSi12% due to conserved internal composition and the absence of corroded layer. However, it is not recommended to encapsulate Al99% since major fraction change of phases is detected in Slag/Al99% sample.

Table 8 Element composition of tested slag samples in normalized weight percentage

Atomic elements	Reference slag	Slag/Al99%	Slag/AlSi5%	Slag/AlSi12%
O	28.85	29.34	27.77	29.16
Mg	5	4.96	3.54	4.26
Al	4.5	5.73	3	5.45
Si	23.76	24.11	26.55	23.79
Ca	32.77	31.37	35.44	33.62
Ti	0.9	0.95	0.79	0.51
Fe	4.23	3.53	2.91	3.22

Figure 10 X-ray diffraction patterns of the slag group (Me : Melilite ; W : Wollastonie)

4.4 Interaction of coal Fly Ashes (CFA) sintered ceramics with aluminium alloys

The first visual inspection of the sample surfaces reveals that the alloys have very high wettability on CFA sintered ceramic. In fact, the alloys seem to have “melted” into the ceramics and form visible

corroded layers in the samples. It is quite interesting to see from Figure 11 that on all three post-contacted surfaces, porosities were filled up with alloys during the interaction. Further inspection on the sample cross-sections (in Figure 12) reveals the substantial change of sample texture if comparing the corroded with non-corroded layers. The corroded layers have compact and dense texture while the non-corroded one has clearly similar porous and arbitrary texture as the reference sample. Further, the thickness of the corroded layers are measured as 0.8-4 mm for CFA/Al99%, 1-1.5 mm for CFA/AlSi5%, and 1.2 mm CFA/AlSi12%. The extreme surface modification shows the opposite result compared with the alumina group. The EDS result reveals the same phenomenon.

Figure 11 Surface topology of CFA sintered ceramic (a) reference sample; (b) Al99% post-contact; (c) AlSi5% post-contact; (d) AlSi12% post-contact

Figure 12 Cross-section topology of CFA sintered ceramic sample (a) reference sample; (b) Al99% post-contact; (c) AlSi5% post-contact; (d) AlSi12% post-contact

The global EDS characterization determined the surface composition as presented in Table 9. The dominating elements are oxygen, aluminium and silicon, indicating the possible composition of aluminium and silicon oxides. In addition, there might be a small amount of iron and calcium oxides. Compared with the reference sample, there is a substantial increase of Al content, and on the contrary, a decrease of Si and Fe content in all post-contact samples. This can be explained by the infiltration of aluminium alloy into the porous structure of the samples. However, it is unknown if any structural modification took place. Therefore, the XRD results are obtained to further understand the process.

The XRD results show that the main phases in the CFA samples include mullite $\text{Al}_{4.52}\text{Si}_{1.48}\text{O}_{9.74}$, solid solution, which crystallizes in the orthorhombic structure space group (Pbam), anorthite ($\text{Ca}_{0.49}\text{Na}_{0.11}$) ($\text{Al}_{11.89}\text{Si}_{0.11}$) Si_2O_8 in anorthic structure (space group P-1) and iron oxide $\text{Fe}_{2.133}\text{O}_{3.2}$ which crystallizes in tetragonal structure (space group P43212). Mullite is a non-stoichiometric compound with the following formula [36]:

$$1) \quad \text{Al}_2^{\text{VI}}[\text{Al}_{2+2x}\text{Si}_{2-2x}]^{\text{IV}}\text{O}_{10-x}, 0.17 < x < 0.59 \quad (\text{Equation-1})$$

derived from the well-known sillimanite (Al_2SiO_5) structure obtained by substituting aluminium atoms by silicon in tetrahedral site, creating oxygen vacancies to preserve the electro-neutrality:

The phase compositions of each sample identified in XRD are presented in Table 7. Compared with reference CFA sintered ceramic, CFA/Al99% and CFA/AlSi12% reveal the appearance of over 40% of α -alumina phase, with a corresponding decrease of mullite phase. CFA/AlSi5% has no mullite phase identified, but a majority of anorthite and a small portion of iron oxide. The presence of the α -alumina phase arises from the oxidation of aluminium during cooling, which fills into the porosity of CFA ceramic samples. It was previously studied and reported in [37] the infiltration of molten aluminium alloys into ceramic structures which results in the creation of a ceramic/aluminium composite. It shows that the infiltration depth is associated with the size of the porosity, the additional agents such as silicon in the molten alloys. The synthesized composite usually presents different mechanical and thermal properties. In our case, there was a structure discontinuity between the infiltrated part and the remained part of the ceramic sample. The infiltrated part fell apart from the original sample block after the samples cooled down.

From the above result, it is observed that apart from mullite and α -alumina phase, certain new phases were generated during the thermal treatment, including anorthite, and iron oxide. The lack of corrosion resistance of CFA ceramic samples is due to the presence of the mullite phase, which exhibits thermodynamic instability in presence of aluminium. The same behaviour was observed in a previous study about mullite in contact with Al-Si alloy [38]. All the evidences from SEM, EDS and XRD

confirmed that CFA sintered ceramic is not thermochemical compatible with either of the tested alloys, and it is consequently not recommended for the encapsulation in the PCM technology.

Table 9 Chemical composition of tested slag samples in normalized weight percentage

Atomic elements	Reference CFA	CFA/Al99%	CFA/AlSi5%	CFA/AlSi12%
O	32.93	21.78	24.05	25.46
Na	0.06	0	0	0
Mg	0.33	1.91	0	0
Al	15.34	57.55	57.88	62.66
Si	30.94	8.11	12.49	6.08
K	3.74	0	0	0
Ca	5.82	3.58	2.02	4.97
Ti	1.49	2.27	0	0
Fe	9.36	1.32	3.56	0.83

Figure 13 X-ray diffraction patterns of the CFA/alloys group (M : Mullite ; An : Anorthite ; Fe : Iron oxide ; A : Aluminum oxide)

5. Conclusions

Prior to this work, numerous studies were dedicated to the compatibility between liquid metals and commercial ceramics [8,10,37], and molten salts with inorganic industrial waste ceramics [13,39,40]. Nonetheless, few researches have reported the compatibility behaviour between liquid metals and the inorganic industrial waste ceramics. With the purpose of examining the potential application for recycled ceramics as encapsulation material for molten aluminium alloys, this paper presents a compatibility study of molten aluminium alloys with recycled ceramics at high temperature. Three industrial waste ceramics, asbestos containing waste (Cofalit), blast furnace slag, and coal fly ashes sintered ceramics were placed in tube furnace in the argon environment for 100 hours at 1000 °C, while being in contact with three Al-based alloys, Al99%, AlSi5% and AlSi12%. A group of alumina samples underwent same treatment to confirm its corrosion resistance and to serve as a reference group for good encapsulation ceramics. The post-characterization with Scanning Electron Microscopy, Energy Dispersive Spectrometry and X-ray diffractometer revealed the following results:

- Alumina presents inert behaviour in all molten aluminium alloys.
- Cofalit has a good conservation of the surface aspect and composition in molten Al99%, but undergoes substantial surface reaction with molten AlSi5% and AlSi12%. Thus, it is recommended to be used in direct contact with molten Al99% but not AlSi5% and AlSi12%.
- Similar with alumina, blast furnace slag has a good conservation of both surface aspect and chemical composition with molten AlSi5% and AlSi12%. So it is recommended to be used in direct contact with these two alloys at high temperature.
- Coal fly ashes sintered ceramics had major chemical interactions with all three alloys. Therefore, it is not recommended to be used in direct contact with these alloys at high temperature.

Judging from the results, Cofalit and blast furnace slag can serve as a potential candidate for the encapsulation in PCM-brick technology mentioned in the introduction [6]. In order to further justify its applicability as an encapsulation material, a design-optimization approach has to be completed. First, it is crucial to design the PCM-based refractory brick with encapsulation ceramic made of proposed recycled ceramics, and conduct the stress calculation to see if it is able to withstand high thermal stress due to significant difference between expansion rates of ceramics and alloy in the dynamic environment. Second, a design optimization based on the heat transfer analysis of the PCM-brick needs to be performed. Thirdly, it is important to conduct the laboratory testing/prototyping of the PCM brick to examine the long-time cyclic performance in terms of buffering effect, system stability and safety of operation.

Since both Cofalit and blast furnace slag are cheaply produced with low embodied energy, they exhibits great potential to be economically viable alternatives to the commercial ceramics. This work identified their excellent corrosion resistance to molten AlSi5% and AlSi12%, which could further help engineers to establish cheap alternative design solutions to their specific high temperature applications.

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