Manufacturing Cordierite Mullite and Mullite Filters from Sanitary Ware Kiln Wastes for Use in Metal Casting Industry

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Abstract: The metallic melts shaped with casting method include impurities within the product. The ceramic foam filters are used for removing these impurities. Proverbially, the mullite based filters is suitable for high temperature applications as its technical features such as low coefficient of thermal expansion, chemical and mechanical stability at higher temperature and thermal shock resistance. Due to these properties, mullite is the potential matrix material for relatively higher temperature applications. In this study, the wasted sanitary ware kiln materials are utilized to investigate as the source of material for mullite and cordierite mullite ceramic filter. In this context, Ece Banyo Sanitary Ware Plant’s kiln roller materials and kiln plates are used (both of which are cordierite-mullite and alumina mullite) in the manufacturing ceramic foam filter. This work is a preliminary study about how to utilize wasted kiln materials in order to manufacture value-added materials. Physical, chemical, mineralogical, thermo gravimetric, micro-structure and sintering behavior tests are made over these prescription samples. Also these tests have been made for nowadays marketing filters-mullite and cordierite mullite-for benchmarking. On the basis of the test results, the best suitable prescription specimen is being selected and shaped with foaming process. Furthermore, the shaped filters are being tested in casting process. It is concluded that a mullite-cordierite based foam filter production which can be used in the metal casting industry is proven to be realized by recycling mullite and cordierite-mullite based ceramic materials that are used in the ceramic sanitary ware industry.

Key words: Sanitary ware, cordierite, mullite, waste recovery.

1. Introduction

Mullite, which is rarely natural phase, is the most common solid phase of alumina and silicate. It is preferred in high temperature applications because of its low coefficient of thermal expansion, high chemical stability and mechanical toughness. It is the most important technologic material which is the mid-phase of Al₂O₃-SiO₂ system. In general, it can be produced as transparent, translucent and opaque.

The mullite—3Al₂O₃·2SiO₂—is the silicoaluminous refractory material for excellence. Its high melting point (≈1,800 °C), good thermal expansion coefficient (≈3.5 × 10⁻⁶ °C), and excellent characteristics to support moderate thermal shocks make it irreplaceable in most of silica-alumina refractory formulations [1].

The different crystal phase transformation shows up in ceramic suspension depending upon thermal efficient and mineral concentration. Kaolinites transform into meta-kaolinite at 500-600 °C. Plasticity is changed due to endothermic reaction at this stage. The composed meta-kaolinite transforms to mullite and cristobalite with strongly exothermic reaction at 830 °C. The terminal breakdown pressure of the anhydrous phase is form to enstatite, sillimanite and quartz at 830 °C [2].

Cordierite and mullite materials have high sensitivity, elevated thermal and chemical resistance and stability, very low coefficient of thermal expansion with features to be used as high temperature application materials. Also they can be used as...
variable temperature application.

The mullite crystal system is orthorhombic and needle-like crystal shaped structure in (001) plane. In Fig. 1, the SEM image of mullite crystals originates, indicating the secondary mullite crystal formations in vitreous phase.

Mullite is used with high temperature applications due to its low thermal coefficient of expansion and high thermal shock resistance. Also mullite has high mechanic resistance and chemical stability at high temperature [3].

Cordierite is the important phase for MgO-Al₂O₃-SiO₂ phase system. It has low coefficient of thermal expansion, perfectly thermal shock resistance, high chemical strength, high refractoriness and high mechanical strength. The sol gel and glass crystallization methods are used in cordierite synthesis. The most commonly used methods are solid phase reaction synthesis and crystallization of glass dusts. High purity cordierite is synthesized with chemical methods like sol-gel.

Metal cast filters are sold on the market in two ways. One of these is used as a honey pellet and is mainly used to provide melt flow into the melt in the mold. The melt-flowed molten metal is poured into the mold without causing any layer or air defect, and the surface quality of the product is better than that of products that are not used in the filter-free molds.

Another type of filter is foam filtration. The main task of foam filters is to remove the inclusions in the molten metal rather than making the flow into a laminate. In this regard, the melt ensures that the slag and non-metallic materials in the metal are retained in the metallic material without mixing and that a high quality product is obtained.

Ceramic foam filter is a product with low bulk density, high porosity and three-dimensional web like structure. Ceramic foam filter has excellent properties such as high temperature resistance, strong chemical corrosion resistance, and large surface area as a result of high porosity; it is widely used in molten metal filtration to remove undesirable nonmetallic inclusions in the melt.

Metal casting process begins by creating a mold, which is the reverse shape of the part. The mold is made from a refractory material such as silica sand. Silica sand is usually used in mold production. The metal casting mold has a feeder which is used for molten metal to enter into mold. The feeder includes filtration part which is needed for ceramic filter (Fig. 2).

Molten metal presents many opportunities for contamination, often with particles as small as a few microns. This contamination may be slag, dross, or pieces of refractory from the melting crucible. Metal that contains impurities will reduce strength, and this usually requires a heavier section thickness to compensate for the lower strength. Impurities also present serious stress points if they are located on the surface of the castings that are subjected to mechanical forces.

Fig. 1  SEM image of secondary needle like mullite phase originated in vitreous phase.
Filters will collect dross particles and inclusions that are larger than the filter hole or pore size on their upstream face. These particles are unable to pass through the casting cavity due to their physical size [4].

Metal casting foam filters are used for filtration in metal casting process. This foam filters provide smooth surface due to laminar flow of metal melt. Also filters filtrate the inclusions in metal melt.

Metal casting filters are shaped as honeycomb, foam and cellular. Ceramic foam filter is the most common and efficient used in metal casting industries. Foam filters gained advantages due to its 3D network shape as high porosity clinker collection, flat surface area, low flow resistance and good filtration. Ceramic foam filters create a simplified feeder to melted metal. Also it regulates the metal product’s metallurgic structure and perfect surface quality after engraving process [3].

Ceramic foam filter’s chief production method is polymer foam shaping method. In this technique, the polymer foam dips into ceramic suspension and makes a burning process before sintering. The polymer foam’s surface quality is important for continuous and smooth coating. The adhesive materials are used for ceramic suspension stick over the foam material’s surface (Fig. 3).

The ability of a ceramic filter to remove inclusions is obviously an important parameter. Ceramic filters are generally more efficient at removing micro inclusions than traditional methods such as extensive running systems and whirl gates (Table 1) [3].

The ceramic foam filters requirements are as follow:
- Excellent stiffness and toughness,
- Filtrate the ashes and clinkers in melted metal,
- Optimum mesh size for permeability,
- Reduce molten metal turbulence and improve molten metal distribution and flow.
Table 1  Advantages and disadvantages of ceramic foam filters [4].

| Advantages                                      | Disadvantages                                    |
|------------------------------------------------|-------------------------------------------------|
| High porosity percentage                       | Expensive                                        |
| The filtration of inclusion increase because of its network shaped | Contamination in melted metal because of its thin network shape and sharp edges |
| Chemical filtration                             |                                                  |
| Screening efficiency is high                   |                                                  |

Fig. 4  Roller kiln’s cordierite roller materials [5].

2. Experimental Procedure

In this study, the waste sanitary ware kiln materials are used for mullite and cordierite-mullite foam filter. Within this scope, Ece Banyo Gereçleri San. ve Tic. A.Ş.’s which is the 3rd biggest sanitary ware manufacturer in Turkey, cordierite and mullite wasted kiln materials are utilized. The roller bars and kiln plates are checked routine and these materials are replaced with new ones. This process takes nearly 3 months for all the materials to be replaced. Also the cordierite-mullite plates used in roller kilns replaced nearly 1 year. These materials are grained and used in foam filter manufacturing (Fig. 4).

Ece Banyo has 3 roller sanitary ware kilns and one tunnel kiln in its production area. The kiln materials used in this kilns are replaced periodically. The materials are changed due to abrasion and cracking. First, these materials are grounded into ball mill and dried in dryers. The cordierite-mullite dusts are used in ceramic foam filter suspension. Ten different filter prescriptions are being prepared and rheological, physical, mineralogical, chemical, thermal and micro-structure analyses are done.

The market filter has been supplied by the People’s Republic of China lately. Although these filters are disposable and partly portable, they are costly for users due to freight costs and shipping costs. Iron casting companies using these filters are limiting their use of filters due to high freight rates.

First of all, the literature search has been done. In this period, the technical specialties and scientific articles and studies are searched. Also the market cordierite and mullite based filter’s chemical, mineralogical, micro-structures and sintering behaviors are/will be examined. The metal casting companies are/will be investigated in Çorum province.

The right prescription is chosen against market filter’s characterization results. The chosen prescription’s rheological and physical specifications are done based on ceramic casting suspension input control test method. These methods are as follow:

- Determination of density test;
- Determination of viscosity test;
- Determination of dry and fired shrinkage;
- Water absorption;
- Loss of ignition;
- Deformation test;

In the second period of this project, the prescription
studies are made for filter manufacturing. The raw materials used in prescription are determined.

The filter’s prescriptions are sintered at different temperatures in experimental kiln in Ece Banyo. Sintered materials will determine the mineralogical changes of foam filtrate at different temperature ranges. Also the sintering behavior tests are made with optical dilatometer.

These tests are performed in Ece Banyo R&D Center’s Ceramic Materials Development Laboratory. Chemical, thermal and mineralogical tests are/will be made in Ceramic Research Center in Anadolu University. Sintering behavior and thermal expansion tests are/will be made in Ece Banyo.

The characteristics of the mullit-based ceramic foam filter to be produced are/will be the same as the mullit-based ceramic filters on the market. The aim of the project is to produce a value-added product to reduce the input costs.

About 21 tons of cordierite mullite bars and 8 tons of mullite kiln plates cast away to wastage per year. The cost percentages of these materials are calculated as 150 k€ which is relatively high in budget.

The prescriptions are/will be made based on cordierite based kiln plates and alumina based kiln rollers. Also a plastic clay and kaolinite based kaolin are/will be used to bond the refractory based materials in suspension. The kaolinite based raw materials have high Al₂O₃. Also plastic clays have some impurities which are Fe₂O₃ and TiO₂. In literature, the cordierite mullite based filters have nearly 6% of MgO and 40-45% Al₂O₃ and SiO₂. Clays and kaolinite based raw materials are suppressed by the cordierite formation. The calcined magnesia is/will be used to generate cordierite inside the glassy phase. Other MgO based materials are/will be used such as dolomite or talc.

The properties of the various raw materials used in the prescriptions will be examined with the cordierite-based refractory materials used as the recycling material. The sintering attempts to be made in this context will be between 1,230 and 1,290 °C, which is the formation temperature range of the secondary mullites.

Ceramic sanitary ware materials have a sintering temperature of approximately 1,200-1,230 °C. Tunnel kilns are usually used in bigger production sites. The burner array in the tunnel kilns is placed in the lower parts of the kiln cars and in the upper parts so as the fire will not come into the products. In this type of kiln design, the temperatures in the lower parts of the kiln cars are 1,250-1,270 °C. Cordierite-based foam filters to be produced within the scope of the study are sintered in the ceramic sanitary ware production furnace according to the sintering temperature resulting from the experimental works and the desired structure. Thus, no energy costs will be incurred for the construction of the filter.

Mullite is a Al₂O₃-SiO₂ based material which is generated at high temperature with these oxides. The secondary mullite phases begin to form within the vitreous phase in a hexagonal loop at 1,230 °C. The secondary mullite phases are mainly due to meta kaolin transformation. Secondary mullite phases are intimately related to the presence of the glassy phase. The secondary mullite crystal’s height growths in glassy phases are depended on grain size distribution of mullite particles.

The middle part of a ceramic filter is depended pressure imposed by the molten metal flow. Filter edges are embedded in the mold and are not in contact with the molten metal. The density of the middle part of the filter is different from the edges and is commonly referred to as the filter bulk density [6]. The bulk density of ceramic foam filter will be obtained due to sample edges.

In third part of the project, the produced foam filter’s characterization specialties will be compared with market filters. The experiments will be carried out in a factory that performs metal casting by taking samples from the produced ceramic foam filters. The parameters that will be observed in these process are:

- Filtration productivity of ceramic foam filter,
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Fig. 5  XRD patterns of the prescription.

- Deformation in thermal heaviness,
- Thermal strength of ceramic filter,
- Maximum temperature strain,
- Blockage of ceramic filters pores with melted metal,
- Thickness of impurities over foam filter.

The shaping and modeling process of ceramic foam filter are difficult and important. Because of filtration efficiency, filtrating part’s particle size and blockage of filter’s pores are depended to the particle size and modeling of the filter. The ceramic foam filters mesh size will determined during the project due to casting tests.

Cordierite, mullite and corundum phases were encountered in the market filter where characterization analyzes were made (Fig. 5). According to chemical analyzes, the MgO ratio is sufficient with respect to cordierite formation. Based on these results, recipe studies will be carried out and a metal casting foam filter will be made which will be the same feature. The thermal expansion coefficient values, resistance temperatures and pore structure of the prepared filter will be examined and the metal casting industry will be tested.

According to the characterization analysis of the first recipe studies, it was observed that cordierite formation was supported due to the increase of MgO ratio in the prescriptions enriched with calcined magnesite. Especially when the results of the chemical analysis and the results of the market filter analysis are compared, it is seen that the percentage of the MgO ratios is similar.

In prescriptions using dolomite (CaO-MgO-SiO₂), shrinkage values and glow losses were found to increase due to the presence of CaO in raw material and recipe.

3. Conclusion

After this work, a mullite-cordierite based foam filter production which can be used in the metal casting industry will be proven to be realized by recycling mullite and cordierite-mullite based ceramic materials that are used in the ceramic sanitary ware industry. In this respect, it will be ensured that the industrial wastes taken into the environment will be evaluated to protect the environment and become a highly usable product with added value. The input costs (excluding labor and grinding costs) of a foam filter were calculated to be 0.1 €. Mullite-cordierite filter is imported between 0.5 € which is more economical.

Cordierite mullite based filters are used in grey iron, ductile iron, aluminum alloy and non-ferrous alloys casting. The expected maximum work temperature is about 1,500 °C. This gives the high temperature resistance and high thermal shock resistance.

The right prescription was selected due to prescription tests. Foam materials were supplied from the market. Based on the FFC slip rheology used in laboratory-based rheology analysis operations, the FFC slip will form the foam material and will have the ability to obtain a better thickness and homogeneous
shape in different rheological properties. After the determined prescription is prepared in laboratory and done in a large scale, the rheological values determined in the rheology studies will be applied and shaped on the foam material.

Foam filters will be sintered at the sintering temperatures determined in the sanitary ware sintering furnaces of Ece Banyo. Sintered products will be tested in metal casting companies and their usability in the sector will be determined.

“Development of alumina-mullite and mullite filters for metal casting industry from fired ceramic sanitary ware wastes” project was done in 2015 at Ece Banyo R&D Center supported by TÜBİTAK. This project was planned to be finalized in 2018. All experiments were finished. The casting tests indicate that honeycomb filter which is produced with sanitary ware wastes has perfect filtration productivity. The casting temperature was at 1,386 °C which was not deformation after casting.

Ece Banyo R&D Center started its activities in 2015 with the approval of Ministry of Science, Industry and Technology. The activities are continuing with 20 researchers, 12 technicians and 2 support staff. Since the establishment of Ece Banyo R&D Center which has knowledge and experience on ceramic materials, high technology ceramics, innovation of ceramic materials, product design, design and development of ceramic machines, have been started in-house projects and ministry supported projects. The projects outcomes are started to use or marketing from these projects.

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