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ENERGY EFFICIENCY ENHANCEMENT IN THE PRODUCTION OF CERAMICS FOR ADVANCED APPLICATIONS: KEY PRINCIPLES

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ABSTRACT

Glass and ceramic industries fall into the category of energy-intensive emitting combustion gases and particulate matter to the air and considered as Integrated Pollution Prevention and Control installations both in the European Union and Russia. Since early 2000s, traditional sub-sectors including tile and brick manufacturing have been participating in a number of pilot projects intended to assess their environmental performance and energy efficiency evaluate opportunities for implementing Best Available Techniques (BATs) at Russian industries. Based on the results of these projects BATs have been identified and first national BAT standards developed.

In manufacturing technical ceramics, a comprehensive study is yet to be done, while existing sector-specific BATs comprise mostly general approaches to energy consumption optimization and emissions control. Considering materials for advanced applications such as alumina, zirconia or carborundum, where these levels are determined by strict process parameters, a generally accepted practice is to reduce energy consumption by adjusting firing temperature. This allows on one hand, to improve environmental performance of the installations, and on the other hand, to suggest candidate BATs providing the desired effect, namely batch composition adjustment, liquid-phase sintering, and the use of eutectic sintering aids.

The present research addresses a combination of these techniques in production of SiC-based structural ceramics including selection of additives based on their physico-chemical properties (melting point, surface interaction) and the use of pre-fabricated sintering aids with enhanced reactivity. The effects of the additives on sintering behavior were studied for a model material consisting of ultrafine SiC and a eutectic sintering aid in $MgO – Al_2O_3 – Y_2O_3$ system. Such ceramics demonstrated excellent mechanical properties (bending strength of 450 MPa, fracture toughness of 4.0 $MPa \cdot m^{1/2}$, and elasticity modulus of 380 GPa), and its sintering temperature didn't exceed 1900 °C. Commercially available samples of liquid-phase sintered SiC require firing temperatures above 2100 °C, which makes this approach a practically suitable basis to develop an energy efficient SiC ceramics processing technology.

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Keywords: energy-intensive industries, advanced ceramics, silicon carbide, environmental performance, Best Available Techniques.

INTRODUCTION

The present-day approach towards the environment protection and pollution prevention took its final shape in 2010, when the European Council issued the Industrial Emissions Directive (IED, ex Integrated Pollution Prevention and Control Directive, 1996 [1]. This document established a concept of environmental permits for installations, based on implementation of Best Available Techniques (BATs) set in the reference documents (BREFs) issued by the Integrated Pollution Prevention and Control Bureau (IPPC Bureau) of the Joint Research Centre.

Since the early 2000s, a large number of BREFs, both sectoral and 'horizontal' (inter-sectoral), has been drawn up and reviewed as part of the exchange of information between the European Union member states carried out in the framework of Article 13(1) of the IED. Ceramics manufacturing was one of the first industries described in terms of BATs, as this sector is extremely energy-intensive and causes considerable environmental impact.

In the Russian Federation, the environmental legislation reform leads to the transfer from single-medium environmental permits to the integrated ones [2]. The 'BAT Law' [2] was passed in 2014 following more than a decade of the implementation of national and international projects, drawing up national standards on BATs (and especially – BATs for energy efficiency enhancement), drafting model environmental acts for the Commonwealth of Independent States [3 – 5].

The European Reference Document on Best Available Techniques in the Ceramic Manufacturing Industry issued in 2007 [6] covers industrial installations for the manufacture of ceramic products by firing stoneware and porcelain. This industrial sector encompasses a wide range of raw materials and manufacturing techniques, but all involve the selection of clays or other mainly inorganic materials which are processed, dried and fired. The Russian BREF issued in 2015 has a similar structure but drawn up as the result of the national environmental and energy efficiency benchmarking and information exchange organised by the Ministry for Industry and Trade and the national BAT Bureau [7]. The major sub-sectors addressed in BREFs, which are based on the ceramic products manufactured are as follows:

- wall and floor tiles;
- bricks and roof tiles;
- table- and ornamental ware (household ceramics);
- refractory products;
- sanitaryware;
- technical ceramics;
- vitrified clay pipes;
- expanded clay aggregates;
- inorganic bonded abrasives.

However, analysis and description of BATs in certain sub-sectors here, especially technical ceramics, lacks in detail due to two main factors. First, sectoral BREFs focus mainly on large-scale production, and this document is of no exception. Second, BREFs are a product of an open exchange of information between operators not only on environment protection measures but also on manufacturing process details (raw and auxiliary materials used, the sources of emissions from the installation, the conditions of the site of the installation et al.), and in case of technical ceramics such transparency is not fully applicable.

APPROACHES TO ENERGY EFFICIENCY ENHANCEMENT IN THE PRODUCTION OF CERAMICS FOR ADVANCED APPLICATIONS

Technical ceramics embraces a broad range of materials with tailored properties for advanced applications in the aerospace and automotive industries (engine parts, catalyst carriers), electronics (substrates, active and reactive units), biomedical products (bone replacement), environment protection (filters) and many others. Technical ceramics manufacturing is without any doubt the most energy- and resource-intensive sub-sector in ceramics production. Due to extremely strict demands on the materials performance, this sector requires the largest variety of raw materials, from high grade clays to rare-earth elements oxides and non-oxide compounds, the highest firing temperatures (i.e., energy consumption), and the most sophisticated processing techniques. Important input and output flows of technical ceramics manufacturing processes, as suggested by the relevant BREF, are presented in the following figure (Fig. 1).

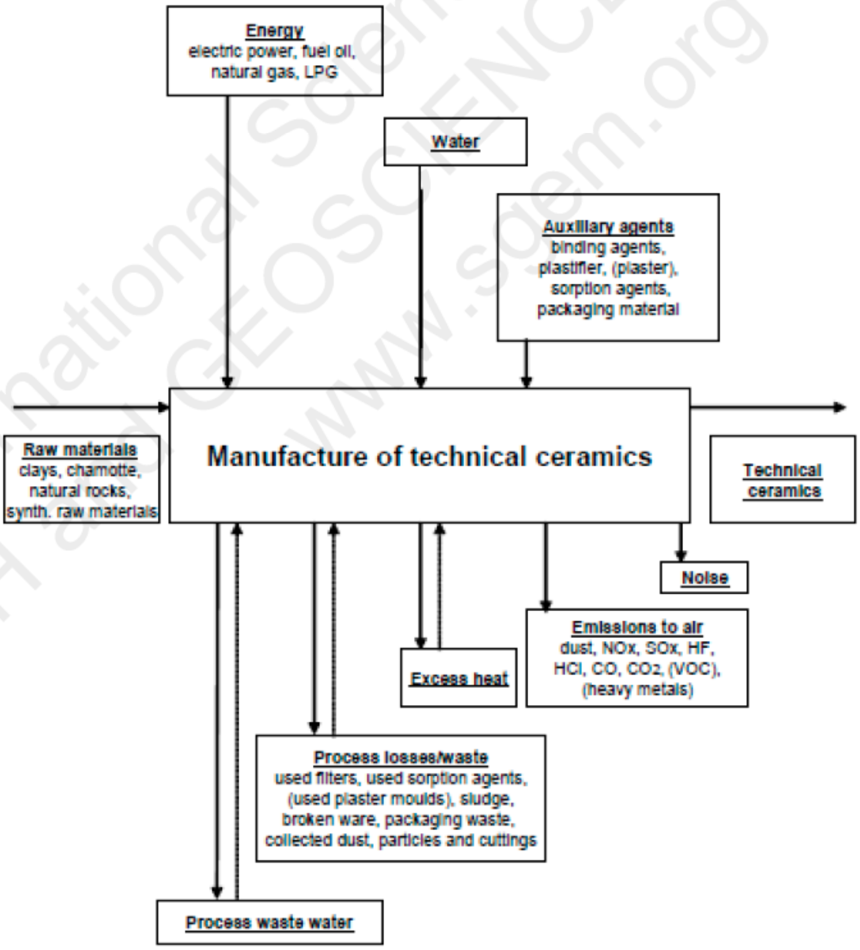

Figure 1. Input and output flows in the manufacture of technical ceramics [6]

The picture is aggravated by a typically poor resource efficiency arising from small-scale production output and a substantial percent defective allowable. For example, product yield for low-temperature cofired ceramics (which includes most commercially available microwave devices) does not exceed 85 % [8], and the rest forms a 'hard-to-recycle' industrial waste, comprising densely sintered bodies of non-ferrous metals, titanium dioxide, alumina, complex rare-earth oxides, boron glasses.

In both the European and Russian BREFs [6, 7], there is a distinction between the primary (built-in, technological) and secondary ('end-of-pipe') Best Available Techniques [9]. No prioritisation of BATs is carried out in the BREFs; although it is assumed that primary solutions providing opportunities for pollution prevention and consumption optimisation are particularly important, while 'end-op-pipe' techniques have also to be considered thoroughly. This approach is selected to recognise the important distinction between techniques for prevention versus control of industrial emissions [10, 11].

In most cases, the sector-specific BATs described in the BREFs [6, 7], comprise emissions control, while a comprehensive study is yet to be done. However, considering conventional materials for advanced applications such as alumina, zirconia or carborundum, where these levels are determined by rigid process parameters, a generally accepted practice is discussed that is to reduce energy consumption by adjusting firing temperature. This allows on one hand, to improve environmental performance of the installations, and on the other hand, to suggest candidate BATs providing the desired effect. Practitioners and researchers typically follow three main routes, namely batch composition adjustment, liquid-phase sintering, and the use of eutectic sintering aids.

SELECTING BEST AVAILABLE TECHNIQUES FOR TECHNICAL CERAMICS: AN EXPERT APPROACH

The present research combined all these routes in manufacturing of high-strength silicon carbide (carborundum) ceramics. At the preliminary stage the manufacturing process was analysed by means of design of experiments procedures, in order to reduce experimental testing especially at high temperatures. The key technological parameters were determined that had most influence on the ceramics properties; those were firing temperature and sintering aid content.

Next, a detailed investigation of the batch influence on materials properties was carried out [12]. This technique is based on closest particle packing structure formation and serves well in the refractories (especially Dinas brick) production to improve mechanical characteristics. However, it is mostly used for materials with coarse structure unlike that of structural SiC ceramics. General provisions for bimodal distribution [13] suggest that the desired particle size ratio should comprise 10:1, and since samples were made of commercially available SiC powder with mean grain size of 3 – 4 μm, the use of sintering aids with mean particle size of 300 – 500 nm was necessary.

Sintering aids were selected based on the results of thermodynamic compatibility analysis among oxide eutectic systems and provided liquid-phase sintering mechanism. The calculated data confirmed the hypothesis, that the most suitable dopants for SiC would be oxides with strong oxophilicity. The higher this value, i.e. the stronger the bond between element and oxygen is, the lower becomes thermodynamic probability of any chemical interaction. This pattern proved most obvious for oxides of metals in Group II of the Periodic table (Ca, Mg, Sr). On the contrary, elements with poor propensity for binding to oxygen (Fe, Mn, Ti, Zr) which showed high mobility of oxygen ions in crystal lattice, were prone to partial reduction and SiC oxidation in a wide temperature range. Therefore, candidate oxides for sintering aids synthesis in the energy-efficient SiC-based ceramics production would be CaO, MgO, SrO, Al_2O_3, Y_2O_3, Sc_2O_3 as well as Ln_2O_3 oxides.

This assumption made, candidate oxide eutectic systems for the present research included $CaO – Al_2O_3 – Y_2O_3$, $Al_2O_3 – ZrO_2$ and $MgO – Al_2O_3 – Y_2O_3$, the content of fine fraction varied from 15 to 50 % vol. in 5 % increments. The densest materials were obtained at fraction ratio 70:30, these samples were uniaxially pressed at 200 MPa and fired at 1900 °C in argon. Process control parameters included open porosity, mean density and bending strength (see Table 1).

Table 1. Structural and mechanical properties of samples with 30 % vol. of eutectic dopant (starting material – α-SiC)

Batch composition	Parameters		
	ρ, g/cm^3	P_o, %	σ_{bend}, MPa
$SiC + CaO – Al_2O_3 – Y_2O_3$	2.73	30.2	94 ± 22
$SiC + MgO – Al_2O_3 – Y_2O_3$	2.84	24.2	132 ± 26
$SiC + Al_2O_3 – ZrO_2$	3.07	26.3	126 ± 24

As it shows from above, the eutectic additive content of 30 % vol. was not sufficient for considerable densification and strengthening of the material. Supposedly, silicon carbide in use was not active for sintering enough to obtain ceramics with improved mechanical properties, gaps between larger SiC grains were too wide to be healed during sintering.

Further tuning of ceramics properties was carried out on compositions with trimodal particle size distribution corresponding to closest trimodal packing principle (particle size ratio – 100:10:1) [13]. Coarse grain size comprising 3 – 5 µm, the finest fraction in such compositions should not exceed 30 – 50 nm. This finest fraction was presented by commercially available silicon carbide nanopowder (n-SiC) with mean particle size 45 – 55 nm. Intermediate fraction with mean particle size 300 – 500 nm, same as above, was presented by eutectic additives which would not only intensify sintering but also form closest particle packing in shaping. With cost concerns in mind the content of n-SiC was kept as low as possible, silicon carbide nanopowder and intermediate fraction content varied from 10 to 20 and from 25 to 35 % vol. respectively in 5 % increments.

It was observed that implying ultrafine dopant makes way for a dramatic increase in structural and mechanical characteristics. Regardless of the eutectics content materials with 15 % vol. of n-SiC exhibited greater strength and far lower open porosity compared to those for ceramics without nano-scale non-oxide constituent. Implementation of ultrafine additive seemingly modifies structure formation process on compacting stage, promotes sintering and alters hardening mechanism, which results in increased mechanical strength of the composite material. Still, ceramics with 15 % vol.

of n-SiC remained porous, and taking into account experimental data on density and porosity of trimodal batches it proved necessary to keep the dopant content at 20 % vol., as displayed in Table 2.

Density and porosity of the samples with $CaO - Al_2O_3 - Y_2O_3$, $MgO - Al_2O_3 - Y_2O_3$ and $Al_2O_3 - ZrO_2$ eutectic additives were quite close regardless of the additive content. As for mechanical characteristics, in otherwise equal conditions ceramics with $MgO - Al_2O_3 - Y_2O_3$ additive exhibited higher values, than that with $CaO - Al_2O_3 - Y_2O_3$ or $Al_2O_3 - ZrO_2$ eutectics. This observation remained true for all investigated trimodal fraction ratios, which clearly favoured magnesia-based additive. According to experimental data, increasing the content of $CaO - Al_2O_3 - Y_2O_3$, $MgO - Al_2O_3 - Y_2O_3$ and $Al_2O_3 - ZrO_2$ additives from 25 to 30 % vol. had little effect on structural properties but significantly augmented bending strength of the material.

Table 2. Structural and mechanical properties of experimental samples containing n-SiC

Batch composition	Parameters		
	ρ, g/cm^3	P_o, %	σ_{bend}, MPa
15 % vol. n-SiC			
SiC + 25 % vol. $CaO - Al_2O_3 - Y_2O_3$	3.08	9.5	220 ± 25
SiC + 30 % vol. $CaO - Al_2O_3 - Y_2O_3$	3.12	8.0	200 ± 20
SiC + 25 % vol. $MgO - Al_2O_3 - Y_2O_3$	3.17	7.5	350 ± 15
SiC + 30 % vol. $MgO - Al_2O_3 - Y_2O_3$	3.29	5.0	310 ± 20
SiC + 25 % vol. $Al_2O_3 - ZrO_2$	3.22	8.5	285 ± 20
SiC + 30 % vol. $Al_2O_3 - ZrO_2$	3.36	6.5	300 ± 15
20 % vol. n-SiC			
SiC + 25 % vol. $CaO - Al_2O_3 - Y_2O_3$	3.33	1.2	380 ± 20
SiC + 30 % vol. $CaO - Al_2O_3 - Y_2O_3$	3.35	1.3	355 ± 15
SiC + 25 % vol. $MgO - Al_2O_3 - Y_2O_3$	3.42	0.4	450 ± 25
SiC + 30 % vol. $MgO - Al_2O_3 - Y_2O_3$	3.47	0.3	400 ± 25
SiC + 25 % vol. $Al_2O_3 - ZrO_2$	3.50	0.5	400 ± 20
SiC + 30 % vol. $Al_2O_3 - ZrO_2$	3.56	0.7	380 ± 20

Values obtained for the composition with 20 % vol. n-SiC apprised LPSSiC armour parameters – almost zero open porosity and bending strength of 450 ± 25 MPa. Thus, the most efficient experimental batch for armour applications among studied was the one containing 30 % vol. of $MgO - Al_2O_3 - Y_2O_3$ eutectic additive and 20 % vol. n-SiC dopant. The experimental procedure also included studies of physico-mechanical features relevant in armour construction, i.e., fracture viscosity K_{1C}, elasticity modulus E, micro-hardness H_V. As expected, ceramics with n-SiC + 30 % vol. $MgO - Al_2O_3 - Y_2O_3$ eutectic additive demonstrated the highest performance capabilities (K_{1C} = 4.0 MPa·m$^{1/2}$, E = 380 GPa, H_V = 19.4 GPa) and was adopted for armour material. Microstructure of such ceramics is shown in Fig. 2.

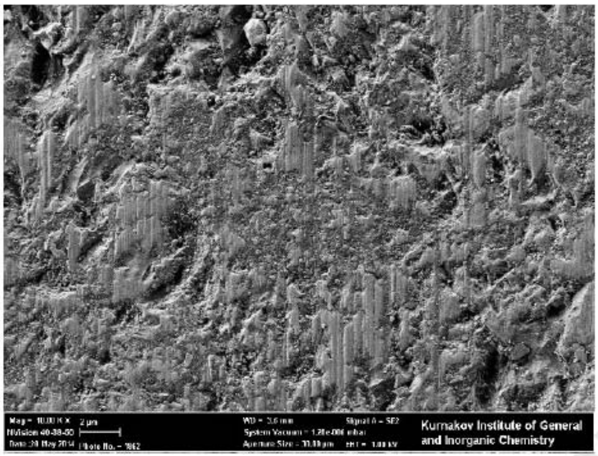

Figure 2. Microstructure of armour ceramics sample with 25 % vol. $MgO – Al_2O_3 – Y_2O_3$ dopant (polished specimen, ×10000)

Results obtained are ready be submitted to the Technical Working Group responsible for the drawing up and reviewing of the Russian BREF ‘The Ceramic Manufacturing Industry’. Prior to reviewing the BREF, national standards on BATs for energy efficiency could be developed (similarly to [14, 15]). As it is already mentioned, in Russia, national BAT-related standards often precede BREFs and tested by the practitioners before being converted into the conditions of the Integrated Environmental Permits.

CONCLUSION

The BAT proposals for technical ceramics manufacturing were estimated for a model material consisting primarily of commercially available raw materials. Achieved environmental benefits for these techniques include less complex firing units and lower firing temperature, which would reduce specific energy consumption and thereby minimise emissions of pollutants formed as the results of firing (first of all – NOx). Driving force for implementation of these techniques are mainly cost-saving issues related to energy consumption. The experimental results proved that a combination of techniques aimed at reducing firing temperature of SiC-based ceramics can easily be implemented in the existing technological process without compromising the environmental performance.

Structural material doped with ultrafine SiC powder and a eutectic sintering aid in $MgO – Al_2O_3 – Y_2O_3$ system demonstrated excellent mechanical properties (bending strength of 450 MPa, fracture toughness of 4.0 $MPa \cdot m^{1/2}$, and elasticity modulus of 380 GPa), and its sintering temperature didn’t exceed 1900 °C. Commercially available samples of liquid-phase sintered SiC require firing temperatures above 2100 °C under pressure, which makes this approach a practically suitable basis to develop an energy efficient SiC ceramics processing technology.

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