Production of Refractory Materials with Silicon Dioxide

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Organization of environmentally-friendly production of refractory materials based on the principles of cost-effective use of energy and material resources through use of energy-saving technologies and replacement of natural raw materials with industrial and agricultural waste is gaining relevance. Scientists are increasingly interested in creating high-temperature materials using silica of plant origin. Its source is rice husk, a multi-tonnage waste from rice production. Organo-mineral in its nature, rice husk determines the uniqueness of the structure and properties of the materials obtained from it. Use of this waste allows to produce porous, high-strength silicon carbide refractories with properties corresponding to classical analogs, while benefiting from environmental, economic and technological aspects.

rice husk | agricultural silicon-containing waste | silica | high-temperature materials

1. Introduction

Effective protection of equipment and technical structures working in high-temperature areas from the damaging effects of aggressive environments has always been a pressing issue for the most important sectors of industrial economies: metallurgical, chemical, petrochemical and others. The feasibility of creating new high-temperature materials to meet the needs of these industries is driven by the increasing demands of consumers and the need to improve the operating conditions and reduce manufacturing energy costs. The modern trend of the development of high-temperature materials' production on the global level is aimed at developing resource-saving composites of a new generation with high fire and heat resistance, including in chemically aggressive environments, while being environmentally friendly and providing improved quality with the final products [1]. Some industries achieve resource conservation using industrial waste as a raw material resource. For example, metallurgical waste is used to create high-quality building materials [2][3][4][5][6][7][8]. The value of its use has also been proven for the synthesis of high-temperature materials [9][10][11].

In recent years, scientists' interest in creating hybrid (organo-mineral) composite materials has increased [12]. The idea of introducing silica ash of rice husk, along with the traditional ingredients, in the composition of high-temperature ceramics and bricks was proposed [13]. Such work has recently been carried out in many countries (Thailand, Vietnam, Malaysia, China, South Korea, South Africa, Brazil). Rice husk is a large-scale biogenic residue within the global economy. Rice is the second most important and common food product. The world production of rice amounts to 800 million tons. Rice husk accounts for about 20–25% wt. of this mass. Known methods of processing this multi-tonnage waste produce even more hazardous waste. The most common process is incineration for energy [14]. However, this produces toxic gases and ash. The formation of the latter is due to the presence of silica in rice husk amounting to ~20% wt. The SiO_2 content in the ash, depending on the feedstock and its combustion conditions, varies within the range of 80–95% wt. [15][16]. This is called biogenic silica. Traditionally, porous silica has been produced on an industrial scale using water glass at high (>1400 °C) temperatures. Yet, it is not only an expensive but also an environmentally harmful process. Each ton of silica produces 0.23 tons of CO_2, 0.74 tons of Na_2SO_4 and 20 tons of wastewater [17]. In this regard, obtaining silica using eco-friendly methods such as biomass recycling is very attractive. Biogenic silica to be used in advanced technologies must not contain carbon and must have a high degree of purity. In addition, it should be characterized by a developed system of pores and have a significant specific surface area. Moreover, its structure should be amorphous. Three main approaches to obtaining biogenic silica from rice husk with the above properties have been proposed in the literature [17] with appropriate references. First of all, is the combusting of rice husk to produce ash; secondly, there is pre-treatment of raw materials; finally, some opt for the post-treatment of rice husk ash.

In the combustion process, the fundamental factors are the temperature and residence time of the raw material. Increasing these parameters increases the degree of purity of the silica produced. However, its degree of crystallization increases, and the specific surface area and total pore volume decrease. The purity of biogenic silica is also affected by the heating rate. The higher it is, the greater the amount of unburned carbon in silica, and 600 °C is typically recommended as the optimum combustion temperature. At this temperature, silica reaches 97.2% wt. purity, whereas the specific surface area is 220 m^2 g^{-1} and the pore volume is 0.26 cm^3 g^{-1}.

Pre-treatment of rice husk before combustion is carried out to improve these indicators. For example, washing with water to remove alkali metals or leaching with acid to remove alkaline-earth elements. The main thing is to exclude the presence of ash-forming elements. Accordingly, after combustion of pre-treated rice husk, its degree of purity increases to 99.8% wt., the specific surface area increases to 353 m^2 g^{-1} and the volume of pores increases to 0.52 cm^3 g^{-1}. The presence of alkali metals influences the degree of crystallization of silica. If the crystallization of silica in the combustion of untreated rice husk occurs already at 600–900 °C, after the pretreatment of rice husk, SiO_2 remains amorphous at higher combustion temperatures (~1000 °C).

To achieve the desired performance of biogenic silica, it is possible to use a combination of pre-treatment methods before combustion, select the combustion conditions and conduct the final treatment of the resulting product. For example, in [18], a series of methods involving treatment of rice husk by hexadecyltrimethylammonium hydroxide solution in an autoclave produced biogenic silica with a specific surface area of 1210 m^2 g^{-1} and volume of pores of 1.0 cm^3 g^{-1}. However, it should be taken into consideration that all these methods increase the cost of silica and are not always eco-friendly. In each case, it is necessary to choose the most appropriate method of silica production. Its purity and characteristics will be determined by the objectives of the further application of the material.

Fine silica, resulting from rice husk burned for energy production, has a low bulk weight, easily gets into the air and has a negative impact on human health. This makes the environmental situation extremely difficult. Many researchers have proposed the use of silicon dioxide ash from rice husk to produce pure silicon and its compounds, concrete, cement and refractory ceramics [13][14][17][19][20][21][22][23][24][25][26][27][28][29][30][31][32][33][34][35][36][37]. It has been shown that rice husk ash, due to its properties (primarily the presence of silicon dioxide in a nanostructured amorphous form with high purity and low thermal conductivity), is a promising source of silicon for the production of ceramics [36], including insulating and high-strength-type (mullite, forsterite, cordierite, carbide-silicon) refractories [14].

In general, there is a large variety of refractory materials, which differ in their properties and so are used differently. Refractories are classified according to a number of features. Depending on the physical and chemical properties of raw materials, they are divided into acidic (silica, aluminosilicate, zirconia), basic (magnesite, dolomite, magnesia-chrome) and neutral (carbon graphite, chromite, alumina) refractories. According to the melting temperature, a distinction is made between normal (1580–1780 °C), high (1780–2000 °C) and super (over 2000 °C) refractories. According to the method of production, they are divided into molded and unmolded, flame retardant and thermally conductive [33].

Kazakhstan, as a country with developed metallurgical, chemical and other industrial sectors, is in need of different types of high-temperature materials. Unfortunately, refractories are fully imported from abroad, although all the necessary raw materials, both natural and anthropogenic, including rice husk, are available in sufficient quantities in the country for production. Despite the great variety of new high-temperature materials with different physical and chemical properties proposed by Kazakh scientists [9][10][11] and the possibility of their widespread use in the above-mentioned industries, the task of organizing the local production of these materials remains unresolved, a problem existing not only in the country. Plus, positive results in the field of studying the possibility of using rice husk ash in the production of refractory ceramics, on a global scale, have not been achieved since 1913 [37]. There are a number of unresolved issues. The main one is detachment from production. All the results have a purely academic orientation. There is a lack of any significant contribution to the refractory industry with the application of new refractories in practice [36][37]. According to the experts [37], solving this problem will produce a real boom in the industry of high-temperature materials, including refractories

2. Porous Refractory

2.1. Diatomite, Rice Husk Ash, Sawdust

Thang [33] obtained refractory composites using the following available raw materials: low-quality diatomite, rice husk ash, sawdust.

This showed that the utilization of agricultural and forest industry waste is useful not only in terms of economic and environmental benefits. With their use as raw materials, lightweight porous refractories were obtained. The researchers plans to study the microstructure of these innovative materials in the future, which will allow for a deeper understanding of the processes under study. At this stage, however, what is important is not just the fact that waste can be used for production of this or that product but also the fact of obtaining new high-quality refractory materials using waste.

2.2. Refractory Clay, Rice Husk Ash, Wollastonite Microfibers

The effect of porosity on the performance properties of refractories was also noted by Silva et al. [34]. They studied the replacement of a part of the refractory clay with rice husk ash and its combination with wollastonite microfibers.

In general, the researchers showed that rice husk ash, due to its high content of silica, mainly in the amorphous form, represents an alternative source of silica for the production of ceramics. When mixed with wollastonite, it provides an increase in porosity and water absorption, which is associated with the incomplete mullitization process and the granulometric aspect.

2.3. Kaolin, Rice Husk Silica, Steel Fibers

Stochero et al. [35] observed a similar pattern of porosity changes to that described above when kaolin was replaced with silica extracted from rice husk and steel fibers were added.

The researchers concluded that replacement of a part of kaolin with silica from rice husk and steel fibers opens up the possibility of producing refractory ceramics with improved mechanical and thermal properties.

2.4. Kaolin, Rice Husk Silica

In [13], refractory ceramics were obtained by replacing part of kaolin with rice husk silica without the addition of other ingredients.

It was showed that the sample, which had the most optimal composition and was characterized as having performed the best, could be recommended for production and application.

2.5. Rice Husk Ash with Additives Compared to Diatomite Silica

The researchers of an earlier work, while not denying the influence of porosity on the thermal conductivity of ceramic thermal insulators, attached more importance to the ordering of the crystal structure. They fabricated thermal insulators based on rice husk ash obtained by burning rice husk at 600–700 °C mixed with wood sawdust by extrusion and pressing methods.

Comparison of the thermal properties of samples prepared (Table 5), depending on the microstructure showed that the higher the degree of structure disorder, the lower the thermal conductivity of thermal insulators.

2.6. Ground and Unground Rice Husk Ash, Rice Husk Sol, Sodium Hexametaphosphate

Considering that rice husk ash or silica, isolated from their composition, are amorphous lightweight materials and contribute to the formation of porous refractories, Hossain et al. [31] tested the possibility of producing insulating bricks using them. As constituents, they used ground and unground rice husk ash (aggregates), isolated by alkaline extraction sol (binder), and added in small amounts of sodium hexametaphosphate (SHMP).

After determining the main characteristics (porosity, strength and thermal conductivity) of the obtained samples and comparing them with literature data and industrial samples of insulating bricks (Table 6), it was shown that the new material obtained at 1000 °C meets the necessary requirements and can be used as an insulating refractory in various furnaces.

2.7. Ghanaian Red Anthill Clay, Sawdust, Rice Husk

Arthur and Gikunoo [38] studied the properties of thermal insulation materials made from Ghanaian red anthill clay enhanced with non-traditional additives. As such, sawdust, rice husk and their mixture were chosen as ingredients, which are very important to dispose of from the environmental point of view.

In general, studies of the physical, mechanical and thermal properties of the new refractory bricks have shown the potential for using the above materials as raw materials for refractory production, with the introduction of rice husk effective at improving the insulating properties of refractory clay.

2.8. Rice Husk Ash, Waste Sediment from Aluminum Anodizing Process, Dregs

Sanewiruch and Saewong investigated the possibility of producing Ca-Al-Si-O compounds as a basis for insulating refractory materials using mixtures of three types of wastes: rice husk ash, waste sediment from the aluminum anodizing process and dregs.

The properties of the obtained composites, presented in Table 8 in comparison to the characteristics of insulating refractory bricks, clearly demonstrate the good prospects for using the mentioned wastes as precursors in refractory production, if the ratio is correct and the conditions of the production process are suitable.

2.9. Porous Silica of Rice Husk Ash

Ahmed et al. [39] investigated silica samples of rice husk ash, obtained at different pressures of compaction, firing temperatures and soaking times (Table 9) for use in ladle lining in steel production.

In concluding the study, optimal modes of production of porous silica compacts, providing the required indicators of porosity (30%) and compressive strength (2.5 MPa) for use in lining ladles, were recommended.

3. High-Strength Refractory

3.1. Quartz, Rice Husk Ash, Clay, Refractory Grog

Bhardwaj et al. [40] investigated the possibility of replacing quartz with rice husk ash used in a mixture with clay and refractory grog, to produce high-strength refractory materials. RHA was used from rice mills. In these mills, rice husk is usually used as fuel. After undergoing combustion at 500 °C, RHA is practically free of any volatile substances, such as carbon. However, the RHA was treated at 600 °C for 2 h to remove any residual carbon content. Using an X-ray fluorescence spectrometer, the following composition of RHA, % wt. was established: SiO_2—92.81; Na_2O—2.658; P_2O_5—1.071; K_2O—1.021; CaO—0.417; Fe_2O_3—0.312; MgO—0.212; RuO_2—0.151; SO_3—0.132; TiO_2—0.112; ZnO—0.091; CuO—0.058; Rb_2O—0.036; BaO—0.031; ZrO_2—0.025; Re_2O_7—0.021; Y_2O_3—0.012; Eu_2O_3—0.010. The SEM method showed that the outer surface of RHA particles has a pronounced relief. The inner surface is porous, which explains the high value of the specific surface area. According to XRD data, the diffractogram of RHA has no sharp peaks. The researchers recorded only one broad halo in the region of 2θ = 20–30°. This character of the diffractogram indicated the absence of any crystalline phases in the studied sample. Amorphous silica is reactive due to the absence of long-range ordering. When interacting with other materials, it provides higher compaction. The C composition is mainly formed by silicon dioxide (52.8% wt.) and aluminum oxide (33.74% wt.). In small quantities' fixed presence, % wt.: Fe_2O_3—0.41; TiO_2—0.06; MgO—0.66; Na_2O—1.28; K_2O—0.7.

To prepare the refractory samples, quartz (90 µm), RHA (106 µm), C (150 µm) and refractory grog (1000 µm) were mixed in an agate mortar using a pestle in the quantities. Then, the necessary amount of water was added for shaping. The samples were pressed on a uniaxial press at 120 MPa at 40 × 10 mm and air-dried in an electric oven at 110 °C for 24 h. Then, they were heated in a muffle from room temperature to 500 °C for 4 h and then to 1200 °C for 5 h. Sintering was performed for 2 h, after which the samples were cooled to room temperature for 8 h.

In general, the results showed that the experimental refractory samples were characterized by good physical, chemical and thermal properties. Increasing the amount of rice husk ash in the refractory composition, when introduced instead of quartz, contributed to the compaction and hardening of the obtained materials. This is explained by the fact that the amorphous silica of the rice husk ash exceeds quartz in reactivity and more actively interacts with other ingredients during sintering of the charge. When reducing the porosity of refractories with increasing RHA in their composition, increased sample shrinkage and increased thermal conductivity are observed. Samples with a higher RHA content show a lower refractoriness (PCE). The researchers of the considered work explain this fact by the lower melting temperature of the rice husk ash silica (1440 °C) compared to quartz (although in [39], the melting temperature of 1600 °C is indicated as a significant advantage of the rice husk silica). The quartz-based refractory showed a maximum PCE temperature of 1580 °C and the RHA-based refractory showed one of 1470 °C. Sample 20Q30R, the production of which involves the replacement of quartz with ash from rice husk at 30% wt., was the most suitable material for furnace lining.

According to XRD data, the intensity of crystallinity of this sample increased significantly compared to sample 50Q. The crystallization process began at 800 °C. At 1000 °C, the sample had a completely crystalline structure represented by cristobalite, tridymite and mullite. The surface morphology had also changed. The distinctive cut of the particles characteristic of the 50Q sample practically disappeared in the 20Q30R sample after sintering at 1200

°C. The surface became smoother as a result of the transformation of amorphous silicon dioxide into a crystalline state.

In general, the promising characteristics of this sample indicate the real prospect of creating high-strength clay-based refractories with rice husk ash for use in most furnace linings where silica refractories are commonly used.

3.2. Rice Husk Silica, Al_2O_3, MgO

One of the excellent refractory materials characterized by the highest melting point among silicate ceramics, high chemical stability and an excellent thermal shock resistance is cordierite. Sembiring et al. [41][42] investigated the possibility of producing this material from rice husk silica at different sintering temperatures [41] and charge ingredient ratios [42]. Silica was obtained by treatment of rice husk with alkali under boiling followed by hydrochloric acid precipitation. Powders of magnesium, aluminum and silicon oxides were mixed in the ratio of 2:2:5 by mass, respectively. Then, these ingredients were mixed with alcohol in a magnetic stirrer for 6 h. After the mixing process, the mixture was filtered off. The solid was dried at 110 °C for 8 h to remove the residual alcohol. The dried solid was ground in a mortar and sifted through a 200-mesh sieve. The powder was pressed in a metal mold at a pressure of 2×10^4 N m^{-2} to obtain cylindrical pellets. The pellets were sintered at temperatures of 1050, 1110, 1170, 1230, 1290 and 1350 °C for 4 h by heating at 3 °C min^{-1}.

The phase changes with an increasing sintering temperature were studied by FTIR, XRD and SEM methods. At temperatures above 1110 °C, using FTIR, the appearance of new bands at 640, 15, 590, 460 and 430 cm^{-1} was observed. Moreover, the higher the sintering temperature, the higher the intensity of these bands, confirming the presence of $MgO–Al_2O_3–SiO_2$ structures. According to XRD data, the presence of cristobalite, μ-cordierite and spinel was detected in the sample obtained at 1050 °C. The formation of cristobalite is due to crystallization of silicon dioxide of rice husk. The presence of μ-cordierite is the result of intra-diffusive processes of interaction between spinel and cristobalite. At 1110 °C, μ-cordierite transforms into α-cordierite. The presence of these phases remains up to 1170 °C. It was found that the α-cordierite phase was predominant at a sintering temperature of 1230 °C. At this time, the reflexes of spinel and cristobalite disappear almost completely. In the region of 1230–1350 °C, cristobalite melts and reacts with the spinel phase, forming α-cordierite. Its amount at 1350 °C reaches 92.7% wt., against 30.8% wt. at 1110 °C. The surface morphology with an increasing sintering temperature changes from small, clearly faceted grains at 1050 °C to large, agglomerated particles with a glassy surface, without evidence of grain boundaries, at 1230–1350 °C.

The sample obtained at 1230 °C was characterized by hardness and high bending strength, while the porosity, density and thermal expansion coefficient corresponded to the formation of the cordierite phase. Aluminum-cordierite samples with different mass ratios of cordierite to aluminum oxide (100:0, 95:5, 90:10, 85:15, 80:20, 75:25, 70:30) were obtained from this material. Aluminum-enriched refractory cordierite is mainly composed of spinel, corundum and cristobalite. Increased aluminum suppresses the growth of cordierite crystals. The XRD data of a Rietveld analysis demonstrate that a binary interaction between MgO and Al_2O_3 producing spinel is preferable to the interaction between MgO and SiO_2. Thus, the spinel formation process is the result of an intra-diffusive interaction of aluminum oxide with periclase. Significant changes in the surface morphology of samples with increasing aluminum oxide addition were recorded by SEM. As a result of aluminum addition, fine grains of α-cordierite were destroyed, with the formation of agglomerated spinel particles, corundum and cristobalite.

Aluminum-enriched refractory samples have high values of density, hardness, flexural strength and thermal expansion coefficient and, on the contrary, a low porosity index. Rice husk silica-based refractory cordierite samples represent a promising insulating material, and aluminum-enriched, dense samples can be used as abrasive materials.

3.3. Rice Husk Ash, α-Al_2O_3

In [43], ash from the industrial combustion of rice husk was used as a source of SiO_2 to produce mullite ceramics. The chemical composition of RHA was as follows % wt.: SiO_2—94.72; SO_3—0.17; CO_2—0.23; P_2O_5—0.51; CaO—0.21; MgO—0.18; Na_2O—0.05; K_2O—0.46; Al_2O_3—<0.05; Fe_2O_3—0.05; Cl^-—0.02; C—3.39. RHA had a melting point > 1200 °C; calorific power—351 cal g^{-1}; specific surface (BET)—11.22 m^2 g^{-1}. According to XRD, RHA contained cristobalite—67.7% wt.; amorphous—30.2% wt.; orthorhombic Si-O—3.1% wt. The particle size distribution of RHA was as follows % wt.: 1.00 mm—0.78; 0.595 mm—5.61; 0.297 mm—42.05; 0.177 mm—24.32; 0.149 mm—5.43; 0.125 mm—6.81; 0.105 mm—2.33; ≤0.105 mm—12.62.

Only α-Al_2O_3 in a stoichiometric ratio of $3Al_2O_3{:}2SiO_2$ was used as the other ingredient. The ingredients were milled in a ball mill (1000 cm^3 for 24 h) and dry-pressed with a pressure of 200 MPa. Disc-shaped samples (∅ = 15.00 mm) were fired in an electric kiln at temperatures from 1100 to 1600 °C for 60 min with a heating rate of 5 °C min^{-1}. After comparing the results of a number of analyses (XRD, SEM) and a study of the properties of the created samples, the researchers concluded that the mullitization reaction begins at 1400 °C and ends at 1600 °C. The lack of SiO_2 is explained by its interaction with inorganic impurities present in rice husk ash. A decrease in the density of the obtained products relative to the density of the initial components, and sample shrinkage at 1400 °C, in their opinion, confirm mullite's formation. The structure and properties of the obtained ceramic materials open up the possibility of their wide use. For example, it is possible to increase the porosity of the final product by introducing combustible additives for its use as insulating materials. On the contrary, to obtain denser materials, strengthening the grinding of the initial components in the preparation stage is suggested. [43] provided enough information to control the process and thereby obtain mullite ceramics with specified properties using rice husk ash.

3.4. Rice Husk Ash, Quartz, MgO

In [44], the possibility of obtaining another type of durable refractory ceramic was shown. People are talking about forsterite refractory, which was prepared using quartz (98% pure) and periclase (99% pure), gradually replacing the quartz with rice husk ash up to complete substitution. The characteristics of the RHA were published elsewhere [40].

To prepare refractory samples, all ingredients (quartz—90 µm, RHA—106 µm, MgO—106 µm) were mixed in two steps. Dry mixing was carried out for 30 min and semi-dry mixing (with the addition of water as a medium) for 20 min. The samples were pressed using a hydraulic press at 123 MPa. Sintering was carried out at 1100 °C for 2 h at a heating and cooling rate of 5 °C min^{-1}.

The formation of the forsterite phase was proven using XRD by the presence of the following bands at 2θ = 20.6°, 41.80° and 62.008°. The characteristic peaks of forsterite in the fired samples were identified by FTIR analysis, for example, 500–620 cm^{-1} (octahedral MgO_6 or SiO_4 bending modes), 650–840 cm^{-1} (Si-O-Si symmetric stretching vibrations), 830–1000 cm^{-1} (stretching vibrations of nonbridging Si-OH) and 1000–1050 cm^{-1} (Si-O-Si asymmetric stretching vibrations). Based on EDX data, amorphous silica extracted from rice husk during its combustion was found to react much more actively with periclase at 1100 °C than with quartz. RHA additives affect the surface morphology of particles and their size distribution, as noted by SEM. The higher the RHA content, the stronger the forsterite formation and the denser the material that is formed. With an increase in the amount of rice husk in the charge of the obtained refractory, a reduction in porosity, a decrease in thermal conductivity, along with increases in the cold crushing strength and density of the finished samples, were observed. However, the complete substitution of quartz by rice husk ash resulted in a material with a density (2.4 gm cc) lower than the theoretical one (3.2–3.3 gm cc) for forsterite, which was explained by the predominance of a closed porosity, which reduced the thermal conductivity. Considering the high density and low thermal conductivity of rice husk ash-based forsterite refractory, this material is recommended for use as thermal insulation in aggregates for steel and cement production.

4. SiC-Based Refractory Compounds

Important ceramic materials for industrial applications, especially at high temperatures, are silicon carbide and products based on it. Silicon carbide combines a set of excellent mechanical, physicochemical, thermal and electrical properties. It has hardness, high strength, thermal conductivity, is characterized by low thermal expansion, is chemically inert, stable in oxidizing environments and is not subject to erosion or corrosion. There are α-SiC and β-SiC polytypes of silicon carbide that differ in their structure, morphology and properties and are formed under different conditions. There are multistage and single-stage processes of silicon carbide production. Its modern production requires the use of simple techniques and cheap raw materials [45][46]. For the latter, the use of ground agricultural waste, such as wheat hulls, corn cobs, sorghum leaves, peanut peels and others, is suggested [47][48][49][50][51][52]. Rice husk, as well as its ash, is a very attractive raw material source in this regard due to its high reactivity and purity, high content of carbon and silicon and their close interaction [19][53][54][55][56][57][58][59]. Moreover, of interest is the carbothermic production method [60][61], which is more cost-effective compared to chemical vapor deposition and the sol-gel method.

Analysis of the results of studies of the process of thermal degradation of rice husk obtained by different researchers [16][62][63][64][65][66][67][68][69][70][71][72][73][74][75][76] shows that the product of rice husk decomposition in the absence of oxygen (in an inert environment, a vacuum, in a waste gas atmosphere) is a silica-carbon nanocomposite (black ash, char, biochar) formed by carbon and silicon dioxide nanoparticles. The structure and morphology of the particles depend on the conditions of the destruction process. Carbon and silicon dioxide are present in an amorphous form [57]. However, carbon has a graphite-like structure [66][70][77]. As the carbonization temperature rises, the degree of ordering of the graphite-like structure increases. As for the silicon-containing phase, up to 800 °C, silicon dioxide is mainly in the amorphous form [65][68]. The presence of $H_2Si_{14}O_{29}·5,4H_2O$ was registered during pyrolysis of rice husk in an exhaust gas atmosphere at 650 °C [69], although [63] described that α-quartz formation was observed in a nitrogen atmosphere at temperatures below 800 °C. Cristobalite appears at temperatures above 800 °C in different atmospheres [62][63][66][68]. In a nitrogen atmosphere at 900 °C, rice husk modified with sodium hydroxide solution decomposes to form graphitic carbon, cristobalite and tridymite [78]. Researchers note that the process of crystallization proceeds most actively in the air [62]. The presence of different silica phases up to tridymite is noted in the product of rice husk combustion in the air [69]. Javed et al. [79] found that pretreatment of rice husk with a dilute solution of potassium permanganate during pyrolysis in the temperature range of 500–700 °C promotes faster decomposition of the organic component but inhibits the crystallization of silica. Silicon carbide formation occurs during the carbonization of rice husk or a mixture of its ash and carbon at higher temperatures (1300–1600 °C and above) [53][54][57][58][59][68][80][81][82]. Despite the known fact that silicon carbide is used as an enhancer of metal and ceramic composites, and though there are examples of silicon carbide being obtained from rice husk, there is little information in the literature about how to obtain refractories based on silicon carbide from rice husk.

Al-Mg-Si Alloy-Based Composites

The researchers of [32] investigated the microstructural characteristics and mechanical properties of aluminum matrix composites reinforced with 10% silicon carbide (SRC) from rice husk ash (RHA, % wt.: SiO_2—91.81; C—4.91; CaO—1.35; MgO—0.50; K_2O—0.41; Fe_2O_3—0.29; others—0.73). The latter were obtained by the carbothermic method. Al-Mg-Si alloy-based composites (% wt.: Mg—0.35; Si—0.59; Mn—0.35; Cu—0.012; Zn—0.002; Ti—0.057; Fe—0.47; Ni—0.035; Al—balance) were prepared by a double-stir casting process. SRC was preheated at 200–280 °C. The Al-Mg-Si alloys were heated in a furnace to a temperature of 710 ± 30 °C until they completely melted. Then, they were cooled to a semi-solid state and heated again to a temperature of 710 ± 30 °C. Finally, they were stirred at 350 rpm for 5–10 min before casting in a sand mold.

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