SUMMARY OF STAGE 1

The research carried out by the NASIPONAC project Consortium is based on the idea of obtaining advanced ceramic materials using the carbothermal method.

The project aims to combine scientific research and commercial interest of the partners from Romania and Turkey, in order to obtain ceramic powders, namely silicon carbide (SiC) and silicon nitride (Si_3N_4) via 2 new technologies, both starting from serpentinite, a mineral used in a small extent.

Serpentinite is a magnesium silicate, found in many regions of Europe, in dumps formed during the former exploitation of asbestos mines, and which can be further processed in mesoporous silica. Through nanotechnology approach (polymerization of a vinyl monomer into the silica nanopores), the process ensures lower price and better quality of the obtained SiC and Si_3N_4 powders than the current technologies. The powders will be used to obtain high performance ceramic products for automotive industry, microwave ovens, military armor.

A significant progress was made lately in developing materials for high-performance technical fields. Among structural ceramics, silicon carbide and silicon nitride are considered the newest and most promising materials. SiC and Si_3N_4 are compounds synthesized by various chemical reactions. The particles are pressed and sintered by well known methods, in order to obtain ceramics with outstanding properties. These materials are dark grey and can be polished to a very smooth reflecting surface. The most interesting properties of ceramics are low density (3 g/cm^3), high resistance to a wide range of temperature, hardness, high wear resistance, good thermal shock resistance, chemical resistance, low friction coefficient.

The use of silicon nitride increases with the development of advanced engineering applications, therefore the demand for finding low cost alternative solutions for obtaining ceramic powders is high. The way to reduce the costs of ceramic powders, proposed by this project, was to use a cheap, available raw material, namely serpentinite found in dumps from the stopped exploitation of asbestos, from Dubova Mehedinti.

In recent decades, silicon nitride was obtained by the CRN (nitration - carbothermal reduction), starting from silica and coal. The main problem in the CRN process is the considerable amount of impurities present. Impurities, such as Ca^{2+} and Fe^{3+} can affect the CRN synthesis process.

Supramolecular chemistry of host-guest type can be an effective method to reduce impurities. This method has multiple advantages: impurities can be reduced by replacing solid carbon with an organic polymer and homogeneous mixture of the reagents, at molecular level, can be formed. Thus, the mineral becomes a reagent suitable for intercalation with the organic polymer such as polyacrylonitrile, that will favor future treatment during the carbothermal process. The aim of the present project is to obtain silicon nitride and silicon carbide powders from such precursors, i.e. host-guest type composites of mesoporous silica and PAN.

Researches achieved within the NASIPONAC project are clearly defined for each partner: INCDMNR -IMNR is responsible for obtaining mesoporous silica by treating serpentinite with mineral acids; the Project coordinator INCDCP - ICECHIM has the task to achieve the synthesis of nanocomposite precursors of the advanced materials, SC CALORIS GROUP has the responsibility to perform the nanocomposites thermal treatments in order to obtain ceramic powders, and MDA SERAMIK, together with Istanbul Technical University have the mission to produce the ceramic objects.

At this stage of the project, a thorough study on the characteristics of the waste serpentinite from Dubova was conducted, regarding: chemical composition, phase structural composition (analyzed by XRD) and mineralogical composition (performed by polarized light microscopy).

Compositional analysis showed that advanced grinding of the starting material and solubilization with concentrated acids, with high oxidation capacity, is required, in order to achieve the project objectives, namely to accomplish the separation of a pure mesoporous silica, with pore sizes below 40nm.

To assess the serpentinite behaviour in grinding, using a Retsch PM 100 drive shaft mill, standard tests were carried out and, following a 2^{nd} order orthogonal experimental plan for 16 experiments, the variation of the following parameters was studied: grinding duration, rotation speed of the mill, material loading.

The solubilization process, followed by phase separation via filtration through filter press (4 bars), provide the necessary conditions to obtain a mesoporous silica with BET specific surface area of more than 300 m2 / g and pore sizes below 10 nm, but impure, with an iron content between 1.0-2.5 %. By magnetic separation of residual insoluble fractions of minerals with magnetic properties from silica, iron concentration limit may be reduced to 0.7-1.0 %.

Intensification of grinding, solubilization and magnetic separation processes of the fractions with high iron concentration can be achieved by irradiating the serpentinites in controlled microwave field, when not only phase transformations occur, but also variation of properties of the minerals in serpentinite composition, along with intragranular micro fissures.

Compounds containing MgO separated by precipitation with alkali (NaOH and Na_2CO_3) from acidic nitrate solutions generated by serpentinite solubilization can be commercially exploited for a wide range of industrial applications: remediating soils contaminated with heavy metals, treating gas streams, treating wastewater and industrial wastewater, fertilizers for agriculture, cement additives for civil engineering, refractory materials, precipitating agents for non-ferrous metals in hydrometallurgy, in steelwork production flow, in catalysis, as hardeners and additives in rubber, plastics, etc.

Hybrid composites were obtained by polymerization of a carbocatenary polymer, acrylonitrile, in porous silica, where both the silica assortment and the concentration of organic compound were varied. The innovative synthesis method consisted in performing both imbibition and polymerization in ultrasound field.

X -ray fluorescence analysis of the samples containing 50 % silica showed that the silica content found was close to the quantity of silica initially introduced. FT-IR spectra of the new synthesized composites, with different content of organic compound, showed all characteristic bands of inorganic host and vinyl polymer guest.

Using thermal analysis, optimum temperatures for thermal treatment of composites were determined, in order to obtain ceramic powders. TGA analysis revealed that the polymer nanocomposites have a content of inorganic component above 35 %.

All hybrid systems presented, regardless of the silica assortment used, show high values of storage modulus versus reference PAN. This indicates that the used silica increases the elasticity of the system throughout the temperature range. Moreover, almost all synthesized composites show two glass transition temperatures: one at a lower temperature than the reference, probably belonging to the surface polymer, of lower molecular weight, and one at a higher temperature than the reference, belonging to the polymer confined within the pores, of higher molecular weight.

The research regarding the hybrid inorganic-organic nanocomposites transformation in SiC and Si_3N_4 allowed the following conclusions:

- the sample 50R12 treated at 1460 °C (without plateau), under N_2 atmosphere, confirms the formation of Si_3N_4, by the absorption bands in the FTIR spectrum at 952 cm^{-1} and 492 cm^{-1}, respectively . The intensities of these bands suggest that Si_3N_4 is not the predominant phase of the sample, SiO_2 remaining the main component;
- the sample 50R12 treated at 1550 °C for 1 hour under N_2 atmosphere (ATD residue) show the formation of a larger quantity of Si_3N_4 (see absorption bands at 930 cm^{-1}, 493 cm^{-1} respectively). In this case, Si_3N_4 is the main component of the analyzed sample;
- the sample 50R12 heat treated at 1460 °C for 3 hours indicates the predominant presence of Si-O bonds (1093 cm^{-1}, 802 cm^{-1} and 472 cm^{-1}, respectively) . The existence of Si_3N_4 is confirmed by the presence of a band at 950 cm^{-1}.

Other results obtained during this stage of the project consist of 8 Scientific papers presented in international meetings and symposia: 4 at the Workshop "Challenges in the obtaining of new ceramic powders starting from inorganic -organic nanocomposites", 2 in "International Symposium on Environment and Industry" – SIMI, 2013, and 2 in the International Symposium "Priorities of Chemistry for a Sustainable Development" - PRIOCHEM – 9^{th} edition, 2013.

Innovative elements were protected by submission of a Patent Application at OSIM, registration no. A/00762/22.10.2013 .