SUMMARY OF STAGE 3

At this stage of the project, research was finalized on getting those 2 ceramic powders targeted in the project: silicon carbide and nitride. During the research the following most important conclusions were revealed:

- Introducing additional operations of serpentinite treatment in a microwave field is beneficial for serpentinite grinding and the results of this operation help to optimize the aimed technology, as follows: leads to a decrease in the particles size in the mill feed (F80, cumulative fraction) from about 817 μm (without microwaves) up to 44%, to values of about 451μm (when applying microwave radiation). It is obtain a milled material (P80 cumulative fraction) thinner by 20%, having an average grain size of 46.6 μm, as compared to an average of 58,94μm. It is reduced the amount of coarse material that it is recycled in closed circuit from 0.48 t / ton of serpentinite (classic grinding) to about 0.34 t / ton of serpentinite (after microwave irradiation), which means a reduction of about 29%. After a recirculation of coarse material (closed circuit grinding), the final size of the material exiting the mill did not differ significantly in the two applied versions, being (P80) in average 42.3 μm (no microwaves) and about 46,1μm (P80) after microwave irradiation . The required amount of serpentinite related to 1 ton of silica (final product) differ slightly, 2.64 t / ton silica obtained being (without microwaves) as compared to 2.89 t / ton silica (microwave irradiation) but the final product, mesoporous silica clearly differs qualitatively in terms of the impurities content, particularly iron, from an iron content of 1.2 - 3% to 0.26-0.34% iron, as Fe_2O_3. When applying microwave irradiation, an acceptable electricity consumption is estimated, to obtain 1 ton of silica 27.8 kWh / ton silica are required;
- Introducing an additional operation of magnetic separation of serpentinite fraction having increased iron content as magnetic compounds, mainly magnetite finely dispersed in milled serpentinite matrix and gravitationally ranked, is beneficial. The iron content in feed can be thus reduced by up to 2%;
- By recirculating a portion of the acid liquid phase, resulted in the operation of washing, the residues wet silica (resulted from serpentinite solubilization with concentrated nitric acid, 50%), up to ½ of the total generated, which can be used to prepare concentrated nitric acid solution in the acid leaching phase, thus a reduction in acid consumption of about 0,006 t / ton of obtained silica being estimated, and implicitly a reduction in fresh industrial water consumption being achieved;
- New silica-PAN hybrids with high Fe content were obtained by host-guest radical polymerization in the ultrasound field using R_{39} silica. It was determined the

influence of different parameters on the synthesis process and on the final properties of the hybrid composites. The investigated parameters were the organic compound concentration, initiator concentration, ultrasonic assisted impregnation time and the time of ultrasonic assisted polymerization, respectively. There were synthesized polymer hybrids with superior features as compared to individual components.

- BET analysis showed that all composites parameters decreased significantly compared to inorganic host structure. The results support the assertion that polymer chains were incorporated into the silica cavities and thus reduce pore sizes of silica original material.
- FTIR results of new composites synthesized by varying different synthesis parameters displayed all characteristic bands of the inorganic host compound and of guest vinyl polymer.
- The thermal stability of polyacrylonitrile embedded within porous inorganic structure was improved as compared to baseline. TGA has also provided important information on the carbonization process (steps 1 and 2 of the polymer degradation) which have been validated in this stage and was subsequently used to obtain ceramics.
- DMA analysis (storage module data, rigidity and glass transition temperature, respectively) revealed also the formation of polymer layers on the host material surface, and an improvement in elasticity of up to 200 ° C as compared to pure silica. All tests and measurements showed the effect of silica reinforcing with polymer.
- The experimental study provides information on thermal generation of silica-carbon nanocomposites by oxidation and graphitization of polymer from nanocomposite. It was shown that different concentrations of carbon can be incorporated into the inorganic matrix and, most importantly phase carbon can be controlled by the initial amount of embedded polymer. Moreover, the used silica sort and the amount of initial treated composite are extremely important for reducing nitriding process but also for the final properties of ceramics.
- An intimate silica-carbon a mixture can be obtained by oxidation and graphitization of acrylonitrile in silica pores after thermal treatments at 290, 550 ^{0}C under an inert atmosphere of nitrogen.
- There were validated technologies for producing polymer nanocomposites and for carbonization of the polymer.

- Research to demonstrate the functionality and utility of technology for producing polymer nanocomposites were twofold: on the one hand verifying the reproducibility of technology and on the other hand making available to the partner P2 nanocomposites necessary for study on carbonization and synthesis of silicon nitride and carbide, respectively.
- It was found that the process shows good reproducibility even when using another sort of silica. Moreover, when working under conditions outside the range that was set as optimum by laboratory technology, it was found that they can finally get advanced ceramic powders, which proves the high elasticity of the developed technology, both the technology of producing the composites and the polymer carbonization technology.
- The quantity and morphology of products obtained after nitridation carbothermal reduction depends on several synthesis factors and on the involved constituents. Porous hybrid precursor materials for getting hybrids together with the impurities in their structure show a major effect on the formation of Si_3N_4 and on the ratio of phases α / β.
- Silica sorts which led to the subsequent obtaining of various composites, as well as the time and the temperature of thermal treatment were modified, finally yielding Si_3N_4 ceramic powder in percentage of over 90%.
- Silica which has yielded over 98% nitride is R_{39}, treated with concentrated nitric acid, presumably due to its higher Fe content, which can play a catalyst role within the reactions for carbothermal nitridation.
- By varying both the maximum temperature treatment and the time of samples maintaining in plateau it concluded that the optimum temperature is 1300 ° C for silica R_{34}, and 1325 ° C for silica $_{R39}$.
- In the studies on silica R_{34}-based composite obtained from polymer nanocomposites with inorganic-organic concentrations of 20-80%, both temperature and duration of maintenance in plateau were modified. The optimum working temperature for Si_3N_4 obtaining was 1375 ° C, and optimum duration of maintenance in plateau 5h.
- The optimal inorganic-organic ratio in polymer composites is 50-50% in order to obtain large amounts of α-Si_3N_4 and 20-80% for the synthesis of silicon carbide.
- Silicon carbide was obtained in 60% percent by the treatment of silica-carbon composites based on R60 silica at 1400 ° C for 6 hours.

- There were validated technologies for producing SiC and Si_3N_4 via polymer nanocomposites by CRN process. Researches proving the functionality and utility of technology for producing ceramic powders were twofold: on the one hand verifying the reproducibility of technology and on the other hand making available to partners from Turkey ceramic powders in the amount of about 100 g Si_3N_4 and 100 g SiC.
- It was found that the process shows good reproducibility even when using another sort of silica. Also, working conditions are outside the range established as optimal in laboratory technology, it was found that they can finally get advanced ceramic powders, which proves the high elasticity of the technology developed.