

MICROSTRUCTURE EVOLUTION OF SILICONE RUBBER-BASED COMPOSITES DURING CERAMIZATION AT DIFFERENT CONDITIONS

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Abstract

The work describes the microstructural changes proceed during ceramization of silicone rubber-based composites at different conditions. Ceramization is a phenomenon which assures compactness of polymer-based composites in the case of its thermal degradation caused by open fire or exposition at a high temperatures.

Polymer-based materials used as a wire covers contain a certain amount of mineral additives. A type, the volume, the grain size distribution of these additives are decisive for shaping of microstructure of ceramized body. Moreover, ceramization condition can strongly influenced its final microstructure. The total porosity, the open porosity, the pore size distribution and ceramized body compactness evolve with degradation temperature changes.

In presented study the microstructure of ceramized composites containing stabilized level of mineral fillers and changing type of selected fluxing agent was described. The ceramization process was conducted at different conditions: rapid burning at temperatures 800 or 1000°C and, relatively, slow temperature increase from 20 up to 1000°C, in electrical furnace. The results were discussed from the point of view of the ceramized phase morphology studied by SEM and the mechanical strength of ceramized samples.

Keywords: composites, silicone rubber, mineral fillers, ceramization

1. INTRODUCTION

Flame resistance of electrical cable covering insulation is very important from the safety point of view of people using means of transport, visiting shopping centres, sport halls, theatres or cinemas. Metal rods in protective covering make the main part of electrical circuits, responsible for distribution of electricity in cars and planes, providing power supply for elevators or fire-fighting systems. Material used nowadays, based on silicone rubber or PVC is incombustible, but the problem concerns its mechanical durability under flame, maintaining circuit integrity and energy supply during fire, indispensable to secure time for evacuation or emergency landing. Integrity of electrical cables can be obtained by application of covering insulation made of polymer composites ceramizing at high temperature arising during fire [1-5]. The paper presents results of investigation on optimization of ceramic phase using stabilized composition of the mineral part of composites and changing fluxing agent.

2. EXPERIMENTAL

Materials used for investigation were silicone rubber-based composites. Composite mixes were prepared using a Brabender (Germany) Plasticorder internal micro-mixer, operating with rotors speed of 20 rpm during incorporation of the components and 60 rpm during their homogenization (10 min). They were composed of a mixture of silicone rubber compounds, filled with a silica, playing the role of a polymer matrix in which minerals: mica, titanium oxide and glassy phases of different compositions, playing the role of a fluxing agent, were incorporated at a fixed amount. The crosslinking agent - dichlorobenzoyl peroxide, was added to the mixes on a David Bridge (UK) two-roller external mixer at 40°C.

The composition of the silicone mixes studied is given in Tab. 1, together with a short description on the fluxing agents applied.

Tab. 1 Composition of the silicone mixes studied

No	Component	Content [phr]
1	Silicone mix, Polsil 60 (50 phr of silica)	70
2	Silicone mix, Polsil 40 (22 phr of silica)	30
3	Fluxing agent *	10
4	Mica (Phlogopite)	15
5	TiO ₂	5
6	2,4 – dichlorobenzoyl peroxide	2.5

* Fluxing agents (frits) used for investigations:

- FR2050 (commercial grade, Reibold & Strick, Germany)
- RC-9 (synthesized at the Institute of Ceramic and Building Materials, Warsaw, Poland, based on their own patents)
- Z-01 (synthesized *ibid.*, according to our instructions)

Frits added for ceramic mixes were subjected DSC/TG (*Differential Scanning Calorimetry / Thermogravimetry*) analyse using Netzsch (Germany) STA449F3 Jupiter equipment.

Ceramization tests were performed using three different algorithms of the furnace temperature increases. The first method of heating was a relatively slow temperature increase from 20°C up to 1000°C with the 300°C/h heating rate and 20 minutes of soaking time at maximum temperature.

The second method of firing was a rapid placement of fired samples in the furnace heated up to 1000°C. The soaking time was also 20 minutes.

The third method of firing was similar to the second one, the maximum temperature was 800°C.

Ceramized samples were subjected to compression tests using a Zwick Roell Z2.5 instrument (Germany). The maximum force required to destroy a composite sample was detected. The mechanical strength of the ceramized materials was calculated as an average value of 5 probes.

Microstructures of ceramized samples were examined by scanning electron microscopy using Nova Nano SEM 200 FEI (UK) apparatus.

3. RESULTS

Diagrams in Figures 1 – 3 show results of thermo-gravimetric analyses of frits used for investigations. Frits differ in transition point temperatures and softening temperatures.

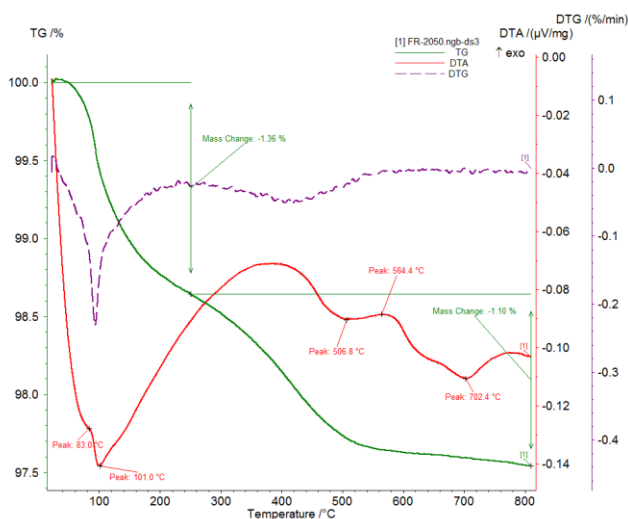


Fig. 1 Thermo-gravimetric curves of FR2050 frit.

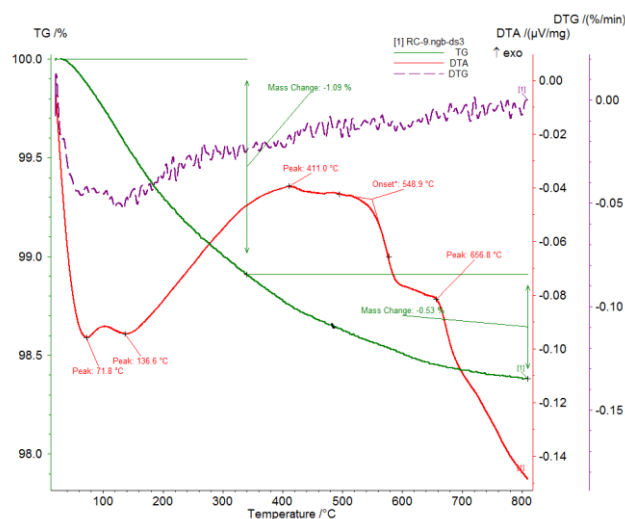


Fig. 2 Thermo-gravimetric curves of RC-9 frit.

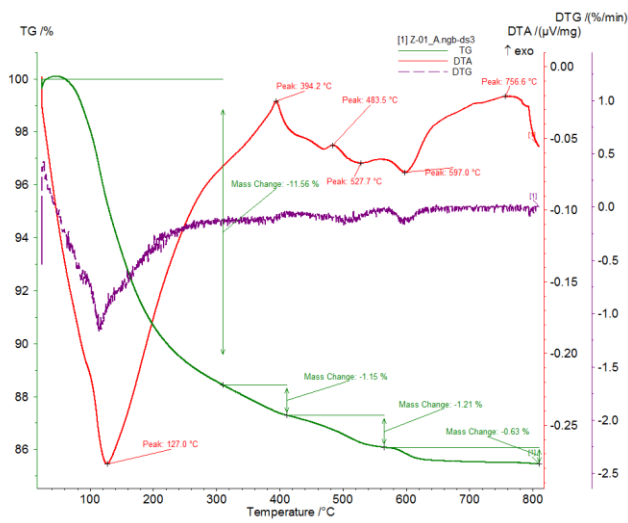
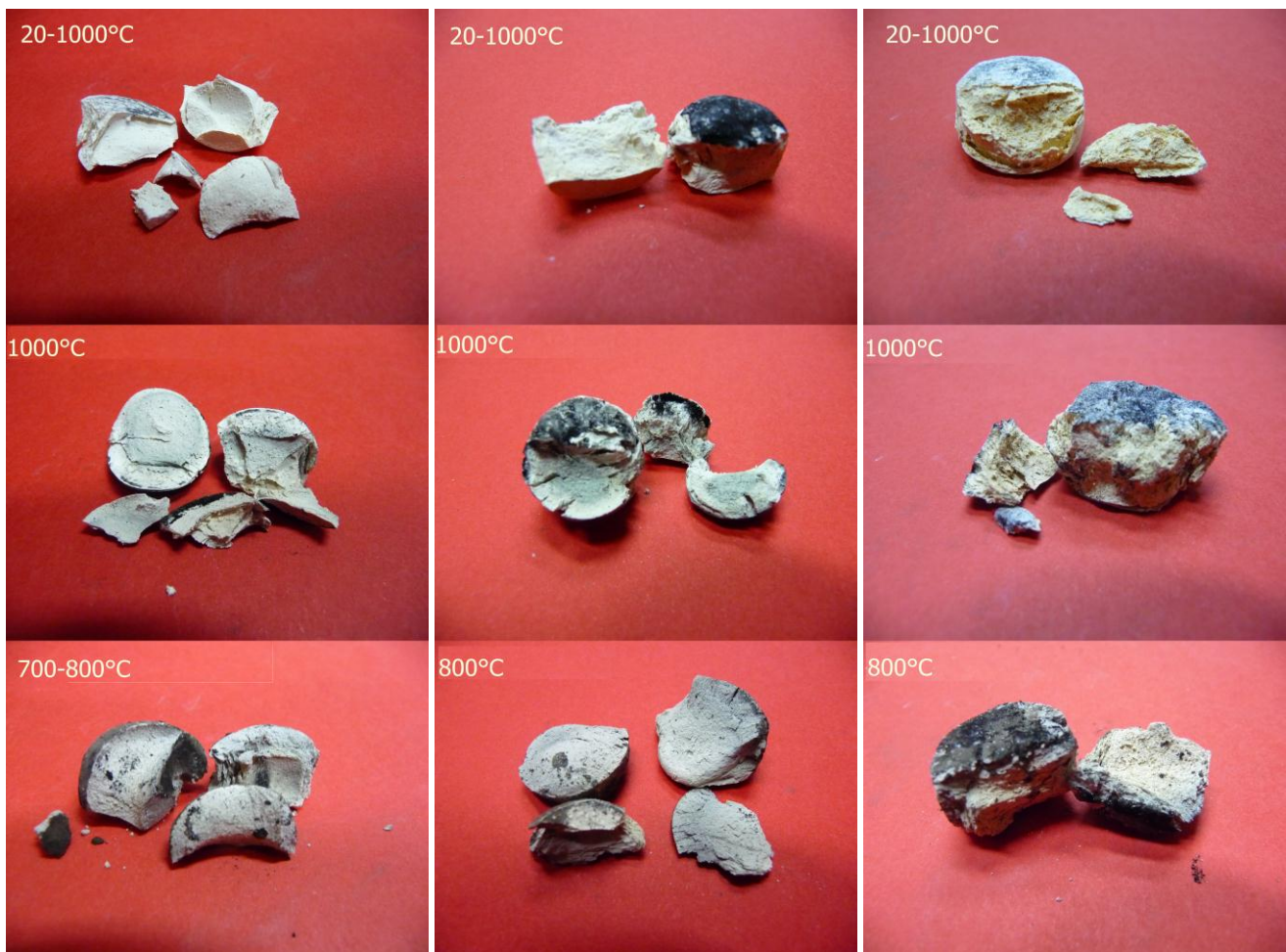


Fig. 3 Thermo-gravimetric curves of Z01 frit.

The macroscopic images of ceramized samples after strength test were collected in the Figure 4. These images illustrate differences in morphology of samples fired at different conditions.



Composite containing FR2050 frit

Composite containing RC-9 frit

Composite containing Z01 frit

Fig. 4 Images of investigated composites ceramized at different conditions after the strength tests.

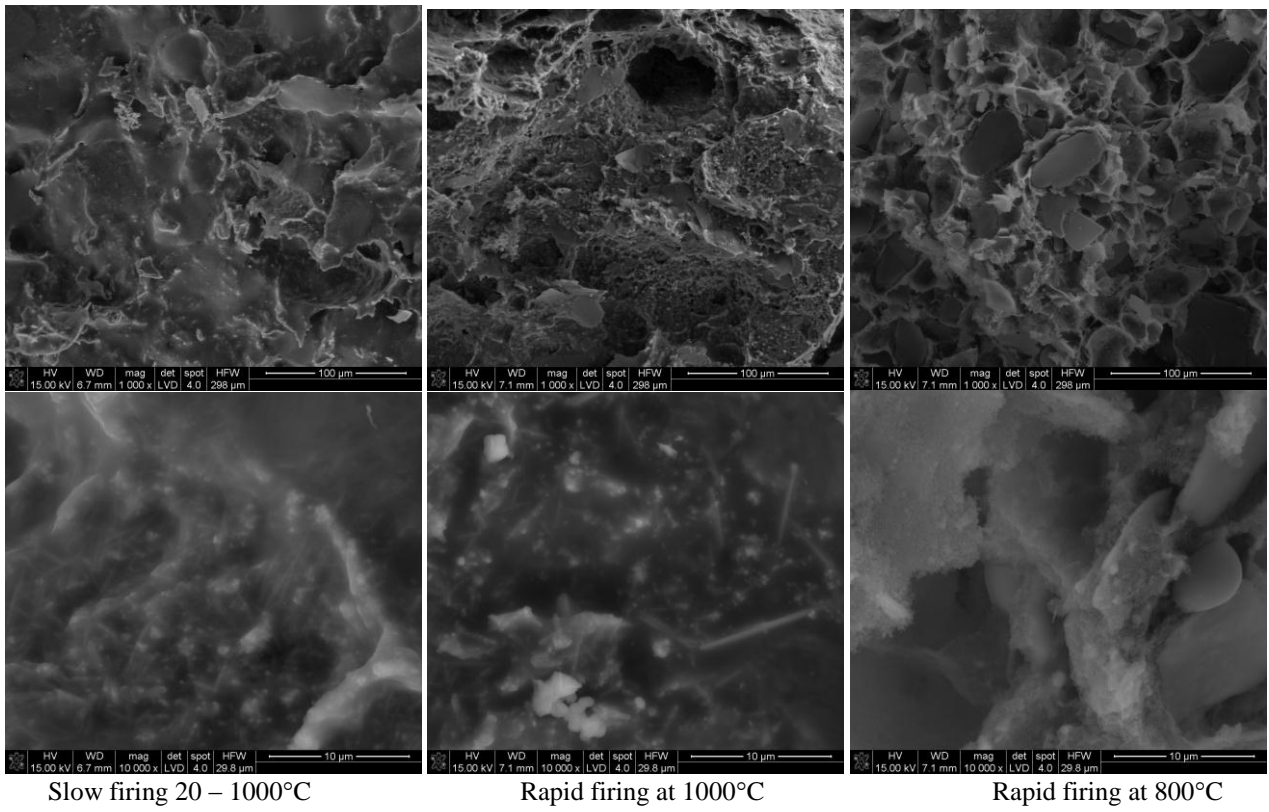


Fig. 5 SEM images of FR2050 frit containing composite ceramized at different conditions.

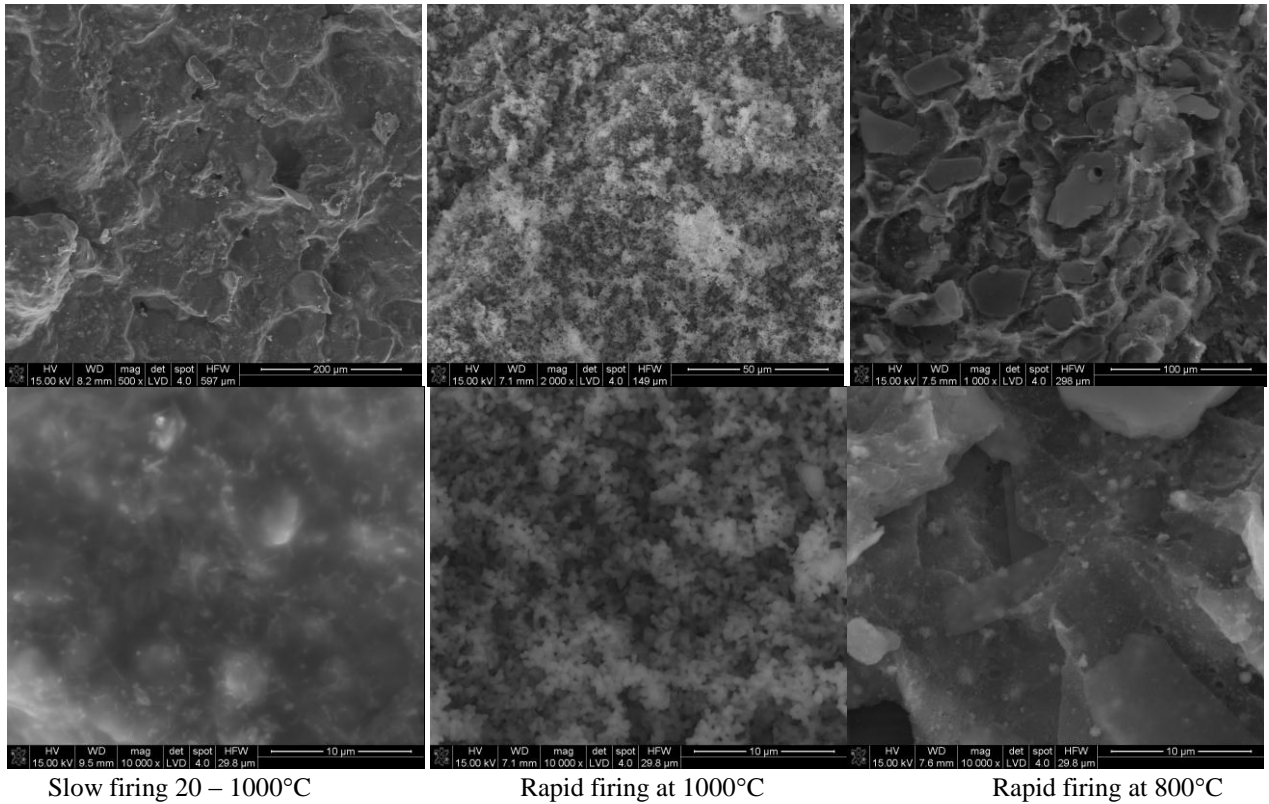


Fig. 6 SEM images of RC-9 frit containing composite ceramized at different conditions.

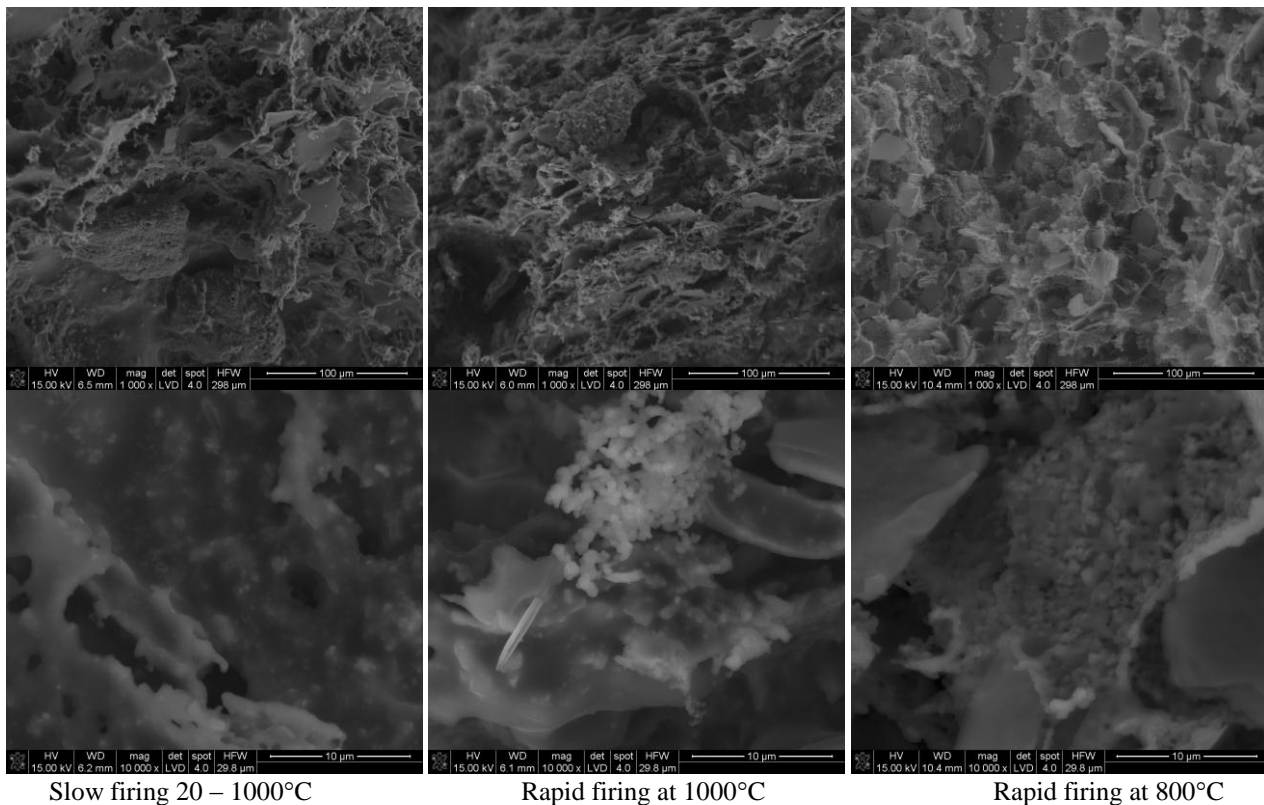


Fig. 7 SEM images of Z01 frit containing composite ceramized at different conditions.

Figures 5 – 7 illustrated ceramized samples morphology in the micrometric scale. There were general similarities in microstructures of composites containing different frits ceramized under similar conditions. Samples fired slowly up to 1000°C showed the compact microstructure. All ceramic components, even mica big grains (flakes), were tight joined with glassy phase produced during ceramization.

The microstructures of samples fired in rapid way were much more porous. In samples heated at 1000°C there was a significant amount of nanometric silica produced during polymer degradation. Fine particles of silica were especially present in the sample containing RC-9 frit. This „free” silica on the ceramized sample surface could be bounded with therest of the material during successive heating, but in the case of the real fire external conditions could make it impossible. Such structure is weaker than compact structure achieved during slow heating.

All samples heated at 800°C have loose microstructure with distinct mica flakes protruding from glassy phase. Particles of nanometric silica were also present.

Tab. 2 Compression strength of the ceramized silicone composites

No	Sample	The average maximum force during compression test [N]		
		800°C	1000°C	20-1000°C
1	FR2050	20 ±5	23 ±6	64 ±8
2	RC-9	48 ±4	48 ±5	431 ±60
3	Z01	67 ±7	26 ±4	76 ±8

± - denotes the standard deviation

Results of the strength tests describes the state of compactness of ceramized bodies. In fact, all investigated samples have the same mineral composition. The only difference is the kind of fluxing agent. Table 2 collected results of measurements of the maximum force noticed during the compaction test. The analysis of this data showed that each tested frit influenced the ceramized composite compactness in the different way. After fast firing at 800°C the maximum strength showed composite containing Z01 frit. Its strength was about three times higher than composite containing FR2050 frit.

The increase of temperature of the fast firing up to 1000°C did not change the strength of composites containing FR2050 and RC-9 frits. The material containing Z01 frit showed significant strength loss ~50%.

Slow firing at temperature range of 20 - 1000°C led to the strongest ceramized bodies for each investigated composition. The difference was in the scale of strength improvement. Material containing FR2050 frit after slow firing was about 250% strongest than fast fired one. Composite with RC-9 frit addition showed almost one order of magnitude strength increase after applying of slow firing procedure.

The using of Z01 frit led to the composite material which showed compactness decrease when fast firing temperature increased. It could not be beneficial for strength of fast ceramized body.

4. SUMMARY

Polymer based composite materials dedicated for electrical cable coverings must show its ability for ceramization in the emergency case when the fire happen. In practice, it is not possible to predict the fire conditions, i. e. the rate of temperature increase, the maximum temperature, etc. The good cable covering should has properties as stable as it is possible. Polymer matrix degradation takes place at temperatures up to 700°C [6, 7]. At higher temperatures ceramic components and products of polymer degradation were responsible for material properties. These properties should be stable or should change in predictable way.

The performed studies confirmed that a type of used fluxing agent strongly influenced the compactness of silicone based composites after ceramization. These studies allowed us to compare the effectiveness of various fluxing agents, which can be applied as a composite components. Depending of used frit composites showed different microstructures and mechanical properties after ceramization. Mentioned properties could distinctly change with ceramization conditions changes. The final microstructure and strength did not depend only on the maximum temperature. Also the firing kinetics is very important for ceramized body properties.

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