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Composites with clay and bentonite matrix: a study of the certain materials behavior for ceramic composites

Simona Matei*, Bela Varga, Tibor Bedo, Mihai Alin Pop, Maria Stoicanescu, Aurel Crisan

Transilvania University of Brasov, Material Science Department, 29 Eroilor Blvd., 500036, Brasov, Romania

Abstract

The paper is a study regarding ceramic matrix composites with clay and bentonite. Ceramic powders (Al_2O_3 and SiC) and metallic particles (Cu, Al and Fe) were used as reinforcement. The materials used for the matrix were first subjected to a thermal analysis. Based on the obtained information from the thermal analysis, the methodology for making the composites was established, namely the mixing of the dry components for a good homogenization, cold pressing for compacting in cylindrical samples and finally sintering at the appropriate temperatures. In this way cylindrical specimens (diameter between 15-16 mm and height between 11-15 mm) were made. For composite materials, the porosity and compressive strength are important parameters that depend on the individual behaviour of the sintering phases, but also on the interactions between the phases at high temperatures [1]. Reinforcing materials were added in composites in two steps. Firstly, clay and bentonite matrix composites with ceramic powders (Al_2O_3 and SiC) were first obtained and analysed, following the effect of these ceramic powders on the properties. Secondly, for each type of composite (with a certain matrix or a certain reinforcement material), metal powders of Al, Cu and Fe (10%) were introduced, again looking at the effect of the ceramic powders as materials of reinforcement on the properties of composites. The study found a significantly different behaviour after the addition of ceramic powders. At the same time, if in the case of composites reinforced only with ceramic powders, the increase in the proportion of powders leads to a decrease in compressive strength, the addition of metal powders radically changes this type of dependence, their compressive strength increasing with the proportion of ceramic reinforcement powders. The behaviour of bentonite matrix composites has always been superior to those of clay matrix, for the same types and proportions of reinforcement materials.

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Keywords: ceramic composites, bentonite, thermal analysis, metallic particles, porosity.

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* Corresponding author. Tel.: +0-000-000-0000 ; fax: +0-000-000-0000 .
E-mail address: simona.matei@unitbv.ro

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1. Introduction

The composite material comprises a base material, the matrix, in which a complementary material is dispersed in the form of particles or fibers, and the properties that are intended to be obtained in an improved form are: tensile strength, wear resistance, density, high temperature resistance, superficial hardness, dimensional stability, vibration damping capacity. [2-9].

Metallic particle-reinforced ceramic matrix composites are promising materials for high temperature applications [10]. Due to the ceramic phase these materials offer the possibility of combining heat resistance, degradation resistance and wear resistance with high mechanical strength and thermal conductivity provided by the metal phase [11]. Thus, composites with ceramic matrix reinforced with metallic particles are classified as low-cost multifunctional materials [12]. These are used for the functional components in the brake assembly, furnace materials, energy conversion systems, gas turbines, thermal engines, etc. [13,14].

The ceramic matrix includes clay, bentonite, silicon carbide, alumina, silicon oxide, zirconium and other elements [4].

In recent years, clay minerals have been widely applied in industrial engineering, agriculture, pharmaceuticals, food, and oil recovery and refining. Several of the important physical and chemical properties that make clay minerals valuable include particle size, surface chemistry, particle shape and surface area [15]. Due to the lamellar structure, large surface area and high ion exchange capacity, clay minerals have great potential to bind to different pollutants, such as heavy metals, paints and organic compounds [16,17]. Bentonite is among the most studied clay that can be used as a low-cost adsorbent material. An important property of bentonite is that it exhibits negatively charged layers and the charge is normally balanced by the hydration ions placed in the intermediate spaces [16]. It has relatively high cation exchange capacity, has good adsorption properties and can effectively remove certain inorganic and organic pollutants from aqueous solutions [18-20].

Clay is a natural inorganic binder consisting of impure oxides, hydroxides, carbonates, feldspars, mica, etc., which is chemically a hydrated aluminum silicate: $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$. Depending on the amount of water absorbed, the clay swells, acquires bonding properties and, through the bonds it creates between the various added particles (Al_2O_3, $2SiO_2$, SiC, etc.), it gives the mixtures mechanical strength and plasticity. Bentonites are a variety of clays with a high montmorillonite content (over 70%). Due to high water adsorption and ion exchange, bentonite can be used in various technological applications, for example, catalysts in the chemical process, additives for plasticizing and handling the viscosity of ceramic pastes or sealing materials. Compacted bentonite is characterized by low permeability, long term stability, self-sealing capacity and high adsorption [21].

Obtaining composites using these materials as matrices requires a good understanding of their behavior depending on temperature. Delage et al. [22] studied the production of bentonite matrix composites by conventional methods and noted that during drying, the phenomenon of contraction results in cracks in the surface of the sample. Chenu and Tessier [23] and Smart and collaborators [24], have studied the production of these types of composites by freezing under liquid nitrogen or propane atmosphere. However, this method resulted in samples with a maximum thickness of 5 μm.

The paper focuses on the synthesis and characterization of some ceramic matrix composites reinforced with ceramic and metal powders.

2. Experimental research

2.1. Materials

For the matrix, two types of ceramic powders were used: clay (37% Al_2O_3, max.2.2% Fe_2O_3, max 60.8% SiO_2) and bentonite (53% montmorillonite, max.2.2% Fe_2O_3, max 60.8% SiO_2). As reinforcing elements Al_2O_3 (50 μm granulation) and SiC (granulation 63÷80 μm) were added, as well as Cu (15÷20 μm granulation), Al (50÷65 μm granulation) and Fe (80÷95 granulation) metal powders. The proportions of the components used to manufacture the samples are shown in Table 1.

Fig. 1. (a) Composite with clay matrix reinforced Al_2O_3, SiC, Cu, Fe si Al particles; (b) Composite with bentonite matrix reinforced Al_2O_3, SiC, Al si Fe particles.

Table 1. The component proportions used to perform the samples

No. crt.	Sample number	Sample type	Components							Compressive strength, MPa
			Clay, %	Bentonite, %	SiC, %	Al_2O_3,%	Cu, %	Al, %	Fe, %	
1	1.1	1.1.1.	94.4		5.6					48
		1.1.2.	88.9		11.1					42
		1.1.3.	83.3		16.7					39
		1.1.1.Cu	85		5		10			20
		1.1.1.Al	85		5			10		41
		1.1.1.Fe	85		5				10	34
		1.1.2.Cu	80		10		10			24
		1.1.2.Al	80		10			10		53
		1.1.2.Fe	80		10				10	42
		1.1.3.Cu	75		15		10			40
		1.1.3.Al	75		15			10		56
		1.1.3.Fe	75		15				10	55
	1.2.	1.2.1.	94.4			5.6				53
		1.2.2.	88.9			11.1				39
		1.2.3.	83.3			16.7				37
		1.2.1.Cu	85			5	10			19
		1.2.1.Al	85			5		10		43
		1.2.1.Fe	85			5			10	26
		1.2.2.Cu	80			10	10			20
		1.2.2.Al	80			10		10		55
		1.2.2.Fe	80			10			10	33
		1.2.3.Cu	75			15	10			38
		1.2.3.Al	75			15		10		62
		1.2.3.Fe	75			15			10	75
2	2.1.	2.1.1.		94.4	5.6					111
		2.1.2.		88.9	11.1					104
		2.1.3.		83.3	16.7					100
		2.1.1.Al		85	5			10		52
		2.1.1.Fe		85	5				10	56
		2.1.2.Al		80	10			10		88
		2.1.2.Fe		80	10				10	68
		2.1.3.Al		75	15			10		96
		2.1.3.Fe		75	15				10	99
	2.2.	2.2.1.		94.4		5.6				135
		2.2.2.		88.9		11.1				111
		2.2.3.		83.3		16.7				90
		2.2.1.Al		85		5		10		58
		2.2.1.Fe		85		5			10	69
		2.2.2.Al		80		10		10		60
		2.2.2.Fe		80		10			10	77
		2.2.3.Al		75		15		10		66
		2.2.3.Fe		75		15			10	141

Dry mixtures were made (according to Table 1) for good homogenization. The obtained mixtures were cold pressed for compaction in cylindrical samples and finally sintered at the appropriate temperatures. In this way cylindrical specimens with diameter between 15-16 mm and height between 11-15 mm were made.

The specimens (Fig. 1a and Fig. 1b) were subjected to the following types of characterizations: surface study by optical microscopy, differential thermal analysis, determination of mechanical properties and porosity assessment.

3. Experimental results

3.1. Surface analysis by optical microscopy was performed using the OmniMet image analysis and imaging system with a Nikon Eclipse MA100 compact reversed metallographic microscope.

The morphology of the sample surfaces after sintering is similar to that presented in Figures 2a-2d. In the case of the clay matrix (figures 2a-2d) and the bentonite matrix (figures 3a-3c) after sintering one can observe a monolithic base mass in which the particles introduced for reinforcement are clearly visible. In Figure 2a, for example, the particles of SiC dispersed in the clay matrix are clearly distinguishable. Similarly, metallic Cu, Fe and Al particles are evenly dispersed in the matrix (figures 3a-3c). Since sintering has been carried out in non-protective atmosphere, the presence of oxides on the surface of the metallic particles is possible.

When using the bentonite matrix, the surface aspects are similar. Figure 3a shows the monolithic matrix with evenly dispersed Al_2O_3 particles. Moreover, Figures 3b-3c show the Fe and Al metallic particles introduced as reinforcement.

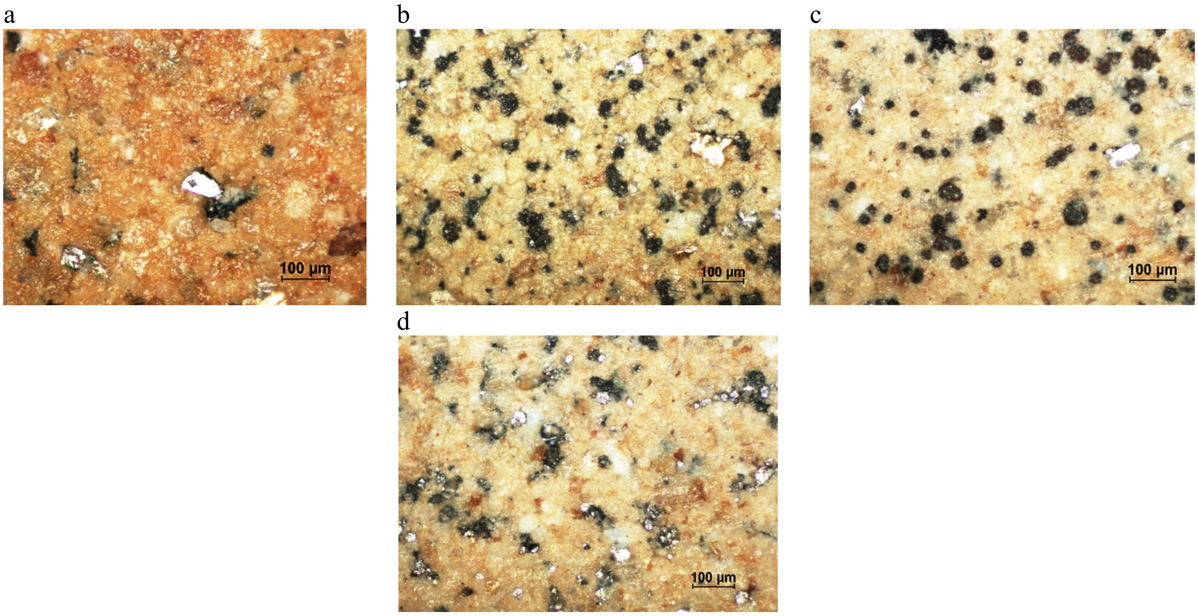

Fig. 2. Surface appearance for clay matrix composite reinforced: (a) SiC particles; (b) SiC and Cu particles; (c) SiC and Fe particles; (d) SiC and Al particles.

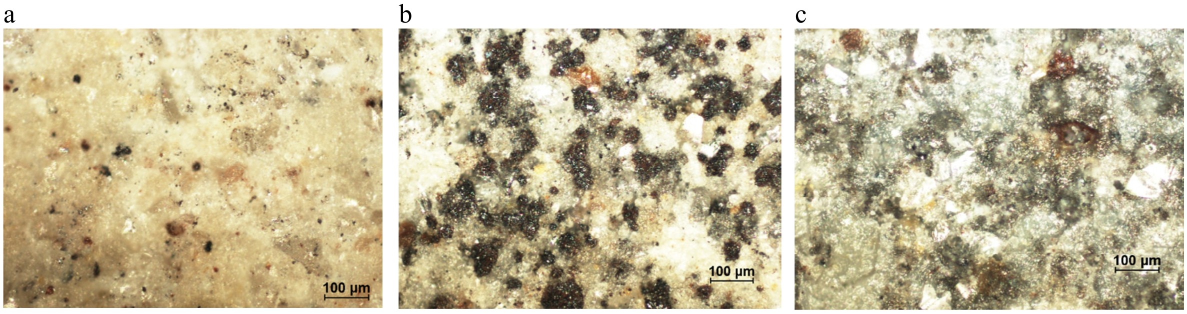

Fig. 3. Surface appearance for bentonite matrix composite reinforced: (a) Al_2O_3 particles; (b) Al_2O_3 and Fe particles; (c) Al_2O_3 and Al particles.

3.2. Differential thermal analysis was performed using the NETZSCH STA 449 F3 JUPITER type TG / DTA with a heating rate of 10 ° C/min, varying the temperature from room-temperature to 900 °C in a nitrogen atmosphere, with a flow rate of 20 ml/min in an alumina crucible.

The graphs obtained from the thermal analysis revealed the temperatures at which important transformations take place, from the point of view of the thermal effects and of the mass variations of the analyzed materials.

Figures 4-5 show the heat analysis diagrams for the materials used as the matrix of the composites, namely clay (figure 4) respectively bentonite (figure 5). These figures show the existence of some specific transformations:

- between 80-200 °C dehydration of the matrix material occurs, accompanied by an endothermic thermal effect and a corresponding mass loss. This transformation is marked as peak 1;
- between 550-700 °C there is loss of chemically bound water accompanied by the conversion of kaolinite into meta-kaolinite according to the reaction [25]:

$$2SiO_2 \cdot Al_2O_3 \cdot 2H_2O \rightarrow 2SiO_2 \cdot Al_2O_3 + 2H_2O \tag{1}$$

This type of transformation was further marked with peak 2.

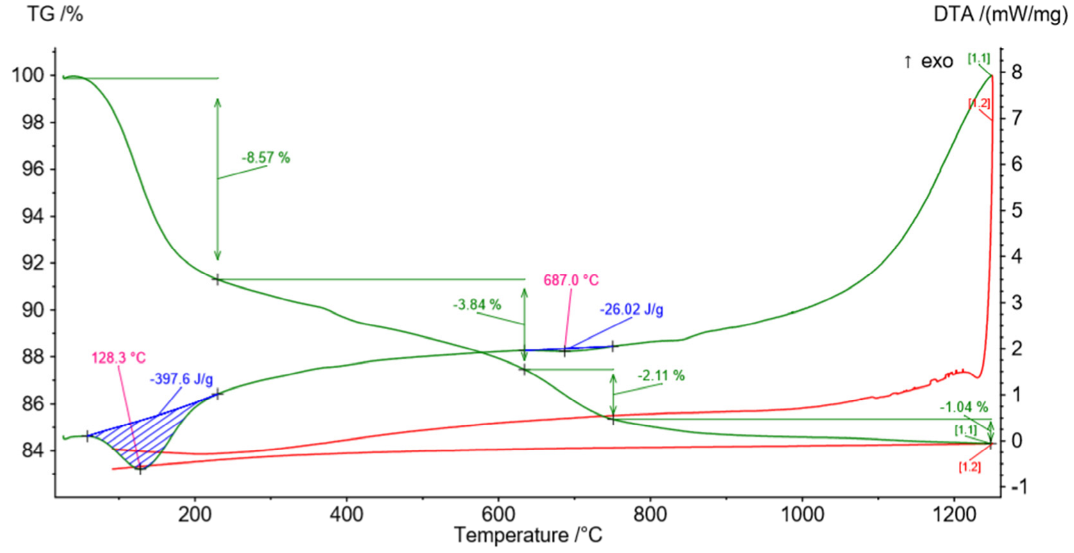

Fig. 4. TG-DTA graph for clay.

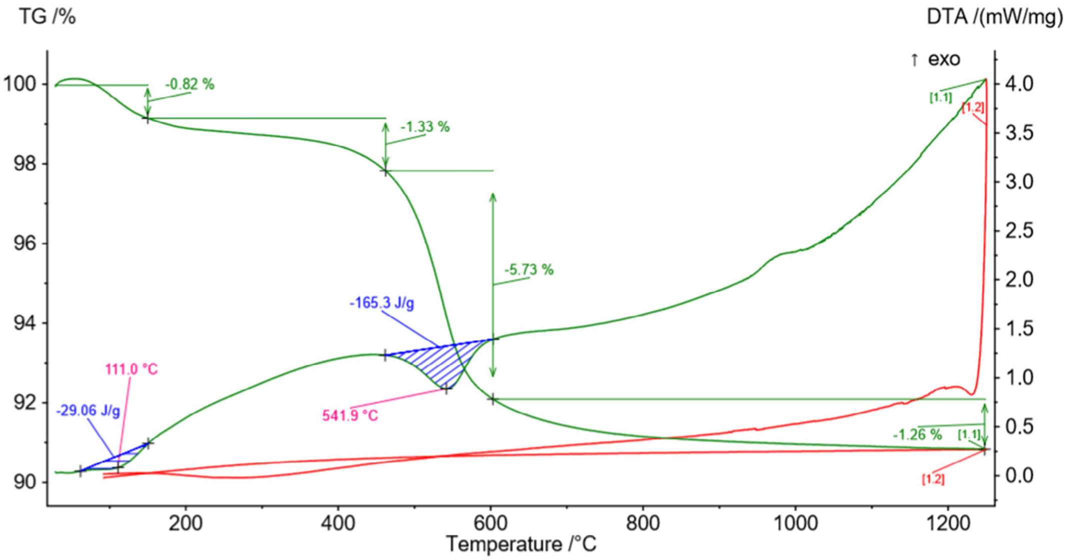

Fig. 5. TG-DTA graph for bentonite.

For composite materials presented here in, the effect of introducing ceramic and metallic particles on these transformations was observed. In this respect, the specific values of the peak 1 and peak 2 transformations for some of the composites are shown in table 2.

Table 2. Specific values of peak 1 and peak 2 for the composites made

No. crt	Sample number	Peak 1			Peak 2			Total mass change, %
		Temperature, ℃	Specific energy, J/g	Mass change, %	Temperature, ℃	Specific energy, J/g	Mass change, %	
1.	1.1.1.	182.9	-0.1693	0.33	521.6	-1.741	-0.02	0.21
2.	1.1.1.Cu	231.2	-4.534	0.36	530	0.3629	0	0
3.	1.1.1.Al	211.1	-8.585	-0.73	561.6	-1.289	0	-0.76
4.	1.1.1.Fe	211.8	-1.51	-0.30	512.3	2.116	-0.10	-73
5.	1.2.1.	246.9	2.759	0.25	496.2	-0.2205	-0.01	0.11
6.	1.2.1.Cu	209.7	-1.785	0.36	506.9	-0.3352	-0.01	-0.14
7.	1.2.1.Al	197.7	0.5613	-0.64	543.3	1.729	0.01	-0.67
8.	1.2.1.Fe	211.8	-0.888	0.18	487.6	2.529	0	0.09
9.	2.1.1.	132.9	12.38	0.25	515.1	-4.865	-0.13	-0.37
10.	2.1.1.Al	214.1	-5.523	0.36	499	-3.729	0.01	0.37
11.	2.1.1.Fe	192.6	-0.386	0.35	440.8	4.251	0	0.34
12.	2.1.2.	167.1	0.2332	-0.13	512.9	-1.636	0.02	-0.15
13.	2.1.2.Al	187.9	0.08799	-0.12	515.8	-0.06209	-0.21	-0.38
14.	2.1.2.Fe	175.6	-0.06314	-0.22	512.7	-2.634	0.02	-0.32
15.	2.2.2.	321.2	-2.223	0.22	506.3	2.135	-0.01	0.14
16	2.2.2.Al	181.9	-0.2993	0.28	532.9	-5.684	-0.03	0.24
17.	2.2.2.Fe	229.1	1.069	0.13	511.8	1.013	-0.05	-0.25

For a more efficient analysis of the effect of the reinforcement material on the transformations, the values shown in table 2 were used for rendering the dependencies shown in figures 6a-6h.

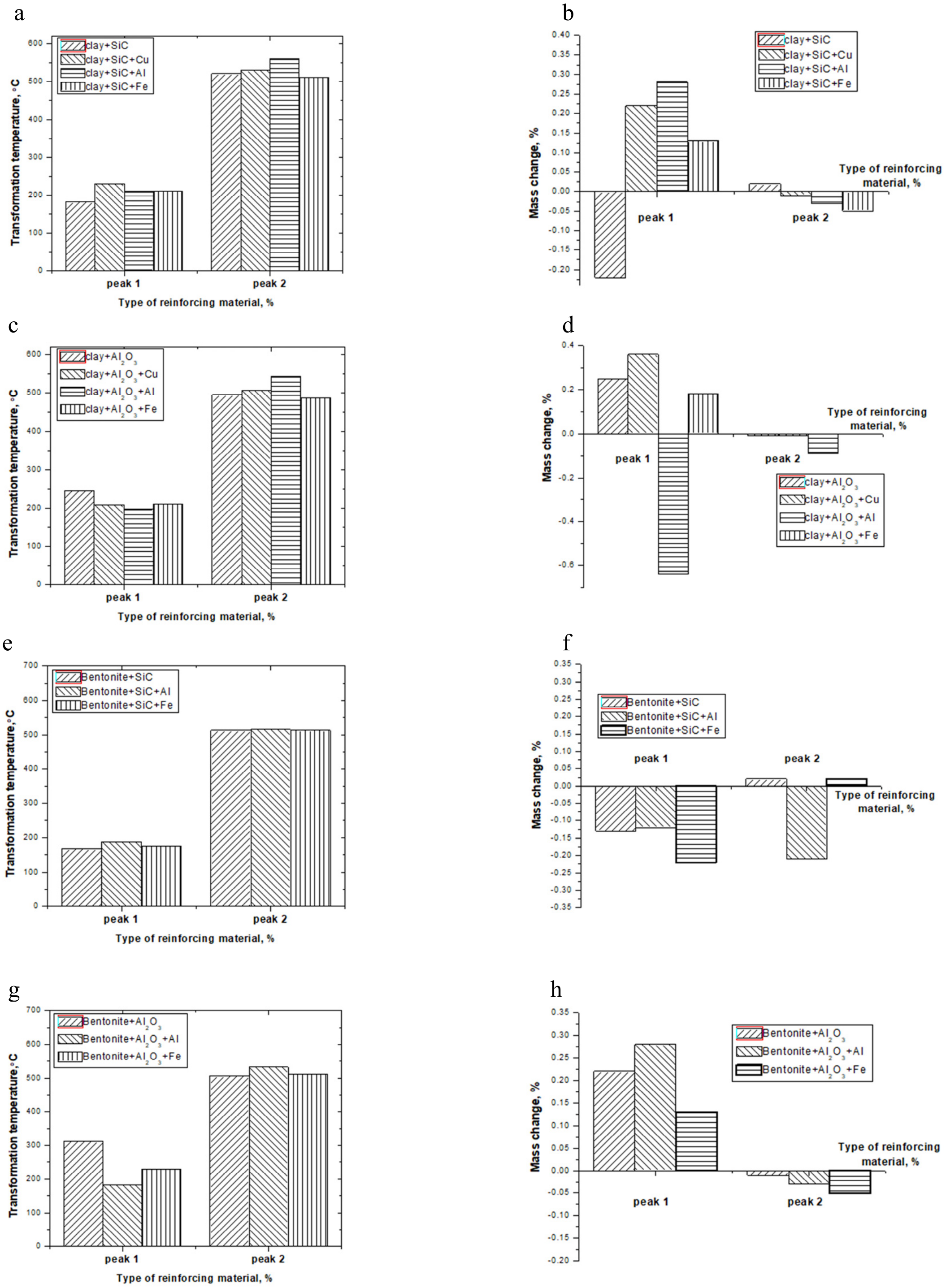

Fig. 6. Variation specific data from thermal analysis depending on the type of composite material: (a) Transformation temperatures; (b) Mass change; (c) Transformation temperatures; (d) Mass change; (e);Transformation temperatures; (f) Mass change; (g) Transformation temperatures; (h) Mass change.

It can be seen from figures 6a, 6c, 6e, 6g that the introduction of reinforcing materials does not significantly change the temperatures at which the transformations observed at peak 1 or peak 2 are occurring. This observation suggests that they do not actually participate in the transformations in question but possibly to a very small extent.

With regard to the mass (and energy) variations that accompany these transformations between the analyzed samples, there are significant differences. These are actually determined by the initial state of the materials under study. Thus, the materials used for the matrices were subjected to the thermal analysis in the natural state (diagrams in Figures 4-5). For all composites, the study was performed on the samples, after sintering. This is actually the explanation for these significant differences in energy and mass.

3.3. Mechanical properties

The compressive strength for the composites was determined on Universal Mechanical Test Machine (model WDW-150S). The results are shown in table 1 and Figures 7a,7b,8a,8b.

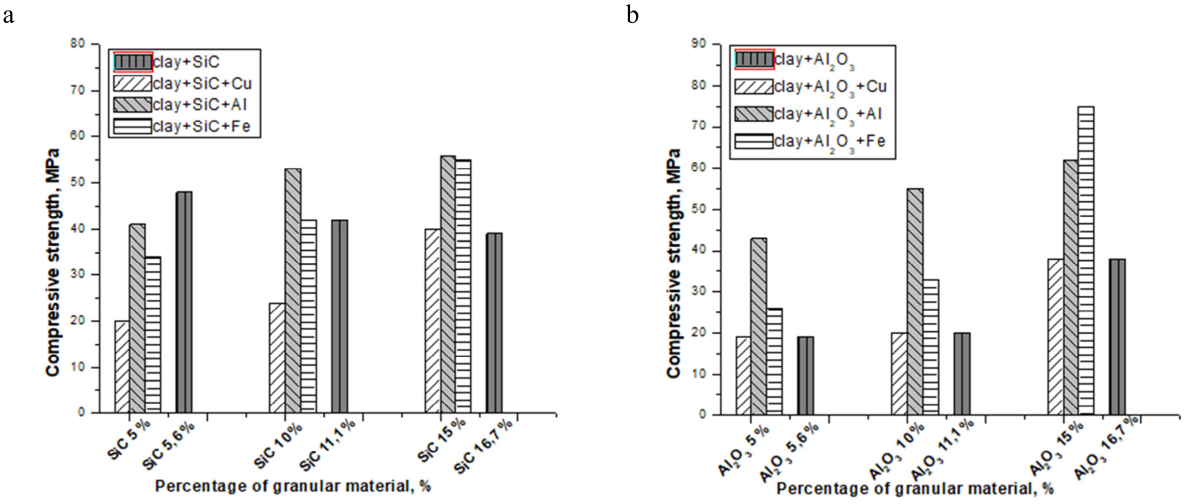

Fig. 7. Compressive strength variation depending on the: (a) SiC content for composites with clay matrix; (b) Al_2O_3 content for composites with clay matrix.

In case of the composites based on clay and bentonite, reinforced with SiC and Al_2O_3 powders, the compressive strength decreases as the percentage of granular material increases (figures 7a,8a,8b). By adding the metal particles to the composite, their behavior changes radically. In all cases, the compressive strength increases with the increase in SiC and Al_2O_3 powders, respectively (figures 7a,7b,8a,8b).

From figures 7a and 7b it can be observed that introduction of Cu in clay+SiC has a negative effect on compression resistance for SiC=5…11.1%, and the introduction of Cu in clay+Al_2O_3 has an insignificant effect on compression resistance.

From figures 8a and 8b it can be observed that introduction of Al and Fe decreases the compression resistance of bentonite+SiC and bentonite+Al_2O_3 composites in the same range, for the content between 5…11,1%. For SiC=16,7%, the effect for the Al and Fe particles are insignificant and for Al_2O_3=16,7%, the Al effect is still negative but the Fe effect becomes positive.

The positive effects of the presence of metallic powders on compressive strength can be attributed to the different behavior of the materials in terms of resisting to the test loads. Metallic powders give an increased elasticity component, also increasing the capacity of the material upon loading.

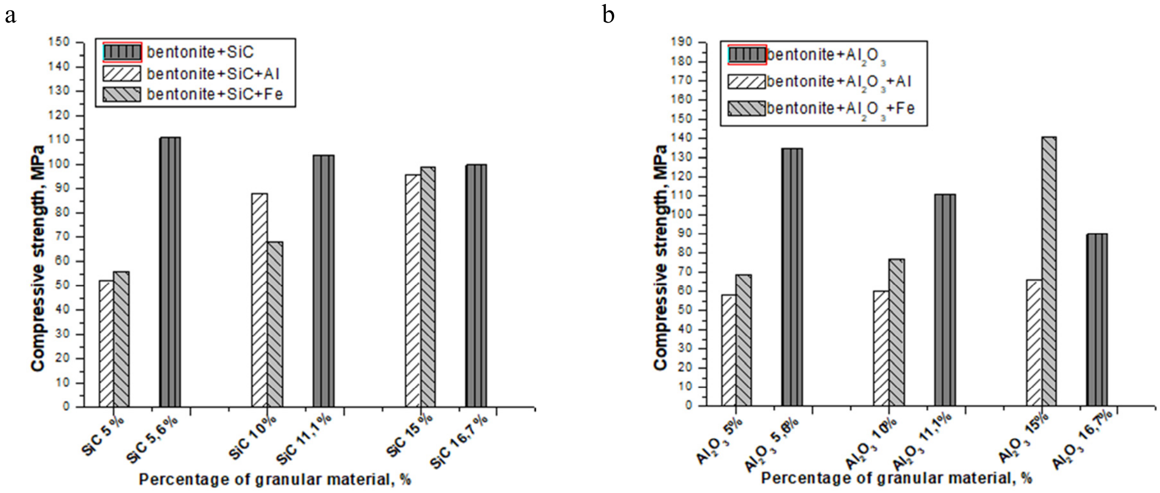

Fig. 8. Compressive strength variation depending on the: (a) SiC content for composites with bentonite matrix; (b) Al_2O_3 content for composites with bentonite matrix.

3.4. The porosity was assessed by measuring the volume of open pores. This was done by measuring the volume and at the same time the mass of water entering these pores in well-determined volume samples. The values obtained for porosity were in the range of 30-40%. They are comparable to the values given for similar materials in the literature [14].

4. Conclusion

Through optical microscopy both the monolithic aspect of the composite matrix and the presence of reinforcement particles was observed.

Thermal analysis showed that the reinforcement particles do not significantly influence the transformations that are produced in the matrix nor show their own transformations highlighted by this analysis. This indicates a contribution of these materials to the thermal stability of the composites.

For composite with clay matrix, the SiC powders cause a decrease in compressive strength and the Al_2O_3 powders cause a increase in compressive strength (figures 7a and 7b).

For composite with bentonite matrix, the ceramic powders (SiC and Al_2O_3) cause a decrease in compressive strength (figures 8a and 8b).

When adding metallic powders, their effect changes significantly. In these situations, the compressive strength increases as the amount of ceramic powder in the composite increases. The effect is correlated with the matrix or the ceramic powder added in the matrix, as follows:

- For SiC clay, the maximum effect is produced by the Fe powder;
- for SiC bentonites the effects of Al and Fe are comparable;
- for Al_2O_3 bentonite the Fe effect is significantly more pronounced than that of Al.

The highest compressive strength was obtained for bentonite-based composites with 15% Al_2O_3 and 10% Fe (141 MPa). In all cases, bentonite-based composites have higher compressive strength than clay-based composites.

Porosity values recommend these materials for uses in the field of micrometric particle filters.

Acknowledgements

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