APPLYING TAGUCHI METHOD TO TIO_2 DOPED SINTERED BASALT

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Keywords: sintered basalt, TiO_2 doping, Taguchi method, full factorial simulation

Abstract: The paper presents a study of the variation of compression resistance of sintered basalt pieces doped with TiO_2. For performing the experiments, a L_8 Taguchi standard matrix was utilized, for which the controlled factors were assigned. For each experimental condition, 5 basalt sintered pieces were manufactured, which were tested to compression. There were sintered 25 parts (probes), analyzing the improvement in compression resistance by doping the basalt with 2% TiO_2. In order to verify the precision of designing the experiments based on a L_8 orthogonal matrix, a full factorial simulation was performed.

1. BASALT SINTERING

Sintering is a processing technique utilized for manufacturing materials with controlled density from metallic powders and/or ceramic powders (including basalt). One of the most important application of sintering is manufacturing sintered basalt parts with high wearing resistance. Figure 1 presents the general process of manufacturing sintered parts. Unlike other manufacturing technologies, the different stages of processing and the corresponding variables must be considered. Depending on the "forming" technique, sintering conditions may change and also the sintering properties can vary considerably. In sintering stage may be used different techniques and process variables that can induce changes in the microstructure and properties of sintered material.

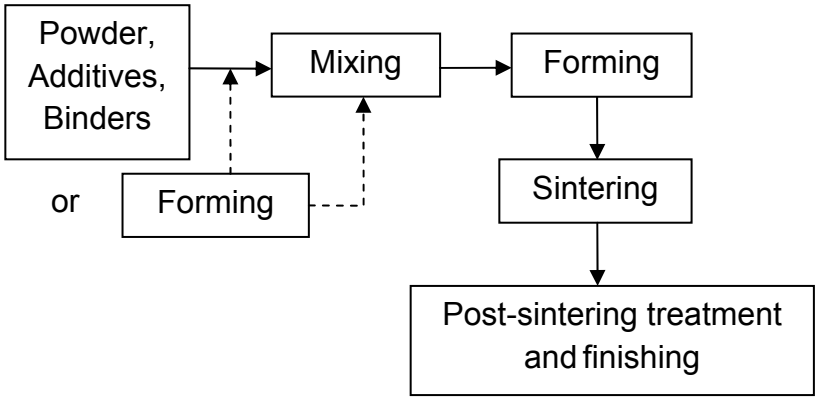

Fig.1 General process of manufacturing sintered parts

Sintering processes can be divided into two categories [4]: solid state sintering and liquid state sintering. Solid state sintering (below solidus line) occurs when the compacted powder is fully densified in solid state at sintering temperature, while the liquid phase sintering occurs when liquid state is present in the compacted powder during sintering. Different types of sintering are explained using a schematic phase diagram, although the optimal type of sintering depends on the material and / or to sintering scope. The "Engine" of sintering process is represented by interfacial total energy reduction. Interfacial total energy of compacted powder is expressed as λA, where λ is the specific interfacial energy and A is total area (interface) of compacted powder. The total energy reduction is expressed in relation (1).

$$\Delta(\lambda A) = \Delta\lambda A + \lambda\Delta A \quad (1)$$

In this relation, the change in interfacial energy (Δλ) is due to densification and the change in interfacial area is due to particle growth. In solid state sintering case, Δλ is related to surface replacement of solid / vapour (interfaces) with solid/solid interfaces. Figure 2 shows how the total interfacial energy reduction occurs through densification and particle growth.

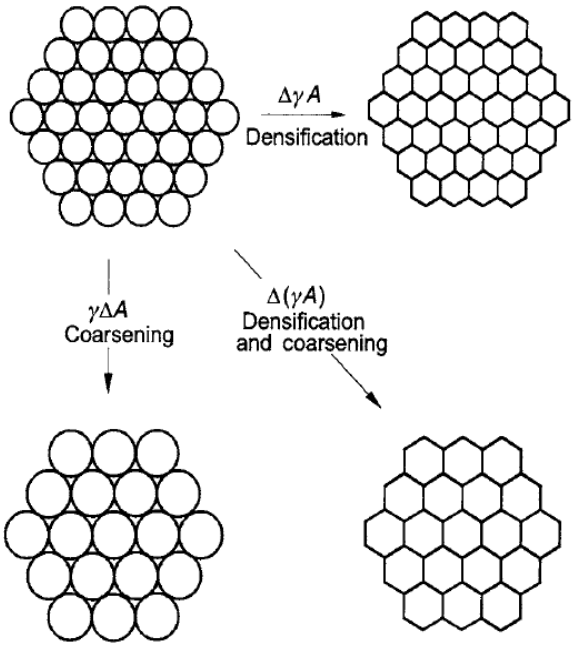

Fig.2 Basic phenomena occurring during sintering [4]

1.1 SINTERING VARIABLES

The variables that determine sinterability and microstructure of sintered parts fall into two categories: material variables and process variables. The material variables are influencing the compressibility of the powder (densification and particle growth). Other variables are mainly thermodynamic variables. Variables affecting sinterability and microstructure of sintered parts are presented in Table 1.

Tab.1 Variables affecting sinterability and microstructure of sintered parts

Material variables	Powder	Shape,size, distribution, agglomeration, mixing possibility etc.
	Chemistry	Composition, impurities, non-stoichiometry, homogenity etc.
Process variables	Temperature, time, pressure, heating and cooling ratio etc.	

1.2 BASALTIC MATERIALS COMPOSITION

Chemical analysis shows that basalt materials are mixtures of binary oxides with a structural range between a maximum percentage of 52% for oxides of silicon and a minimum of 2% for oxides of titanium, and a variety of covalent-ionic type structural links

for the elements silicon and aluminium, ion type links for alkali metals (Na, K) and alkaline earth (Mg, Ca) and the metal type links for transitional elements (Fe, Ti) respectively. The three types of chemical bonds present affects the structure and properties of chemical compounds. During sintering, depending on the substance introduced into recipes and temperature, in the mass of the sample held a series of structural changes caused by chemical reactions that occur between oxide compounds participating in the formation of basalt. Being under the granular form, mixed oxides from the chemical reaction, causes the formation of oxide compositions in moles, existing the possibility of forming, at contact surfaces between granule constituents, of some mixed compounds. Chemical reactions (molar ratio 1:1), which can occur in the process of sintering (combination of various binary oxides) shows that: sintering process causes the occurrence of combinations of ternary oxides (metasilicates,metatitanates, cyclosilicates) and mixed oxides (metatitanates, spineles), with composition corresponding to normal valences or stoichiometric interstitial combinations; binary oxides participate in the sintering process in a relatively small percentage, even if the reaction is complete, if one takes into account that reactions occur between the surfaces of granules.

1.3 SOLID STATE BASALT SINTERING PROCESS AND TECHNOLOGY

In the present study were used basalt rocks from Luncani, Timis county, Romania. This natural basalt rock, of volcanic origin, crystalline, compact, composed of a mixture of silicates, is the raw material for obtaining parts and is represented by: Tectosilicates - plagioclases feldspars (albite anorthite), organized in three-dimensional networks of structures that allow cleavage and crystallizes in triclinic system. In a proportion below 20% have a favourable effect on the process of crystallization; Nesosilicates - olivine, isomorphous compounds, consisting of forsterite and fayalit with island structure, allowing cleavage and crystallizes in rhombic system. The presence of large quantities in finished products is undesirable; Inosilicates - pyroxenes (metasilicates of Mg, Fe, Mn, Ca, Al) with simple chain structure, looking slightly fibrous and cleaving, crystallizes in monoclinic and rhombic system. Pyroxenes are the main phase of basalt and are in quantities between 34% and 80%. Pyroxenes gives final products good chemical and mechanical properties, in mineralogical components containing less than 60% and a content less than 10% magnetite and olivine, favours the crystallization process. Operations of forming and sintering, which causes interatomic links between particles, is the essence of the process of obtaining products by aggregating powders. Through forming, is aimed at processing powders in intermediate states, in order to facilitate and ensure obtain prescribed properties. The customary procedure for forming is pressing in a mold at compacting pressures ranging between (2-10) x 10^3 daN/cm^2. Sintering is a heating operation of the semi-fabricate at a temperature at least equal to or greater than recrystallization temperature, basically the sintering temperature being $T_s = (2/3 – 4/5) \cdot T_f$, where T_f represents the melting temperature of principal component. During sintering occurs an increase in compactness (more pronounced in the direction of pressing), a phenomenon influencing decisive the mechanical properties of finished products. Porous structure of sintered products, ranging from 1 to 30%, depends on the porosity obtained from the operation of forming and on sintering temperature and duration. Basalt, as raw material, in order to become a finished product through sintering process, undergoes through a series of operations such as: choosing the raw material, processing to obtain the powder form, forming, calcination and sintering. Table 2 presents the oxide composition of basalt rocks from Luncani, Timis county, Romania, in comparison with the mean values from other basaltic basins from Romania and a some value considered as optimum conditions.

Tab. 2 Oxide composition of basalt from Luncani, Romania and optimum conditions

Oxide composition [%]	Mean values in basalt structures		
	Luncani	Romania	Optimum
SiO_2	47,65	44 – 52	43,5
Al_2O_3	15,84	14 – 16	11 – 13
Fe_2O_3 + FeO	10,06	9 – 14	5 – 8
CaO	8,92	9 – 12	10 – 12
MgO	8,80	7 – 10	8 – 11
Na_2O+K_2O	5,50	3 – 8	3 – 5
TiO_2	2,30	2 – 3	2 – 3,5
P_2O_5	0,11	-	0,3 – 1,0
MnO	0,10	-	0,2 – 0,3
P.C.	0,72	-	-

Operations performed on rocks in order to obtain basalt powder are: washing, drying, sorting, crushing-sifting, disposal of metallic debris, milling and powder sifting. The next step is to prepare the powder-binder mixture in order to ensure the necessary powder compactness for forming. Basalt powder is mixed homogeneously with a binder consisting of a special glue, olein and water. To form and pressing the pieces of basalt, the process of pressing in die was used. The die slots have dimensions increased by about 15%, depending on the rate of contraction of the mixture. Figure 3 presents a newly designed pressure die for the purpose of this study.

Fig. 3 Pressing die

Because, according to the designed study, there is the need of obtaining two pressures of p_1 = 1500 daN/cm^2 and p_2 = 2000 daN/cm^2 respectively, the two needed pressing forces are F1 = 1695 daN and F2 = 2260 daN respectively. Drying and calcination was done by placing compacted raw parts in boxes and calcinatinatig them in a furnace an the two imposed temperature regimes of 900 °C and 950 °C respectively. Sintering and cooling of compacted basalt parts was performed in a sintering furnace able to achieve sintering temperatures of 1000 °C and 1100 ° C, heating durations of 8 h and 10 h and holding

duration of 1 h and 1.5 h respectively. Figure 5 presents sintered and cooled parts. Also to be noted that the sintering and cooling was achieved, as a premiere, in quartz capsules.

Fig. 4 Sintered and cooled basalt parts

To analyze the components of sintered basalt parts, microanalysis technique with X-rays (EDAX). Surface images of sintered basalt were analyzed using a scanning electronic microscope (SEM), as shown in figure 5.

2. EXPERIMENTAL RESULTS USING TAGUCHI METHOD

Unlike the classical (traditional) approaches which looks over the mean and the variability separately, Genichi Taguchi [1],[2] uses for evaluating a product or process quality a synthetic measure of performance which takes in account simultaneously the mean and the variance (Signal-to-Noise ratio).

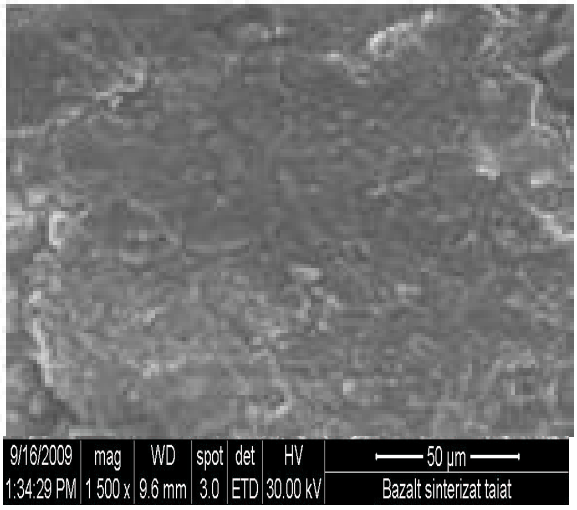

Fig. 5 Sintered basalt surface (SEM)

For performing the experiments, a L_8 Taguchi standard matrix[3] was utilized, for which the controlled factors were assigned, determining their levels and the random order for the 8 experimental conditions. The choosen quality characteristic of sintered parts is Compression resistance (daN/cm^2) and the seven controlled factors are: Composition; Calcination temperature; Cooling duration; Sintering temperature; Heating duration; Holding duration; Forming pressure. For each experimental condition 5 basalt sintered pieces were manufactured, which were tested to compression. Figure 6 presents the

controlled factors levels and figure 7 the experimental results and S/N ratios. Furthermore, all possible interactions between controlled factors were studied.

	Factors	Level 1	Level 2
1	Composition	0% TiO2	2% TiO2
2	Calcination temp	900 C	950 C
3	Cooling duration	4 h	5.5 h
4	Sintering temp	1000 C	1100 C
5	Heating duration	8 h	10 h
6	Holding duration	1 h	1.5 h
7	Forming pressure	1500 daN/	2000 daN/cm2

Fig. 6 Controlled factors levels

Conditions	Sample# 1	Sample# 2	Sample# 3	Sample# 4	Sample# 5	Sample# 6	S/N Ratio
Trial# 1	1125	1200	1150	1175	1160		61.298
Trial# 2	1175	1210	1165	1190	1180		61.464
Trial# 3	1300	1285	1250	1290	1295		62.168
Trial# 4	1230	1210	1220	1245	1235		61.782
Trial# 5	1310	1295	1275	1285	1300		62.23
Trial# 6	1290	1310	1285	1300	1275		62.224
Trial# 7	1250	1240	1210	1220	1215		61.774
Trial# 8	1695	1675	1685	1680	1700		64.541
							62.185

Fig. 7 Experimental results and S/N ratios

The presence of an interaction, regardless how severe, doesn't mean necessary that is significant. If an interaction is significant or not can be tested by using the ANOVA method (figure 8). Changes in optimal condition, necessary due to an interaction presence, must be performed only if that interaction is significant.

The order of importance of controlled factors was established, in the optimums table being denoted the predictive equation for performance at optimal condition and any other condition. The expected performance calculation includes only the significant factors (figure 9), the optimal condition being determined based on the selected quality characteristic.

One can observe that optimum factors levels are consistent with the one obtained after analyzing the factors mean effects and factors interactions. Another method to show the performance improvement is the presentment of modification in normal distribution (figure 10). Thus, the improved S/N ratio at optimal condition correspond to a reduction of standard deviation. In order to verify the precision of designing the experiments based on a L_8 orthogonal matrix, a full factorial simulation (2^7 = 128 experiments for full factorial experiment) was performed.

Col # / Factor	DOF (f)	Sum of Sqrs. (S)	Variance (V)	F - Ratio (F)	Pure Sum (S')	Percent P(%)
1 Composition	1	2.055	2.055	36.571	1.999	27.788
2 Calcination temp	1	1.162	1.162	20.686	1.106	15.378
3 Cooling duration	(1)	(.056)		POOLED	(CL= *NC*)	
4 Sintering temp	1	.806	.806	14.353	.75	10.431
5 Heating duration	1	1.109	1.109	19.738	1.053	14.638
6 Holding duration	1	.619	.619	11.03	.563	7.835
7 Forming pressure	1	1.382	1.382	24.605	1.326	18.44
Other/Error	1	.057	.057			5.49
Total:	7	7.194				100.00%

Fig. 8 ANOVA table

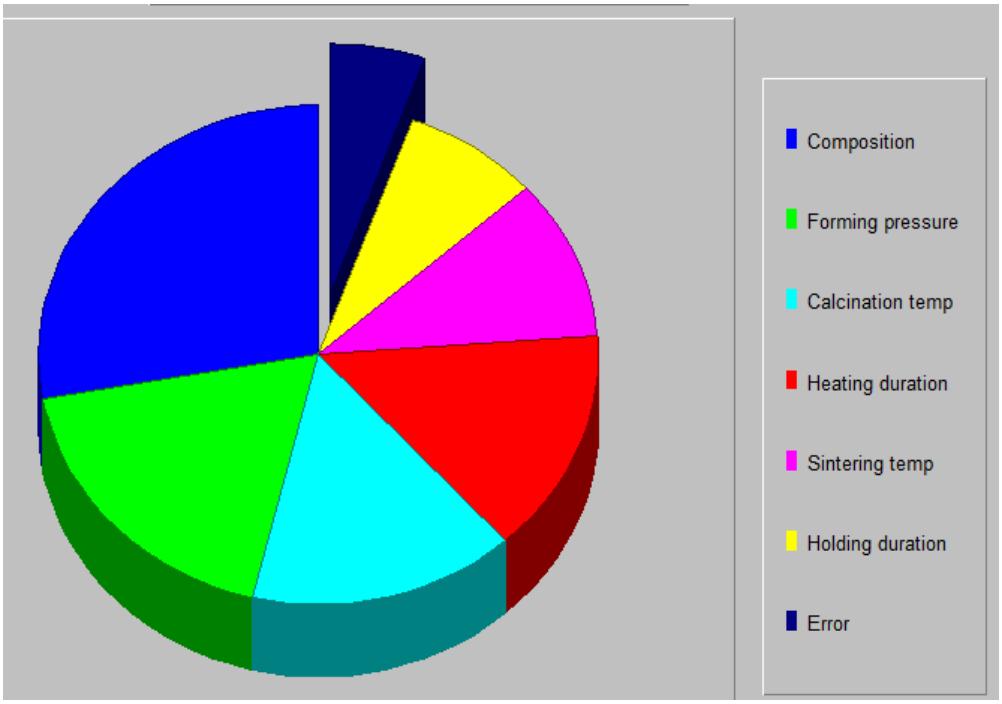

Fig. 9 Significant factor and interaction influences

There is the possibility to work with a predefined set of equations which can be solved in full factorial condition (all possibilities). It has been utilized in first instance o generalized non-linear relation between the performance characteristic (Y= Compression resistance) and the seven controlled factors (A = Composition; B = Calcination temperature; D = Cooling duration; E = Sintering temperature; F = Heating duration; G = Holding duration; F = Forming pressure).

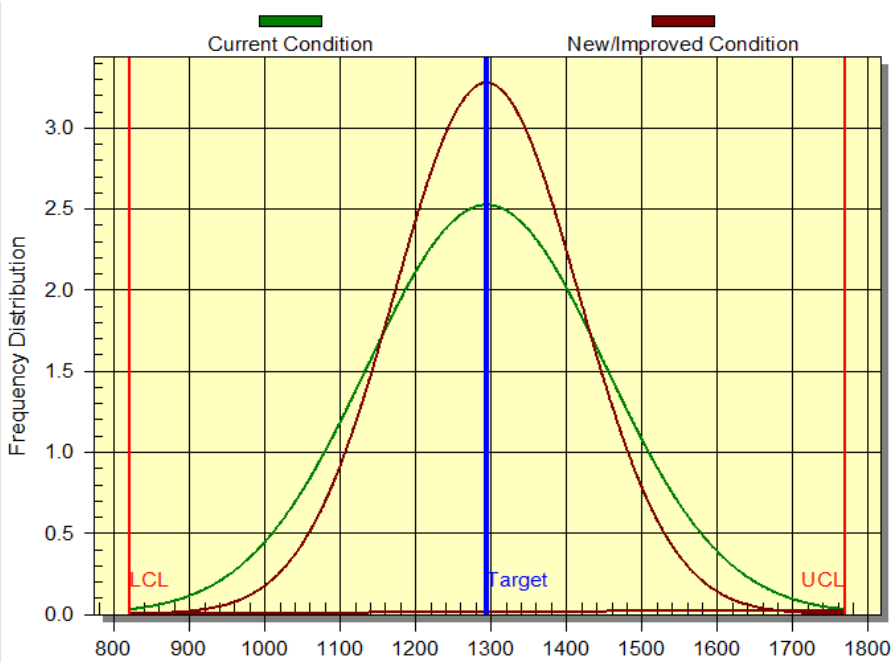

Fig. 10. Variation reduction plot based a on assumed Normal Performance Distribution

Assuming that the characteristic equation represents the system behaviour, the maximum value obtained from full factorial experiment combinations, can be regarded as exact solution which can be compared to the solution of the experiment based on orthogonal array L_8. Also performance at optimal conditions can be compared with the exact solution in order to determine the L_8 experiment accuracy of prediction. Relation (2) presents the equation obtained from simulating the full factorial experiment. The error using an L_8 orthogonal array instead of a full factorial experiment is only 0.9%.

$$Y = (10A)^{1.97} + (0.1B)^{1.55} + \frac{(10C)^{0.61}(0.1D)^{1.13}(10E)^{1.53}}{(5F)^{0.82}(0.1G)^{1.95}} \qquad (2)$$

3. CONCLUSIONS

Applying Taguchi's robust design to sintering basalt parts allowed to identify the most important factors to be controlled in order to obtain the best products. Also it was demonstrated that by using 2% of TiO_2 as dopant, one of the major drawbacks of basalt sintered parts was partially eliminated. Thus, the compression resistance of sintered basalt parts was significantly improved. It was demonstrated also that by using an L_8 orthogonal array (8 experiments), the error that was made was very low by comparison with using a full factorial experiment, (128 experiments). Further researches will be focused mainly in reducing the brittleness of basalt sintered parts.

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