

## RECOVERY OF ORGANIC WASTE WITH COMBUSTION CAPACITY

Dumitru DINCĂ<sup>1</sup>, Alexandra Raluca MIRON<sup>2</sup>, Cristina MODROGAN<sup>3</sup>

*High-temperature synthesis of refractory compounds is of wide interest. We consider reactions in a binary system in which the rise and fall of the temperature during the reaction is such that one of the reacting elements melts but not the other. The reactions take place in a binary system in which raising and lowering the temperature is done so that, one of the reactive material is melting and the other not. Carbon products manufacturers create waste packing material products which undergo graphitization and at first sight are difficult to ignite but once ignited due to external initiators can cause fire difficult to be annihilated. A packaging waste recovery by converting them into refractory products and soil contamination by waste disposal is attempted.*

**Keywords:** graphitization, waste, soil

### 1. Introduction

The synthesis of solids possessing desired structures, composition and properties continues to be a challenge to chemists, material scientists and engineers. Formation of solids by the ceramic method is controlled by the diffusion of atoms and ionic species through reactants and products, and thus requires repeated grinding, pelletizing and calcination of reactants (oxides or carbonates) for longer durations (than soft chemical routes) at high-temperatures. Attempts have recently been made to eliminate the diffusion control problems of solid synthesis by using various innovative synthetic strategies [1]. One such approach is ‘combustion synthesis’ also known as ‘self-propagating high-temperature synthesis’ and fire or furnaceless synthesis. The process makes use of highly exothermic redox chemical reactions between metals and nonmetals, the metathetical (exchange) reaction between reactive compounds or reactions involve redox compounds/mixtures. The term ‘combustion’ covers flaming (gas-phase), smouldering (heterogeneous) as well as explosive reactions. The combustion method has been successfully used in the preparation of a large

<sup>1</sup> PhD eng., Bioresources and Polymers Depart., University POLITEHNICA of Bucharest, Romania, e-mail: cristinamodrogan@gmail.com

<sup>2</sup> Assist. PhD, Faculty of Applied Chemistry and Materials Science, University POLITEHNICA of Bucharest, Romania, e-mail: andra3005@yahoo.com

<sup>3</sup> PhD eng., Faculty of Applied Chemistry and Materials Science, University POLITEHNICA of Bucharest, Romania, e-mail: c\_modrogan@yahoo.com

number of technologically useful oxide (refractory oxides, magnetic, dielectric, semiconducting, insulators, catalysts, sensors, phosphors etc.) and nonoxide (carbides, borides, silicides, nitrides etc.) materials. To date more than 500 materials have been synthesized by this process, many of which are commercially manufactured in Russia [2-4].

In recent years, there has been tremendous interest in the combustion synthesis of materials because it is simple, fast, energetically economic and yields to high purity products compared to the conventional routes used to prepare these materials. As it is a high-temperature process, only thermodynamically stable phases can be prepared. At the same time, rapid heating and cooling rates provide the potential for the production of metastable materials with new and unique properties [5-9].

Production of graphite electrode involves a final stage of graphitization at 2500 °C, phase in which the electrodes are packaged in a mixture of sand and coke. After graphitization, the packaging material represents a waste hardly usable, which is stored in heaps.

Graphite fine dust and sand is taken by the wind and deposited on the ground, thus introducing an inert material, which affects soil fertility.

The material has high calorific value and can cause fires in the case of combustion initiation. The two electrodes factories from Slatina and Titu are important deposits for such packing materials which contribute particularly to the decrease of soil fertility [10].

The literature describes the preparation of another refractory material.

Thermo physical properties were investigated for zirconium diboride ( $\text{ZrB}_2$ ) and  $\text{ZrB}_2$ -30 vol % silicon carbide ( $\text{SiC}$ ) ceramics. Thermal conductivities were calculated from measured thermal diffusivities, heat capacities, and densities. The thermal conductivity of  $\text{ZrB}_2$  increased from  $56 \text{ W}\times\text{m}^{-1}\times\text{K}$  at room temperature to  $67 \text{ W}\times\text{m}^{-1}\times\text{K}$  at 1675 K, whereas the thermal conductivity of  $\text{ZrB}_2$ - $\text{SiC}$  decreased from 62 to  $56 \text{ W}\times\text{m}^{-1}\times\text{K}$  over the same temperature range. Electron and phonon contributions to thermal conductivity were determined using electrical resistivity measurements and were used, along with grain size models, to explain the observed trends. The results are compared with previously reported thermal conductivities for  $\text{ZrB}_2$  and  $\text{ZrB}_2$ - $\text{SiC}$  [11].

The thermal reaction sequence of  $\text{MoSi}_2$  formation from Mo and Si powder mixtures was investigated by SEM using quenching techniques. It was observed that the mechanism of  $\text{MoSi}_2$  formation depends on the Mo particle size. In the case of small particles, the final structure consists of equiaxed  $\text{MoSi}_2$  grains. The large particles, however, cannot be completely dissolved and remain unreacted surrounded by thin solid-state diffusional layers of  $\text{Mo}_5\text{Si}_3$  and  $\text{Mo}_3\text{Si}$  [12, 13].

In this paper we try to transform these materials in refractory bricks superior bricks to those made of pure clay or alumina, because their resistance to high temperatures is around 2000 - 2 500 °C with 70-80 % more than the best refractory bricks (1500-1600 °C).

Due to the difficulties of separation on the one hand, and to the temperature resistance on the other hand, we investigated the possibility of transformation of this material in refractory bricks. The use of the material in the production of ordinary carbon products is not possible due to the low thermal conductivity (quartz and silicon carbide are not conductors).

The researches have been developed for obtaining a silica-carbon mass through specific processes of carbon products obtaining.

The laboratory researches were developed by the research of the influence of grain and binding material in order to obtain materials which after baking at 1000 °C (under similar conditions to carbon products) to form refractory lining plaques. Such plaques could be used for cladding various equipments which are carrying melts at high temperatures. Thus, it is possible to obtain from a material without specific uses, a refractory material with special qualities.

## 2. Materials

The solid material was a powder sample with the characteristics presented in table 1.

*Table 1*

**The characteristics of solid material sample used**

Characteristic	Units	Values	Determination method
Moisture	%	0.50	STAS 5264/1995
Cinder	%	26.50	STAS10274/1983
Free quartz	%	23.15	the infrared spectrum
Kaolinite	%	1.85	the infrared spectrum
Temperature cinder fusion	°C	1550.00	the infrared spectrum
Sulfur	%	0.45	STAS 8754/1996
Carbon	%	72.00	STAS 5268/1990
High calorific power	kcal/kg	5145.00	STAS 928/1995

## Composition recipe

The material was milled with a ball mill and the particle size sorts below 1 mm were chosen, and the recipe shown in Table 2 was made.

Table 2

**The used recipe**

Characteristic	Units	Value
Solid material 0.4-1 mm	%	10
Solid material under 0.071mm	%	65
Pitch molten	%	25

**The used binder**

As binder coal tar A- STAS 3360-69 type with characteristics shown in table 3 was used.

Table 3

**The characteristics of the binder used (coal tar A STAS 8351/2-83 type)**

Characteristics	Units	Values
Softening point	°C	81
Benzene insoluble substances	%	32
Ash	%	0.28
Water	%	0.21
Volatiles	%	48.15
Fixed carbon	%	51.85
Materials insoluble in anthracene oil (resin $\alpha$ )	%	8.25
$\beta$ Resins	%	23.15
Coke in $\beta$ resins	%	92.35
Distillation		
0 – 270 °C	%	0.80
270 – 300 °C		9.00
Swelling index for coke in the case of benzene insoluble substances	-	2

**Samples preparation**

From the recipe presented in section 2 with the pitch introduced in the molten state at 200 °C were taken 600 g and hot manually mixed (150 °C) for 30 minutes, and then were pressed with a mechanical tests machine at a pressure of 300 kgf/cm<sup>2</sup>  $\phi$  = 60 mm, and subsequently cooled in order to be ripped. Baking was done up to 1200 °C in an oven with temperature diagram shown in table 4.

Table 4

**Ripening Chart**

<b>Time(h)</b>	<b>Temperature (°C)</b>
25	60
50	100
75	250
100	350
125	480
150	720
175	1 000
200	1 200
225	1 200
250	950
275	850
300	775
325	680
350	640
375	600
400	520
425	450
450	375
500	240

After complete cooling of the samples, they were tested for compressive strength, bending strength, bulk density, true density, porosity and resistivity [12-16].

### 3. Results and discussions

#### The compressive strength of samples

The compressive strength of samples was determined according to STAS 10537-76 and the results obtained are shown in table 5.

Table 5

**The compressive strength of samples**

<b>Sample</b>	<b>Units</b>	<b>Compressive strength</b>	
		<b>On the pressing direction</b>	<b>Perpendicular to the pressing direction</b>
1	MN/m <sup>2</sup>	21.0	17.0
2	MN/m <sup>2</sup>	20.0	16.0
3	MN/m <sup>2</sup>	19.0	16.0
4	MN/m <sup>2</sup>	17.0	15.0

5	MN/m <sup>2</sup>	22.0	19.0
6	MN/m <sup>2</sup>	18.0	16.0
7	MN/m <sup>2</sup>	23.0	18.0
8	MN/m <sup>2</sup>	18.0	16.0
9	MN/m <sup>2</sup>	21.0	17.0
10	MN/m <sup>2</sup>	19.0	16.0
average	MN/m <sup>2</sup>	19.8	16.6

Compressive strength of the resulting material about 20 MN/m<sup>2</sup> is similar to the anodes. The material can be successfully used to warm lining material (melt), loose and which does not react with carbon.

### Flexural strength of the samples

The flexural strength was determined according to STAS 10537-76. The results are shown in table 6.

Table. 6

Flexural strength of evidence			
Sample	Units	Flexural strength	
		On the pressing direction	Perpendicular on the pressing direction
1	MN/m <sup>2</sup>	5.0	4.0
2	MN/m <sup>2</sup>	6.0	5.0
3	MN/m <sup>2</sup>	4.0	3.0
4	MN/m <sup>2</sup>	5.0	4.0
5	MN/m <sup>2</sup>	3.0	2.0
6	MN/m <sup>2</sup>	5.0	4.0
7	MN/m <sup>2</sup>	6.0	5.0
8	MN/m <sup>2</sup>	5.0	4.0
9	MN/m <sup>2</sup>	4.0	3.0
10	MN/m <sup>2</sup>	5.0	4.0
average	MN/m <sup>2</sup>	4.7	3.7

Flexural strengths of about 5 MN/m<sup>2</sup> are considered to be satisfactory for a coating material.

### The apparent density of the samples

The apparent density of the samples was determined according to STAS 8160/8-81. The results obtained are shown in table 7.

The increase of apparent density is not due to a more advanced baking, but is related to the free quartz and silicon carbide content of the material.

Table 7

**The apparent density of the samples**

Sample	Units	Values
1	g/cm <sup>3</sup>	1.75
2	g/cm <sup>3</sup>	1.64
3	g/cm <sup>3</sup>	1.80
4	g/cm <sup>3</sup>	1.60
5	g/cm <sup>3</sup>	1.62
6	g/cm <sup>3</sup>	1.74
7	g/cm <sup>3</sup>	1.80
8	g/cm <sup>3</sup>	1.66
9	g/cm <sup>3</sup>	1.78
10	g/cm <sup>3</sup>	1.59
average	g/cm <sup>3</sup>	1.7 +/- 0.11

**The real density of the samples**

The real density of the samples was determined according to STAS 8160/8-81. The results are shown in table 8.

Table 8

**The real density of the samples studied**

Sample	units	values
1	g/cm <sup>3</sup>	2.33
2	g/cm <sup>3</sup>	2.23
3	g/cm <sup>3</sup>	2.28
4	g/cm <sup>3</sup>	2.29
5	g/cm <sup>3</sup>	2.22
6	g/cm <sup>3</sup>	2.36
7	g/cm <sup>3</sup>	2.37
8	g/cm <sup>3</sup>	2.37
9	g/cm <sup>3</sup>	2.34
10	g/cm <sup>3</sup>	2.41
average	g/cm <sup>3</sup>	2.32 +/- 0.1

The real densities appear larger than the ones of the ripped carbon product (1.9 g/cm<sup>3</sup>) due to the presence of quartz and silicon carbide, materials with higher densities. They are acceptable for a ripped material used in plating.

**Samples porosity**

Samples porosity was determined according to STAS 8160/8 - 81 and the results are presented in table 9.

Table 9

Porosity of the studied samples		
Sample	Units	Value
1	%	24.9
2	%	26.5
3	%	21.1
4	%	30.0
5	%	27.1
6	%	26.6
7	%	24.1
8	%	30.0
9	%	24.0
10	%	34.1
average	%	26.8 +/- 8

The resulted porosity is similar to the one obtained for the ripped products.

### Electrical resistivity

Electrical resistivity was determined according to STAS 4829-80.

The results are shown in table 10.

Table 10

Electrical resistivity of the samples studied		
Sample	Units	Values
1	$\Omega \cdot \text{mm}^2/\text{m}$	274
2	$\Omega \cdot \text{mm}^2/\text{m}$	265
3	$\Omega \cdot \text{mm}^2/\text{m}$	236
4	$\Omega \cdot \text{mm}^2/\text{m}$	282
5	$\Omega \cdot \text{mm}^2/\text{m}$	274
6	$\Omega \cdot \text{mm}^2/\text{m}$	264
7	$\Omega \cdot \text{mm}^2/\text{m}$	272
8	$\Omega \cdot \text{mm}^2/\text{m}$	282
9	$\Omega \cdot \text{mm}^2/\text{m}$	275
10	$\Omega \cdot \text{mm}^2/\text{m}$	295
average	$\Omega \cdot \text{mm}^2/\text{m}$	272 +/- 23

The material has an electrical conductivity three times less than the ripped products due to quartz and silicon carbide contained impurities, which leads to the decrease of thermal conductivity in about the same rate.



#### 4. Conclusions

From the research study several results can be highlighted. The fire hazards and soil contamination with inert material is completely reduced. It is possible to manufacture a resistant coating material from the waste packaging resulting from wards graphitization. The material manufacturing is similar with ripped carbon materials manufacture, namely, the grain size recipe making, specific coal tar bonding and ripening after a given chart. The material withstands well at temperatures up to 2500° C. The material is characterized by good mechanical strength (the anisotropy with respect to the pressing direction). Real and apparent densities of the material are greater than the one of the ripped carbon products, due to the SiO<sub>2</sub>, and SiC<sub>2</sub>. The electrical conductivity of the material is about three times higher than the one of the ripped products, so, it cannot be used for electrodes. The material is a cladding thermoresistant material of good quality.

#### Acknowledgements

The work has been funded by the Sectoral Operational Programme Human Resources Development 2007-2013 of the Ministry of European Funds through the Financial Agreement POSDRU/159/1.5/S/134398.

#### REFERENCES

- [1]. *CNR Rao*, Combustion synthesis. In Chemical Approaches to the Synthesis of inorganic Materials. New Delhi: Wiley Eastern Limited, 1994, p. 28-30.
- [2]. *J.J. Moore, H.J. Feng*, *J Mater Sci*, **39**, 1995, p. 243-273.
- [3]. *J.J. Moore, H.J. Feng*, *J Mater Sci*, **39**, 1995, p. 275-316.
- [4]. *J. T. Abrahamson, M. S. Strano*, *J. Phys. Chem. Lett.*, **1** (24), 2010, p. 3514–3519
- [5]. *N. Shingo, E. Takaya, H. Ken*, *Ceramics International*, **35**, 6, 2009, p. 2145–2149
- [6]. *A.G. Merzhanov*, *Int J Self-Propag High-Temp Synth*, **2**, 1993, p. 113-158
- [7]. *A.G. Merzhanov*, In Chemistry of Advanced Materials: A Chemistry for the 27s' Century. Edited by Rao CNR. London: Blackwell; 1993, p. 19-39.
- [8]. *J. Subrahmanyam, M. Vijayakumar*, *J Mater Sci* **27**, 1992, p. 6249-6273.
- [9]. *C. Pascal, R. M. Marin-Ayral, J. C. Tedenac*, *Journal of Materials Synthesis and Processing*, **9**, 2001, 6, p. 375-381
- [10]. *C. Sierra, A. J. Vázquez*, *Intermetallics*, **14**, 7, 2006, p. 848–852
- [11]. *M. Samadi Khoshkhoo, M. Shamanian, A. Saidi, M. H. Abbasi, M. Panjehpour, F. Asgharzadeh Javid*, *Journal of Alloys and Compounds*, **475**, 1–2, 5, 2009, p. 529–534
- [12]. \*\*\* *Groupe francais d'etude des carbones – Les Carbones* vol. II Ed. Masson & Cle 1965, p. 5 – 34.
- [13]. *M. Ienciu, F. Barca*, *Produse cărbunoase (Carbon Products - in Romanian)*, Ed. I.P.B. 1985, p. 46 – 14.
- [14]. \*\*\* *Enciclopedia de chimie (Chemistry Cyclopaedia – in Romanian)*, vol. 6, Ed. Științifică și Enciclopedică 1989, p. 137 – 141.

- [15]. *M. Ienciu, F. Barca* – Îndrumar de laborator – produse carbunoase (Laboratory Guide – Carbon Products – in Romanian), Ed. I.P.B. 1987, p. 92 – 105.
- [16]. *F. Barca, R. Roman* – Compozite carbonice (Carbon Composites – in Romanian), Ed. Protech, 2011, București
- [17]. STAS 8351/2-83 Smoala de huiă. Determinarea conținutului de substanțe insolubile în benzen sau toluen (Pitch Pitcoal. Determining Insoluble Substances in Benzene or Toluene – in Romanian)
- [18]. STAS 10537-76 Materiale carbonice. Determinarea rezistenței la compresiune, încovoiere și tracțiune (Carbonic Materials. Determining the Resistance at Compression, Bending and Traction – in Romanian)
- [19]. STAS 4829-80 Electrozi și nipluri carbonice, grafitate pentru cuptoare electrice cu arc (Carbon Electrodes and Nipples, Graphited for Electric Arc Furnaces – in Romanian)
- [20]. SR 5264/1995 Combustibili minerali solizi. Cărbuni. Determinarea umidității (Solid Mineral Fuels. Types of Coal. Determining Humidity – in Romanian)
- [21]. STAS10274/1983 Determinarea conținutului de sulf total (Determining the Total Sulphur Content – in Romanian)
- [22]. SR EN ISO 8754:2002 Produse petroliere. Determinarea conținutului de sulf. Metoda prin spectrometrie de fluorescență de raze X dispersivă de energie (Oil Products. Determining Sulphur Content. Energy Dispersive Method of X-Rays Fluorescence Spectrometry – in Romanian)
- [23]. SR 5265:1994 Cărbuni. Determinarea cenușii prin metoda rapidă (Types of Coals. Determining Ashes by Rapid Method – in Romanian)