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Thermal plasma for materials engineering

***Abstract**. The paper presents thermal plasma applications directed towards receiving near zero emission of any hazardous residuals of wastes. The final material obtained after the plasma treatment is environmentally safe. It can return to the environment as a useful material or product. The paper also describes a CNT's synthesis microwave plasma method. It allows producing CNT's in the powder form or making deposits on substrates such as silica, metals and on refractory insulators.*

***Streszczenie.** W artykule przedstawiono zastosowania plazmy termicznej ukierunkowane na zapewnienie zerowej emisji jakichkolwiek szkodliwych pozostałości. Końcowy materiał może powrócić do środowiska jako użyteczny produkt. Przedstawiono również plazmową metodę syntezy CNTs przy użyciu generatora mikrofal. Umożliwia ona wytwarzanie CNTs w postaci proszku lub nanoszenie warstw CNTs na podłożach. **(Plazma termiczna dla inżynierii materiałowej)**.*

Keywords: thermal plasma, waste treatment, nanomaterials.
Słowa kluczowe: plazma termiczna, utylizacja odpadów, nanomateriały.

Introduction

Thermal plasma in the state of LTE (Local Thermodynamic Equilibrium) or near LTE (in a reduced pressure) can be an efficient medium for breaking bonds of unwanted molecular chains. It can be used for gas and fluid waste destruction and solid waste conversion into valuable materials or products. Another application of near LTE plasma is carbon nanotubes (CNTs) synthesis. CNTs deposited on various substrates are urgently required for many technological applications such as electron emitters, supercapacitors, rechargeable batteries, photovoltaic cells, etc.

Plasma environmental applications

One of the most important thermal plasma technological applications is a destruction of hazardous waste keeping zero emission conditions. This can be fulfilled by organic waste incineration or its limited oxidation combined with smelting of inorganic residues possibly enriched with hazardous industrial mineral wastes. Such process gives no post-incineration residues, makes the system clean and generates the product friendly to the environment. The above approach has been widely studied in the European Union Project G1RD-CT-2001-000468 with the acronym WASTILE [1]. In Figure 1 the flow chart of classic fuel burning incinerator combined with plasma vitrification system of all solid residues is presented.

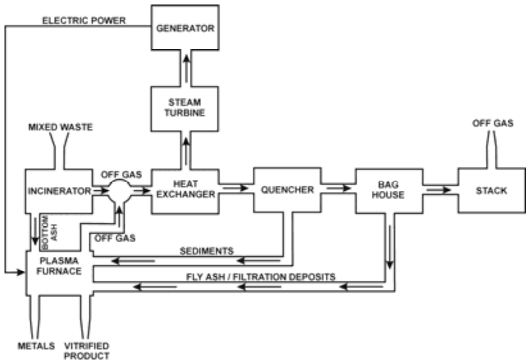

Fig.1. Flowchart of plasma zero-waste incineration process

The system is self-supplied in the electric power and it employs only single plasma furnace for vitrification of solids. All the post incineration residues: ash, slag, filter deposits, sedimentation residues are heated to a sufficient temperature and their minerals and toxic heavy metals, melt and glassify. This way every classic waste incineration plant can be converted to zero waste emission system. The excess of energy in the form of electricity or steam can be sold. The novel approach here to the material processing is the use of a DC arc submerged in the feed charge. Plasma utilization process might be a continuous one if the feeding of the charge and collection of the product are continuous.

Detailed requirements concerning the design principles of the furnace are:

- the arc initiation is caused by short-circuiting of the electrode and the crucible following by the electrode enhancement,
- the continuous casting of the bath starts as soon as the feed is liquefied,
- the tap hole should be at sufficiently high temperature all the time, what makes impossible coagulation of the bath,
- the tapping should be hold without the furnace move.

In axially - symmetrical configuration (Fig. 2) of an anode - the crucible (1) and a cathode – the rod electrode (3) the mineral feed charge files a space between them (2). Initially (in solid state) the feed does not lead an electric current. Anode has got in its bottom a hole enabling flowing out of excess of gas as well as tapping of the melt (bath). A DC arc, burning in the environment formed by gaseous mineral substance was named here the gas-mineral-arc (GMA).

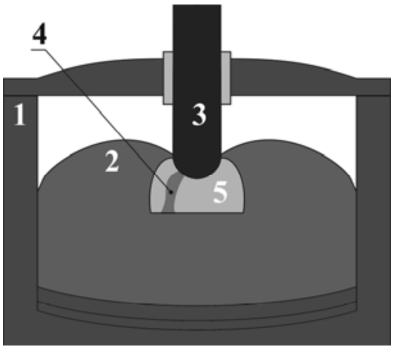

Fig.2. The sketch of GMA idea [2]

The idle current starts to flow following the short-circuiting of the cathode and anode. After electrodes separation to a short gap (usually below 1 mm) a stable arc discharge named here the idle arc is initiated (4) using a gas matter (argon, nitrogen or air) from side of the hole. The increase of the feed temperature effects in the gas coming from gradually evaporating compounds according to their boiling points enters the arc atmosphere. The arc discharge produces a gas sheath (5) from the side of charge which is of mineral origin. The melted material can be continuously tapped on the cold conveyor to receive "cakes" formed by the coming down fluid droplets or tapped to some forms to make the shape of the cast as shown in Fig. 3. This way the process of toxic wastes conversion into useful ceramic tiles has been demonstrated [1].

Fig.3. The casted from waste: "cakes" - left and triangular tiles in color glaze – right [3]

In the second approach a thermo insulating foam glass production, which utilizes vitrified ash formed in the process of toxic waste destruction, have been elaborated.

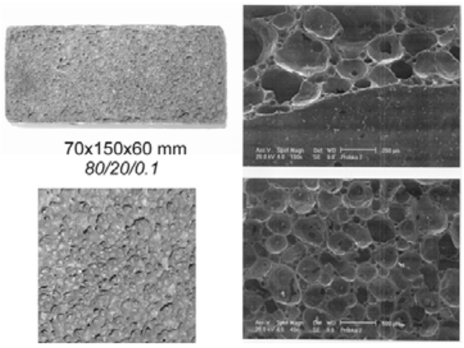

Fig.4. The foamed tiles made from grinned vitrified waste – left and their cross-section – right [3]

Table 1. Concentration of metals in aqueous solution after vitrificates washing [mg/dm^3] [3]

	Medical ash without additions	Medical ash + 15%SiO$_2$	Fly-ash from heat and power generating plant Belchatow	Sludge from industrial treatment plant
Na	89	20	3.985	29.551
Ca	16.15	4.68	137.76	69.273
K	8.3	2.4	1.27	1.013
Zn	1.29	0.28	0.013	0.044
Mg	0.53	0.086	0.0127	0.034
Co	0.49	0.09	0.033	0.004
Fe	0.32	0.09	0.0198	0.015
Cu	0.178	0.054	0.026	0.006
Pb	0.166	0.0371	0.625	0.53
Ni	0.016	0.004	0.11	0.081
Cr	0.009	0.002	0	0
Cd	0.005	0	0.022	0.024
Mn	0.04	0.005	0.024	0.028

The foam glass obtained is highly porous material of closed pores (porosity 92%) it does not absorb water (absorbility below 5%), it is inflammable, and does not emit toxic fumes, light (app. density 180-225 kg/m3), strength (compression str. about 2.4 Mpa) posses thermal conductivity 0.06 W/mK, and high chemical and biological durability. Thus it represents a highly valuable material for various applications mainly in building industry and engineering.

One of the most important features of the vitrificate is leachability level of heavy metals. This property decides about wide use of the vitrificate and about possibility of returning it to the natural environment. Results of chosen investigations for leaching tests were placed in Tab.1. The next criterion determining a usefulness of the final product was the mass loss test. The results are presented in Tab. 2. It can be seen, the best effects have been reached for the vitrificate samples made of fly ash from heat and power generating plant Belchatow and the sludge from the municipality treatment plant.

Table 2. Mass loss in aqueous solution [3]

	Sample	Mass loss in aqueous solution [%]
1	Medical ash + 35% PCB	2.9
2	Fly-ash from heat and power generating plant Belchatow	1
3	Sludge from industrial treatment plant	9.28
4	Sludge from municipality treatment plant	1

Measured Vickers hardness of the vitrificate is typical for usual kinds of glass. It suits for producing of building materials, road aggregates, etc.

Plasma assisted CNT's synthesis

Carbon-Nano-Tubes (CNTs) in the form of free fibers or forests growing on substrates are needed for many technological applications such as special reinforced materials or electron emitters, supercapacitors, rechargeable batteries, photovoltaic cells, etc [4]. In this paper the microwave plasma process (Fig. 5) being able to carry out the CNTs synthesis are presented. The carbon atoms can be delivered to the system with acetylene, benzene, ethylene, methane, propylene, CO and other gases containing carbon and also from evaporated solid material such as ferrocene. Catalysts are mainly iron, cobalt and nickel. Synthesis appears during a flow of the carrier gas such as Ar or N2 which are mixed with gases containing carbon when they are reaching temperatures ranging from 800 to 1200 K. To deposit a layer of freely oriented CNTs it is possible to move in the cross section of the outgoing pipe (Fig. 5) a porous material which will be able to catch the CNTs that are flowing out from the plasma.

One of the main challenges to obtain the optimal product properties is to work out a process of continuous synthesis and uniform dispersion of CNTs on a substrate. In this case the substrate surface must be pretreated to implant a matrix of catalyst islands. Then the substrate should be heated in the temperature about 1000 K and the carbon gas must be applied. The synthesis of CNTs can be done in one compact microwave plasma system [5]. We present here exemplary research results for randomly depositing CNTs in the collector and uniform forest deposited on silica wafer (Fig. 6). The near LTE microwave plasma may be used as an activator of the synthesis process of carbon nanotubes.

It can be applied at the entrance to the furnace CVD. Then the tube furnace is used to ensure the conditions necessary for the synthesis process. However the microwave plasma takes also part in preparation (activation) of catalytic gas and mixing it with carbon carrying gas.

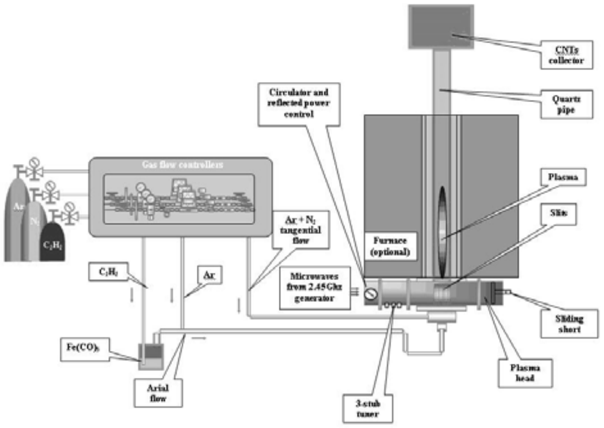

Fig.5. The microwave plasma system for CNTs synthesis

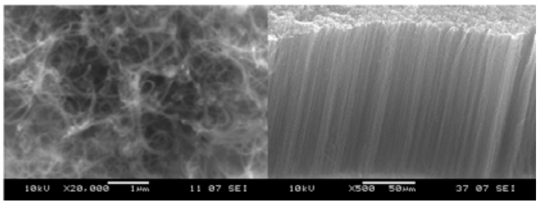

Fig.6. SEM images of multiwall CNTs deposits captured in the microwave plasma furnace collector – left and grown on silica wafer - right column

Our studies have shown that microwave plasma may itself lead to the synthesis of carbon nanotubes without the use of CVD furnace. The vertical geometry of the quartz reactor tube causes symmetrical heating gas flowing at a positive impact on the homogeneity of the product, preventing the local overheating of the quartz tube. This is much easy to maintain solution with fast start up and cooling rate.

Acknowledgement
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