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GASIFICATION OF RAM MEMORY WASTE

ZGAZOWANIE ODPADÓW PAMIĘCI RAM

Abstract

RAM memory is a basic part of printed circuit computer board. It consists of organic (resin) fraction, mineral substance (fiberglass) and metals, predominantly copper and precious metals: Ag, Au and Pd. Processing RAM memory by steam gasification on the laboratory scale has been presented in the paper. This process transforms original solid material into easy separable fractions, without organic phase. Lightly sintered original RAM memory parts after gasification were crushed and separated according to diameter and magnetic properties and analyzed for valuable metals concentration. The process may be applied to other composite waste materials.

Keywords: electronic waste, RAM memory, steam gasification

Streszczenie

Pamięci RAM są podstawową składową komputerowych płyt głównych. Zawiera frakcję organiczną (żywic), mineralną (najczęściej włókno szklane) i metale, głównie miedź, a także metale szlachetne: Ag, Au oraz Pd. W pracy przedstawiono rezultaty zgazowania w atmosferze pary wodnej w skali laboratoryjnej pamięci RAM. Proces ten pozwala na przekształcenie oryginalnego, zwartego materiału w łatwo rozdzielany na frakcje produkt, pozbawiono fazy organicznej. Lekko spieczony produkt zgazowania był kruszony i rozdzielony na frakcje w zależności od rozmiarów ziaren i właściwości magnetycznych. We frakcjach tych oznaczono stężenia wybranych metali, w tym szlachetnych. Proces zastosowany może być do innych materiałów złożonych.

Słowa kluczowe: odpady elektroniczne, pamięci RAM, zgazowanie parą wodną

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1. Introduction

RAM (*Random Access Memory*) is a computer data storage device, commonly used in personal computers. In waste processing, waste RAMs detached from computer mainboards are a separate commercial product, one of the most valuable. RAM consist of two different types of structures: printed circuit boards, PCBs, are the first one, and integrated circuits, ICs, mounted onto boards, are the other one. Processing of ‘empty’ boards (in particular without memory chips) or boards with memory chips and other components (printed circuit assemblies, PCAs) may be considered different procedures. Integrated circuits are mounted on printed boards as encapsulated, usually by ceramic material, chip (integrated circuit packaging). The method of encapsulating, as well as integrated circuits themselves, have changed over time and there is a variety of packages now. One of more common is TSOP system (thin small-outline package), usually applied for RAM and flash memories. As an example, Integrated Silicon Solution, Inc., CA USA published a material composition sheet of the specific package – 54 TSOP II, Table 1 [1]. It may be noticed that there is only 7.74 wt.% of organic fraction in the package. Silica prevails, SiO₂, but the content of iron and nickel is also significant (21.26 wt.%). The presence of elemental silicon (5.47 wt.%) and gold (0.14 wt.%) is worth mentioning. Printed circuit boards characteristics are systematically published in the literature. Their composition and structure is varying but usually they are a combination of fibreglass and epoxy resins or cellulose with phenolic resins which are a substrate for generally metallic (copper) structure of the circuit [2]. A typical elemental composition of 8-layer PCB (FR-4, bare boards) is given in table Table 2 [3]. The elemental composition does not represent entirely material combination of the board; according to [3] weight ratios of metallic copper, fibreglass and resins are 1:1:1. It corresponds to fuel characteristics (approximately): 70 wt.% of solid combustion residue (together with metals), 21 wt.% of volatiles, 8.5 wt.% of fixed carbon and 0.5 wt.% of moisture. The information whether processed PCBs are bare boards or populated ones (or how they were disassembled) is often not precisely given in the literature. Maybe this is the reason for significant variation of material composition of this waste – an example is given in Table 3 [2].

Table 1

Material composition of Thin Small Outline Package (54 TSOP II), ISSI [1]

	Mass [mg]	Material	Mass [mg]	wt. %
Die	29.790	Si	29.612	5.47
		Al	0.089	0.02
		Cu	0.089	0.02
Leadframe	115.037	Fe	66.721	12.33
		Ni	48.316	8.93
Die Attach Adhesive	2.136	polyimide resin polyether amide imide	1.068 1.068	0.20 0.20
Bonding Wire	0.768	Au	0.768	0.14
Encapsulation	389.673	Epoxy resin	21.432	3.96
		Phenol resin	17.535	3.24
		Carbon black	0.779	0.14
		Silica	349.927	64.66
Solder Plating	3.795	Sn	3.795	0.70
total			541.200	

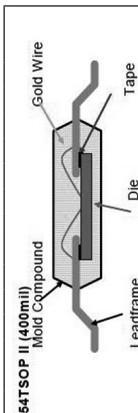


Table 2

Elemental composition of PCB (FR-4, bare boards), [3], wt.%

C	O	Si	Cu	Al	Ba	Br	N	S	H
24.80	24.16	14.76	26.30	2.88	0.12	4.30	0.48	0.28	1.94

Table 3

Material composition of printed circuit boards, [2].

Material	Average content	Content, [wt.%] (ppm)
Cu	metals – 40 wt.%	10 – 27
Al		1.3 – 4.8
Pb		1.0 – 4.2
Zn		0.2 – 2.2
Ni		0.3 – 2.4
Fe		1.2 – 8.0
Sn		1.0 – 5.3
Sb		0.06 – 0.4
Au		80 – 1000 ppm
Pt		4.6 – 30 ppm
Ag		110 – 3300 ppm
Pd		10 – 290 ppm
SiO ₂		ceramics – 30 wt.%
Al ₂ O ₃	6 – 7	
Alkaline and alkaline earth oxides (CaO)	6 – 7	
Titanates, mica, etc	3	
Polyethylene	plastics – 30 wt.%	10 – 16
Polypropylene		4.8
Polyesters		4.8
Epoxies		4.8
Polyvinyl chloride		2.4
Polytetrafluoroethane		2.4
Nylon		0.9

2. Gasification

Steam plays a double role in gasification experiment: on the one hand it enables transferring of residual carbon to a gaseous phase after an intensive pyrolysis step (equilibrium of reaction $C + H_2O = CO + H_2$ is shifted to the right at high temperatures) but on the other hand it enables also subsequent conversion of complex organic compounds in gases to simpler forms. However, the purpose of this experiment was to determine how parts of the RAM memory are converted in the gasification process (pyrolysis under steam at normal pressure) and what fractions may be separated from this product.

Gasification experiments have been carried out in a quartz reactor, presented in Fig. 1. Original RAM memory (Fig. 2) was cut into two pieces suitable for the reactor and heated under steam flow of 0.37 g H_2O/min to 750°C at 10°C/min. The heating under steam flow was continued at 750°C for 1 hour, then the temperature was increased to 790°C and after the next 20 minutes the reactor was cooled down (also at 10°C/min and under the same steam flow). After cooling to ambient temperature the reactor was opened and gasification products removed. The products are presented in the following three illustrations Fig. 2.

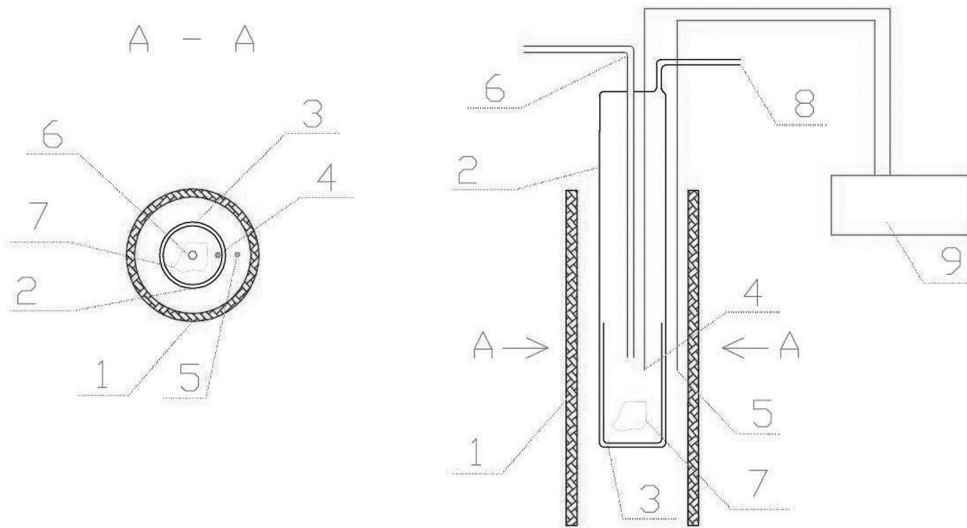


Fig. 1. Quartz reactor used in gasification experiments. 1 – heating elements, 2 – quartz tubes, 3 – quartz container, 4 – measuring thermocouple, 5 – controlling thermocouple, 6 – steam inlet, 7 – gasified elements, 8 – outlet of process gases, 9 – control unit

Rys. 1. Reaktor kwarcowy użyty podczas eksperymentów zgazowania. 1 – element grzewczy, 2 – reaktor kwarcowy, 3 – tygiel kwarcowy, 4 – termopara pomiarowa, 5 – termopara sterująca, 6 – doprowadzenie pary wodnej, 7 – wsad, 8 – odprowadzenie gazów procesowych, 9 – układ kontrolny

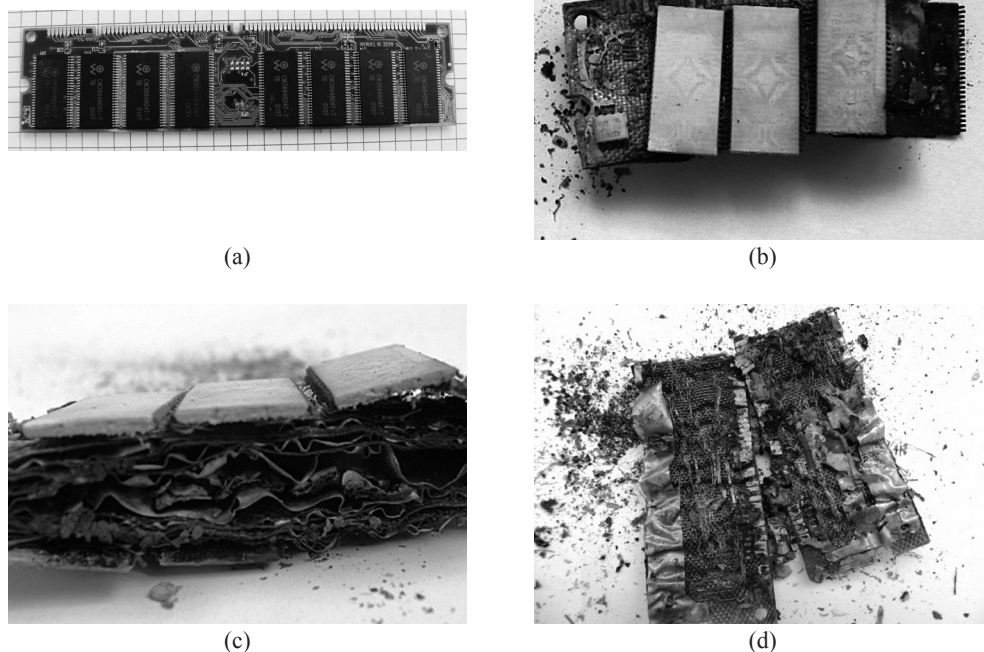


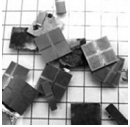
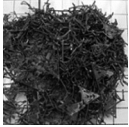
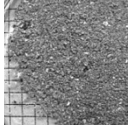
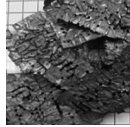
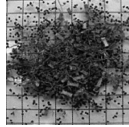
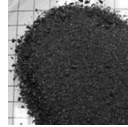
Fig. 2. Gasified RAM memory – original (a) and after gasification process (b–d)

Rys. 2. Pamięć RAM – oryginalna (a) i po procesie zgazowania (b-d)

3. Results

Gasification process does not change the general shape of gasified elements, which can be seen in Fig. 2: some unbroken integrated circuits are still attached to the printed board whereas the board is clearly stratified. Two of eight IC elements dropped spontaneously during the process and the six remaining ones were easily separated without any damage to the board or circuits. The separated ICs were crushed in a porcelain mortar and original dies (fraction 1.1 in Table 4), ferromagnetic elements of leadframes together with current leads (fraction 1.2) and a gray powder – residue of encapsulation (fraction 1.3) – were extracted. Crushing of gasified board and manual separation (sifting) gave next three fractions: larger metallic fragments (generally copper foil, fraction 2.1 in Table 4), coarse metallic elements (grains > 0.4 mm, fraction 2.2) and fine mineral (grains < 0.4 mm, fraction 2.3). Fine fractions, 1.3 and 2.3, were heated in the air at 600°C for 12 hours in order to complete oxidizing of carbon residues. Both fractions became slightly brighter and fine metallic particles became reddish. These changes were accomplished by a small, 1-2 wt.%, decrease of sample masses, consequently the concentration of residual carbon should be low.

Products of steam gasification of RAM memory

Fraction ^{#)}	1.1	1.2	1.3	2.1	2.2	2.3
[wt.%]	47.7			52.3		
	4.3	14.2	29.2	13.1	6.8	32.4
^{#)} – details in the text						

The concentration of metals: Ni, Fe, Cu, Ag, Au, Pd, Pb, Zn in product fractions was determined by atomic absorption spectroscopy (F-AAS) with atomization in acetylene-air flame. Fraction 1.1 was powdered in a porcelain mortar and fraction 2.1 was cut into small, 2x2 mm, pieces. Other fractions were used unchanged. Weighted samples (approximately 0.2 g of each fraction 1 and 0.5 g of each fraction 2) were digested without heating in 5 cm³ of aqua regia (concentrated HCl:HNO₃ in a ratio 3:1) for 24 hours, then were heated to 90 °C and digested for the next 1–2 hours (adding aqua regia, if necessary). The solutions together with solid residues were displaced to volumetric flasks (100 or 200 cm³) and analyzed.

The results of analyses, recalculated to wt.% of each metal in the product fractions, are presented in table Table 5. Fractioning of metals is characteristic for a processed substrate (RAM memory). Fraction 1.1, corresponding to the original IC elements (dies), does not contain metals in general (concentration of Au, Pd and Ni below detection limit). A high concentration of Fe and Ni characterizes fraction 1.2 of leadframes and current leads. There is also Ag (120 ppm), Au (1070 ppm) and Pd (370 ppm) in this fraction. Silver and gold are present at high concentrations also in the fraction 1.3 (a residue after encapsulation), at 270 and 890 ppm, respectively, but the Pd concentration is only 40 ppm. Taking into account that fractions 1.1-1.3 correspond to the original integrated circuit, the determined concentration of gold generally fits to the value given in table Table 1 (exemplary integrated circuit). There was no silver and lead in this exemplary integrated circuit and only traces of copper (these metals could be transferred in the gasification process from other components), but the concentration of gold was 1400 ppm. Fractioning of copper is well marked for fractions 2.1–2.3, the products of printed circuit board gasification. Naturally, the highest concentration of copper is fraction 2.1 (copper foil), however the concentration of copper in fraction 2.2 (coarse metallic grains) exceeds 30 wt.% accompanied by 2 wt.% of nickel. Some copper is also present in fraction 2.3 (fine mineral fraction) – this fraction constitutes 32.5 wt.% of the products and contains 10% of copper (at concentration of 4.9 wt.% Cu). Silver was detected in fractions 2.1 and 2.2 at concentrations of 120 and 110 ppm, respectively, and in fraction 2.3 at concentration of 290 ppm. Palladium in almost the same concentrations is present in fraction 2.1 (440 ppm) and in fraction 2.2 (420 ppm). The palladium concentration in fraction 2.3 equals to 110 ppm but, taking into account that it is a major fraction of the products, up

to 19% of total palladium occurs in this fraction. The average concentration of metals in all fractions is given in a bottom row of table Table 5. These data may be compared with the concentrations given in table Table 3. The concentration of copper, as well as nickel and iron, is at the expected level. The concentration of zinc and lead is lower. Considering precious metals, there is 190 ppm of palladium (expected 10-290 ppm, Table 3), 560 ppm of gold (expected 80-1000 ppm) and only 210 ppm of silver (expected 110-3300 ppm). This means a significantly lower concentration of Ag, with a typical content of Au and Pd.

Table 5

Concentration of metals in product fractions of RAM memory gasification, in wt.% (% of total quantity of particular metal in the fraction is given in brackets).

Fraction ^{#)}	Ni	Fe	Cu	Ag	Au	Pd	Pb	Zn
1.1	< 0.0025	0.074 (0.06)	0.19 (0.05)	0.0045 (0.9)	< 0.006	< 0.004	0.019 (0.5)	0.25 (2.2)
1.2	11.8 (76)	34.5 (92)	2.6 (2.4)	0.012 (8.1)	0.107 (27)	0.037 (28)	0.15 (13)	0.090 (2.7)
1.3	0.58 (7.7)	0.92 (5.1)	1.6 (3.0)	0.027 (38)	0.089 (46)	0.0040 (6.1)	0.055 (10)	0.20 (12)
2.1	0.57 (3.4)	0.043 (0.1)	83.6 (70)	0.012 (7.5)	0.011 (2.6)	0.044 (30)	0.019 (1.6)	0.040 (1.1)
2.2	2.4 (7.4)	0.034 (0.04)	33.3 (14)	0.011 (3.6)	0.036 (4.4)	0.042 (15)	0.15 (6.4)	0.14 (2.0)
2.3	0.45 (6.6)	0.26 (1.6)	4.9 (10)	0.029 (45)	0.032 (18)	0.011 (19)	0.33 (67)	1.2 (81)
Average concentration in all fractions	2.2	5.3	15.7	0.021	0.056	0.019	0.16	0.48

^{#)} details in the text.

4. Conclusions

Gasification of printed circuit boards with mounted integrated circuits with steam under normal pressure allows easy, automatic separation of integrated circuits, metallic fractions and copper foils and almost complete removal of organic carbon. It was found that 70% of copper was in a form of copper foils. Palladium was distributed in copper foils, elements of leadframes, the fine fraction of the board and the coarse metallic fraction (30%, 28%, 19% and 15%, respectively). 46% of gold was concentrated in the fine fraction from integrated circuits, 27% in leadframe elements and 18% in the board fine fraction. The highest concentrations of silver were found in fine fractions from the board (45%) and integrated circuits (38%).

References

- [1] *Quality and Reliability Manual*, Integrated Silicon Solution, Inc., 1940 Zanker Road, San Jose, USA (<http://www.issi.com>).
- [2] Williams P.T., *Valorization of Printed Circuit Boards from Waste Electrical and Electronic Equipment by Pyrolysis*, Waste Biomass Valor, 1, 2010, 107-120.
- [3] Jinhui L., Huabo D., Keli Y., Lili L., Siting W., *Characteristic of low-temperature pyrolysis of printed circuit boards subjected to various atmosphere*, Resources, Conservation and Recycling, 54, 2010, 810–815.