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PROCESSING OF ALUMINUM WASTE FROM THE FOOD PACKAGING

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ПЕРЕРАБОТКА АЛЮМИНИЯ, ПОЛУЧЕННОГО ИЗ ПИЩЕВОЙ ТАРЫ

The aim of this experiment was to melt down aluminium beverage containers and making use of the recycling process to acquire an aluminium material of a certain chemical composition for another production process with the aim of manufacturing aluminium semi-products and products. The aluminium material extracted in this way was subsequently analysed chemically and metallographically. These experiments were carried out within three casts and in all three cases the batch was formed by 100% of aluminium scrap in the form of finely shredded aluminium cans (Fig.1) and from the point of view of the complex efficiency assessment of the recycling process a calculation of the yield of the acquired aluminium alloy was undertaken. At the same time, considering that the aluminium waste was coated with plastic materials, paper and varnish/lacquer, it was necessary to identify the content and composition of the substances released in the course of the melting process in the form of gas and assess their possible negative impact on the environment.
Keywords: aluminium alloy, beverage containers

Introduction. Analysis of gases released from aluminium beverage containers by means of the gas chromatograph and the mass spectrometer.

With respect to aluminium scrap an analysis of the composition of the releasing gases in the form of chemical compounds at the temperature of 200 °C and 300 °C was carried out according to the following detailed description: Approximately 1 gram of shredded and crashed aluminium scrap was weighed and inserted into a glass capillary tube. Afterwards the tube was inserted into a furnace in which the temperature was set at 200 °C and the first desorption was carried out by pumping/drawing one litre of helium through the tube for a period of 20 minutes. The released substances were sorped into the sorption tube which was filled with Carbotrap 300 (which is a combination of 3 sorbents placed one after the other, i.e. Carbotrap, Carbotrap C and Carbosieve SII). The acquired sorption tubes were processed by thermal desorption in the apparatus Aerotrap 6000 (Tekmar, USA). Subsequently, the desorbed volatile organic substances were analysed by a tandem of the gas chromatograph – the mass spectometer MD800 (Fisons, UK) while applying separation silica columns SPB-1 Sulphur, 30m long, with the internal diameter of 0,32 mm and 4 μm thickness of film. The identification of eluted compounds was carried out by means of an interpretation of the measured mass spectra. The record of thermogravimetry (Fig.2) shows approx. a 4% loss of weight of the aluminium scrap in the form of gases with temperatures ranging between 300° and 600 °C. Therefore it is possible to reach the conclusion that the heating of aluminium scrap to a temperature higher than 300 °C and up to the melting point, leads to the release of gases in a quantity that corresponds to the decline of approx. 4 % of the weight from the total weight of the aluminium scrap.

Description of individual compounds which most frequently occurred at 200°C from the point of view of the ecological and health risk (Fig. 3): *Styrene* - (Phenylehylene, Vinyl benzene) is a colourless to yellow liquid with an intensive sweet odour. Styrene has narcotic and locally irritable effects. When it comes to contact with the skin, it causes defatting dermatitis and irritation. In the case of eye contact, it results in the irritation of the cornea and it may even cause its permanent damage. Chronic exposure to styrene is manifested by neurasthenic disorders and changes in liver functions and a drop in blood pressure; *Ethyl benzene* – is a non persistent substance which is biodegraded or exposed to photo oxidation in the environment. With the exception of its extensive leakage from a point source it does not cause a lot of damage to the eco system. Acute and chronic toxicity of ethyl benzene is relatively low. Ethyl benzen irritates respiratory paths and eyes, influences brain functions and damages skin, causes dizziness and damages liver, kidneys and eyes; *Methanol* - (apart from the chemical that is labelled according to the Czech spelling rules only “methanol”), methyl alcohol, carbinol is the least complex aliphatic alcohol. It is volatile, flammable and highly toxic. The narcotic effect of methanol is slightly less than with ethanol, it is excreted from the body gradually and this is also the reason why drunkenness lasts longer. Convulsive abdominal pains and visual disturbances are the two main symptoms of poisoning by this methanol. It also damages chemical substances in the cornea, which may result in blindness; *Benzene* **-** is an organic chemical substance with a sweet odour and a toxic liquid well known for its carcinogenous effects. Breathing in a small quantity of benzene may cause headache, fatigue, rapid heart beat, shivering and the loss of consciousness. A large concentration of benzene in the air may even cause death. Benzene damages bone marrow and causes anaemia. The IARC classifies benzene as a carcinogenous substance of group 1 (i.e. substance carcinogenous for man), in particular because it causes leukaemia and lung cancer; *Methyl Methacrylate* – is highly flammable, irritates eyes, respiratory organs and skin, it can also cause sensitization by skin contact.

Description of the individual, most frequently occurring compounds at the temperature of 300 °C from the point of view of the ecological and health risks (Fig. 4): *Chloromethane* - (Methyl Chloride) CH_3Cl, Methylene Dichloride (Dichloromethane) CH_2Cl_2, Chloroform (Trichloromethane) $CHCl_3$ a Carbon Tetrachloride (Tetrachloromethane) CCl_4 – is produced by methane chloration. These are, in general, carcinogenous compounds with narcotic effects; *Chlorethen* - (Vinyl Chloride) $CH_2{=}CHCl$ is a carcinogenous gas, the whole production of which is used for the manufacture of Polyvinyl Chloride, one of the most frequently used plastic materials. These are carcinogenous compounds; - *Acetone* – is a trivial name given to propane-2-one or also dimethylketon. Acetone is a colourless liquid with a specific odour, flammable, and can freely be mixed with water. Acetone is a basic raw material of the chemical industry; *Phenol* – is, under ordinary conditions, a colourless solid crystalline substance with the odour of tar. Its formula C_6H_5OH gives a true picture of its composition; the molecule is formed by one hydroxyl group attached to the hydrocarbon residue of the benzene ring called phenyl. This means that phenol is an aromatic compound. Due to its antiseptic effects, it is used in the manufacture of various antiseptics, and in the manufacture of pharmaceuticals. It is the initial material in the industrial manufacture of aspirin, herbicides and synthetic resins, for instance Bakelite; *Cyclopentanone* – is a colourless liquid of an agreeable odour with a density of 0.95 g.cm-3 and a boiling point of 131°C, less soluble in water, but easily soluble in organic solvents.

Melting tests of aluminium beverage containers and those of the metal yield

The batch containing 2.5 kg of the finely shredded aluminium beverage scrap for each of the casts (No1, 2 and 3) was at first weighed. Precise scales, VEB Wägetechnik Rapido, with a range from 5g to 1000g and a precise level of 0.1g, were used for weighing exact quantity of the shredded cans. Then the batch was crammed into a graphite crucible and placed in the electric resistance furnace LAC s.r.o. with a power supply 13.8 kVA and a nominal heat output of 7.5 KW (Fig. 5). The batch was melted in the graphite crucible at a temperature of 780 °C and after melting the aluminium waste a small amount of salt was used (20g) for the better separation of the smear from the metal. The melting metal was stirred to take smears from the surface of the liquid metal. The molten metal from each of the three batches was cast into pieces of a circular shape (Fig. 6) and after it was cooled, it was weighed according to the calculation of the metal yield by the following formula:

$$\text{Metal yield} = \frac{\text{weight of metal after melting}}{\text{total weight of the batch}}.100\ [\%]$$

The metal yield in the individual casts ranged from 70 to 80 % and the following results of the metal yield were obtained: Cast No. 1 – 70.5 %, Cast No.2 – 79.5% and Cast No 3 – 79.7 %. When recycling aluminium beverage containers on an industrial scale with the aim of achieving a higher level of the metallic yield, the more suitable way of preparing the batch is to use the method of crushing cans into small pieces and the subsequent compacting of aluminium scrap by pressing it into “briquettes”.

Spectrometric sample analysis after the process of melting

With cast Nos. 1, 2 and 3 the required samples for spectrometric analysis were taken after melting and the casting of aluminium into a shaped piece with the aim of determining the precise chemical composition of the individual samples. The apparatus employed was SPECTROLAB, manufactured by the company Spectro, i.e. an optic emission spectometer which makes use of special CCD detectors for identifying the light of the spectral lines of the individual chemical elements. As a whole, 27 elements were analysed within individual samples. The results of the individual analyses in Casts No. 1, 2 and 3 are presented in the following tables.

All analysed casts are, as far as their chemical composition is concerned, close to the AlMn1 alloy (EN AW 3103 or EN AW 3003) with a content of Mn 0.452 – 0.606 %. The content of the main impurities ranges between: 0.341 and 0.90 % in Fe, 0.307 % and 0.341 % in Si and 0.015 and 0.264 % in Zn. The aluminium content ranges between 96.3 and 97.9 %.

Table 1

Cast No. 1

Element	**Si**	**Fe**	**Cu**	**Mn**	**Mg**	**Cr**	**Ni**	**Zn**	**Ti**
Value in %	**0,337**	**0,90**	0,094	**0,452**	**0,67**	0,043	0,156	0,**264**	0,026
Element	**Ag**	**B**	**Be**	**Bi**	**Ca**	**Cd**	**Co**	**Ga**	**Li**
Value in %	0,026	0,02	0,0007	>0,03	>0,012	0,02	>0,05	>0,042	>0,0004
Element	**Na**	**P**	**Pb**	**Sb**	**Sn**	**Sr**	**V**	**Zr**	**Al**
Value in %	>0,02	>0,0084	>0,048	<0,002	>0,06	>0,0085	0,05	>0,036	96,3

Table 2

Cast No. 2

Element	**Si**	**Fe**	**Cu**	**Mn**	**Mg**	**Cr**	**Ni**	**Zn**	**Ti**
Value in %	**0,307**	**0,48**	0,085	**0,606**	0,004	0,009	0,003	**0,132**	0,027
Element	**Ag**	**B**	**Be**	**Bi**	**Ca**	**Cd**	**Co**	**Ga**	**Li**
Value in %	<0,0001	0,0011	0,0001	0,0007	<0,0000	0,0002	<0,0001	0,0114	<0,0000
Element	**Na**	**P**	**Pb**	**Sb**	**Sn**	**Sr**	**V**	**Zr**	**Al**
Value in %	0,0017	0,0038	0,0067	0,0287	0,0014	<0,0001	0,0054	0,0013	98,3

Table 3

Cast No. 3

Element	**Si**	**Fe**	**Cu**	**Mn**	**Mg**	**Cr**	**Ni**	**Zn**	**Ti**
Value in %	**0,341**	**0,341**	0,098	**0,530**	**0,72**	0,013	0,00065	0,015	0,021
Element	**Ag**	**B**	**Be**	**Bi**	**Ca**	**Cd**	**Co**	**Ga**	**Li**
Value in %	<0,0001	0,0013	0,0004	>0,001	0,002	0,001	0,0005	>0,016	0,0001
Element	**Na**	**P**	**Pb**	**Sb**	**Sn**	**Sr**	**V**	**Zr**	**Al**
Value in %	0,0029	0,0025	0,0039	<0,002	<0,001	<0,0001	0,01	0,0026	97,9

Metallographic evaluation of the procedure of casting

The acquired aluminium smelts from individual casts which were cast into a circular shape, and subsequently cut vertically, always in the central area prescribed for taking samples and for the preparation of metallographic cuts with subsequent metallographic microscopic evaluation. The samples were cast and subsequently cut and polished with a final etching in 10% phosphoric acid for a period of 5 minutes for better visibility of its structure. The microstructure of Cast No. 1 was fundamentally different from the other two casts since Cast No. 1 contained an increased content of iron which manifested itself in the occurrence of a higher number of crystalographically developed rough needles of the inter metallic phases of the $FeSiAl_5$ type (spatially understood as blankets) with a size of 300 – 700 μm (Fig.7). The microstructure of Cast No. 2 (Fig. 8) and also that of Cast No. 3 show the ramified intermetallic phases of the AlFe(Si)Mn type, often called "Chinese Script", which reach a size of from 80 to 200 mm. The microstructure of all casts shows an increased level of local interdendritic porosity (Fig.9) with occurrence of oxide membranes of different shapes.

Fig. 1. The Weighing of Finely Shredded Cans

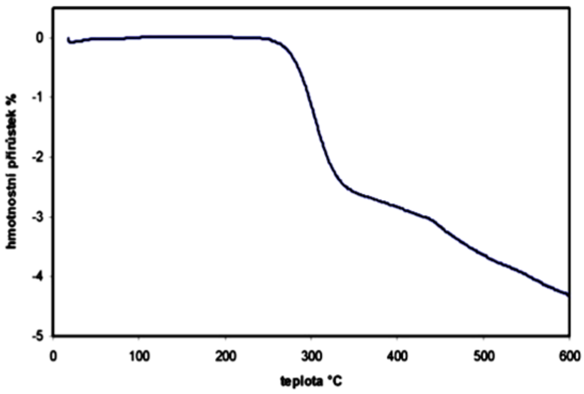

Fig. 2. Thermogravimetric Record

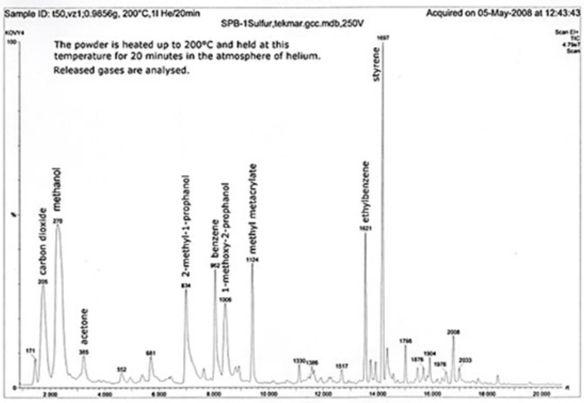

Fig. 3. Measured Mass Spectra of Compounds at 200°C

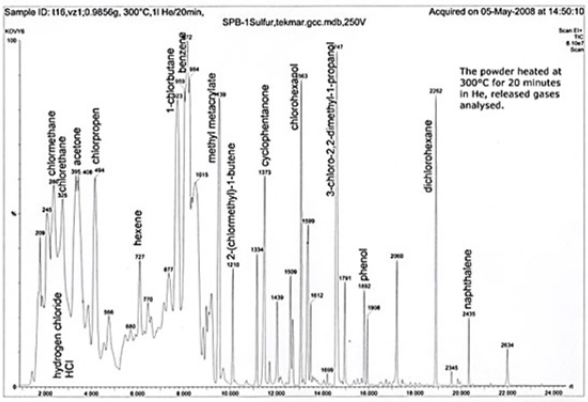

Fig. 4. Measured Mass Spectra of Compounds at a Temperature of 300°C

Fig. 5. Electrical Resistance Furnace LAC

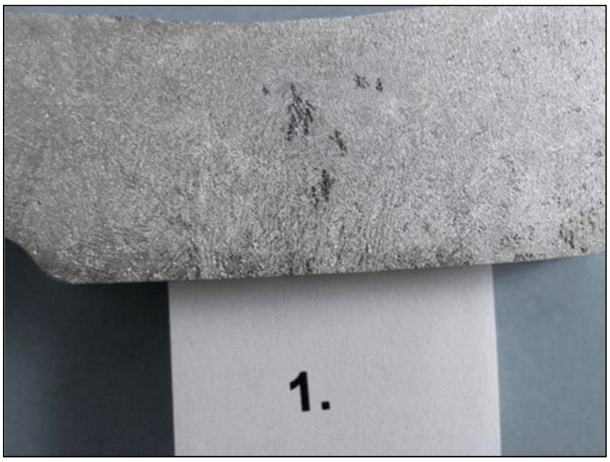

Fig. 6. Macrostructure of Cast No. 1

Fig. 7. Microstructure of Cast No. 1

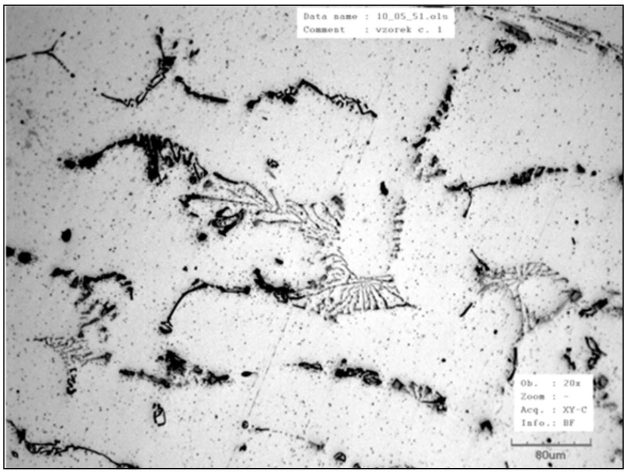

Fig. 8. Microstructure of Cast No. 2

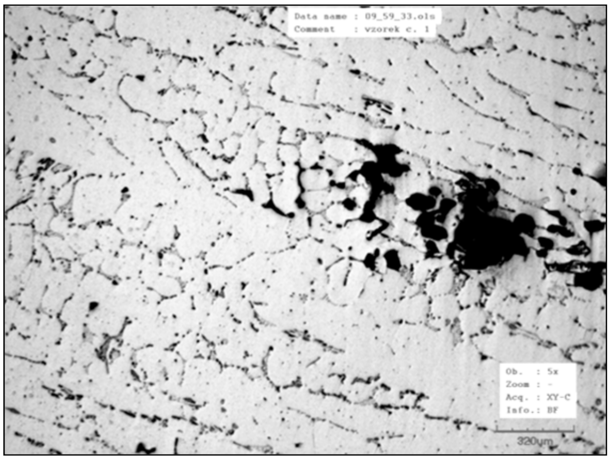

Fig. 9. Microstructure of Cast No. 3

Conclusions

At temperatures ranging from 200-300 °C, aluminium releases a long line of dangerous chemical compounds. The thermo gravimetric record points to an approx. 3-4% loss of the aluminium weight from the total weight of waste (scrap) in the form of gases.

From the above-mentioned facts it is possible to hypothesise that aluminium granules contain 3-4 % of impurities (remnants of lacquers, plastic materials, paints, etc.), which are released in the form of volatile gases when temperatures are increased. The substances which are released from aluminium beverage cans are dangerous for human health and are mainly the following: methanol (strongly poisonous, it may damage the retina and further lead to visual disturbances), benzene (a carcenogenous substance of Group 1, causes leukaemia and lung cancer) and methyl methacrylate. Also the compounds containing chlorine (Chloromethane, Chloroethene, Hydrogen chloride, 1-Chlorbutane, Chlorhexanol, etc.), from which chlorine or hydrogen chloride (carcinogenous and irritant gases) may be released. It can be concluded that the melting of a larger quantity of these aluminium beverage cans represents, without prior alteration (or alteration of the technological process of melting) and without removal of these substances, a considerable risk to security and health.

All analysed casts are, with respect to its chemical composition, close to the AlMn1 alloy (EN AW 3103 or EN AW 3003) with a content of Mn 0.452 – 0.606 % and Fe, Si and Zn. The content of Al ranges between 96.3 and 97.9%.

From the obtained results of from the melting of individual casts, it was possible to hypothesise that the yield was moving within a range of 70 – 80%, which is a very good result from the point of view of shredded non-compacted waste. When compacted input waste pressed into briquettes was used, it was possible to achieve the yield with an increase of up to 80%.

From the results of individual casts it is possible to reach the conclusion that the entire volume of the acquired aluminium material is compact and homogenous, without any evident shrinkage, holes, pipes and remnants of the re-melted scrap. From the point of view of the metallurgical quality of the microstructure of all samples, we can observe occurrence of carbides, due to burning plastic residues, paints and dyes, and their subsequent reaction with aluminium. Also the inter- dendritic porosity has increased by the content of oxide membranes and fine oxides. For that reason, in order to acquire a better metallurgical quality, it would be necessary to carry out refining and degassing processes, possibly supplemented by filtration through a ceramic filter.

Анотація. *Метою цього експерименту було розплавити алюмінієві контейнери для напоїв і при використанні процесу переробки отримати алюмінієвий матеріал певного хімічного складу для іншого процесу виробництва з метою виробництва алюмінієвих напівфабрикатів і продукції. Алюмінієвий матеріал, витягнутий таким чином згодом був проаналізований хімічно і металографічно. Ці експерименти проводилися на трьох злитках і у всіх трьох випадках пакет був сформований із 100% алюмінієвого брухту у вигляді тонко подрібнених алюмінієвих банок. З точки зору комплексної оцінки ефективності утилізації розрахунок прибутковості отриманого алюмінієвого сплаву не проводився.*
Ключові слова: алюмінієвий сплав, контейнери для напоїв.

Аннотация. *Целью этого эксперимента было расплавить алюминиевые контейнеры для напитков и при использовании процесса переработки получить алюминиевый материал определенного химического состава для другого процесса производства с целью производства алюминиевых полуфабрикатов и продукции. Алюминиевый материал, извлеченный таким образом впоследствии был проанализирован химически и металлографически. Эти эксперименты проводились на трех слитках и во всех трех случаях пакет был сформирован из 100% алюминиевого лома в виде тонко измельчённых алюминиевых банок (рис. 1). С точки зрения комплексной оценки эффективности утилизации расчет доходности полученного алюминиевого сплава не проводился.*
Ключевые слова: алюминиевый сплав, контейнеры для напитков

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