



Thermal Cleaning and Melting of Fine Aluminium Alloy Chips

P. Palimaka

AGH University of Science and Technology, Faculty of Non-Ferrous Metals,
 al. A. Mickiewicza 30, 30-059 Cracow, Poland

* Corresponding author. E-mail address: palimaka@agh.edu.pl

Received 24.05.2020; accepted in revised form 24.09.2020

Abstract

Production waste is one of the major sources of aluminium for recycling. Depending on the waste sources, it can be directly melted in furnaces, pre-cleaned and then melted, or due to the small size of the material (powder or dust) left without remelting. The latter form of waste includes chips formed during mechanical cutting (sawing) of aluminium and its alloys. In this study, this type of chips (with the dimensions not exceeding 1 mm) were melted. The obtained results of laboratory tests have indicated that even chips of such small sizes pressed into cylindrical compacts can be remelted. The high recovery yield (up to 94 %) and degree of metal coalescence (up to 100 %) were achieved via thermal removal of impurities under controlled conditions of a gas atmosphere (argon or/and air), followed with consolidation of chips at a pressure of minimum 170 MPa and melting at 750 °C with NaCl-KCl-Na₃AlF₆ salt flux.

Keywords: Environmental protection, Aluminium recycling, Aluminium chips, Turnings, Melting of aluminium scrap

1. Introduction

Aluminium alloy chips from the machining process are one of the scrap categories defined by European Scrap Standard EN 13920 [1]. Due to the large surface, which is covered by a thin layer of Al₂O₃, remelting this material is much more difficult than in the case of other types of aluminium scrap (profiles, sheets, ingots, etc.). Depending on the type of machining (cutting, sawing, grinding, turning, drilling, milling), the chips may have larger or smaller dimensions; they may be elongated or spiral in shape, short, discontinuous, or in the form of dust or powder. Among the above mentioned machining methods, sawing is the method that generates significant amounts of waste aluminium and its alloys in the form of small size semi-continuous chips that are not suitable for recycling in melting processes [2]. This is due to the oxidized and large surface contaminated with lubricants and emulsions used during machining. Additionally, direct melting of small chips can be dangerous. It is assumed that aluminium

powder, swarf or chips with dimensions below 420 μm suspended in the air or deposited in the form of a layer pose a real risk of explosion in contact with the ignition source (open fire, sparks, electrical devices, hot surfaces, etc.). The minimum explosive concentration for aluminium chips suspended in the air is 40÷60 g·m⁻³, while for aluminium powder it is the value of 40÷140 g·m⁻³, with ignition temperatures amounting to 600÷700 °C and 550÷800 °C, respectively [3]. Such conditions may arise during loading of chips into the furnace, where high temperature (750÷800 °C) can be the factor leading to the ignition of the resulting mixture. Low-temperature processes that do not use metal melting are an alternative to remelting chips of this type. Bingbing Wan [4] describes techniques that use severe plastic deformation (SPD), such as hot extrusion, equal channel angular pressing (ECAP), cyclic extrusion compression (CEC), friction stir extrusion (FSE), high pressure torsion (HPT) and screw extrusion, or techniques based on powder metallurgy. Compared to remelting, these methods have several advantages, including low metal losses, low energy consumption and nearly total

absence of harmful gas emissions [2]. Techniques based on strong plastic deformation consist in consolidation of the chips to a semi-finished solid product, followed by extrusion of the final product [5-11]. On the other hand, in the techniques based on powder metallurgy, metal chips are pulverized to produce metal powders from which components can be made by high-temperature methods of sintering [12]. All of the above-mentioned methods require, however, chips from one source, relatively clean and homogeneous in terms of chemical composition. There is no possibility in the case of these methods to correct the chemical composition, especially to remove unwanted admixtures or impurities, because any interference in the chemical composition to produce metal with the required composition is possible only when this metal is in the molten state. In this research work, attention was focused on the possibilities to melt the chips formed during mechanical cutting (sawing) of aluminium alloy. The dimensions of individual chips, described in more detail in the next section, was less than 1 mm. Therefore, every attempt undertaken in this work to melt the test material was preceded by the consolidation of properly prepared stock. Melting was performed with chloride and fluoride salts flux. The aim of the research was to determine the effect of compacting pressure on the degree of metal coalescence and recovery yield, to select optimal melting conditions, and to indicate the advantages and disadvantages of the proposed process.

2. Materials and Methods

Microscopy observations were carried out on chips with dimensions below 1mm formed during machining (sawing) of aluminium alloy. The appearance of the chips is as shown in Figure 1 a-d.

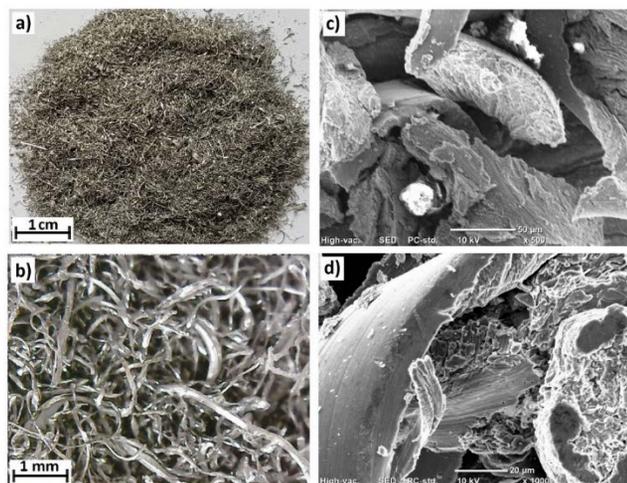


Fig. 1. The appearance of aluminium chips: b) - optical microscope, c) and d) - SEM

Particularly interesting is the SEM image. It indicates that the size of some of the chips is even less than 30 µm (Figure 2d), their shape is irregular and the edges are jagged. Hence the specific surface is large and also covered large amount of Al_2O_3

and other impurities. The tested material was pressed into a cylindrical form and analyzed by EDXRF technique (MINIPAL 4, PANalytical B.V., Espoo, Finland). The appearance of the compacts and analysis results for the five samples are shown in Figure 2.



Fig. 2 The appearance of five compacts and its chemical composition

Because of strong fragmentation of the tested material and the expected large amount of oxides (Al_2O_3) as well as other impurities on its surface, the salt fluxes were used in all the melting experiments. The salt composition was based on the equimolar NaCl – KCl system (i.e. 44 mol% NaCl – 56 mol% KCl, the eutectic temperature of about 650 °C [13]). The addition of cryolite to this mixture was to increase the interfacial tension between the salt and the molten metal, enhancing the removal of Al_2O_3 film from metal droplets, favour the metal coalescence and reduce the aluminium loss by metal entrapment into salt [13]. Each of the samples was remelted in alumina crucible with the salt flux containing KCl - NaCl mixtures with the addition of 5 wt.% Na_3AlF_6 . The melting temperature was 750 °C and the time was 30 minutes. The relation salt : compacts was 10 : 1 and was selected experimentally. At lower amounts of salt (with maximum compacting pressure), the coalescence did not occur. It could be explained as the amount of Al_2O_3 and impurities on the surface of the chips was so large that the small amount of salt very quickly got saturated with Al_2O_3 and impurities and lost its ability to facilitate metal coalescence.

After melting, the solidified products were pre-grounded in a steel mortar and then placed in a beaker with hot water to completely dissolve the salt. The obtained metal was separated into two fractions, i.e. above 3 mm (considered coagulated) and below 3 mm (considered non-coagulated). Both fractions were weighed, and the metal recovery yield n and the degree of coalescence c were calculated using Equation (1) and (2), respectively.

$$n_{\%} = \frac{m_{fr(n)} + m_{fr(c)}}{m_t} \times 100 \quad (1)$$

where: $m_{fr(n)}$ - mass of non-coagulated metal [g], $m_{fr(c)}$ - mass of coagulated metal [g], m_t - mass of the compact before melting [g].

$$c_{\%} = \frac{m_{fr(c)}}{m_{fr(n)} + m_{fr(c)}} \times 100 \quad (2)$$

where: $m_{fr(n)}$ - mass of non-coagulated metal [g], $m_{fr(c)}$ - mass of coagulated metal [g].

During the thermal cleaning process, a 20 g sample of material was placed in an alundum crucible and in a laboratory tube furnace (Figure 3). After closing the furnace tightly, the heating rate was set at $13\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ until reaching a temperature of $500\text{ }^{\circ}\text{C}$. At the same time, an air pump was started, feeding the air to the reactor at a rate of $5\text{ dm}^3\cdot\text{min}^{-1}$. The gas composition analysis was made every 10 seconds as a function of the time of the experiment lasting 40 minutes using a CO/CO₂ gas analyser (ABB Advance Optima 2000, Germany). In the case of thermal cleaning in a protective argon atmosphere, the reactor was flushed with argon for 24 hours before heating the furnace. Other parameters and steps were the same as described above.



Fig. 3 The appearance of laboratory stand for thermal cleaning process

In turn, the two-stage experiment consisted in the initial removal of impurities in argon done in accordance with the procedure provided for this gas, with the maximum temperature in the second stage being reduced to $350\text{ }^{\circ}\text{C}$ and air fed instead of argon into the reactor for 40 minutes.

3. Results and discussion

3.1. Compacting

At the beginning of the experiments, aluminium chips were compacted at different pressures to determine their compressibility. A cylindrical die with a diameter of 21 mm was used. The compacting pressure was $170\text{--}720\text{ MPa}$. Figure 4 presents the compressibility of the aluminium material.

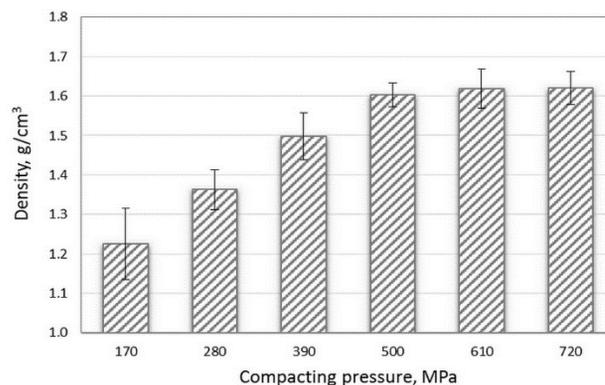


Fig. 4 Effect of compacting pressure on the density of compacted chips

Figure 4 indicates that the higher compacting pressure than 500 MPa did not increase the density significantly. The maximum pressure applied (720 MPa) produced the compacted chips with a density of about $1.63\text{ g}\cdot\text{cm}^{-3}$.

3.2. Thermal cleaning

There were two reasons for conducting experiments with thermal cleaning of chips. The first reason was derived from industrial processes in which chips not containing fine fractions (<1mm) are subjected to thermal purification in a controlled atmosphere prior to melting. The second reason was the behaviour of compacted chips during the preliminary process of melting. After placing the pellet in molten salt ($750\text{ }^{\circ}\text{C}$), the appearance of flames was observed. This indicated the ignition of flammable impurities. Additionally, the salts after melting were black and difficult to break in a steel mortar. The author's experience shows that salts that get saturated only with Al_2O_3 resting on the surface of molten aluminium scrap are light grey in colour and relatively easy to disintegrate by manual grinding. Thus it was decided to remove impurities by thermal processing. Sample results of CO and CO₂ concentration changes in gases obtained during experiment carried out in the air are shown in Figure 5.

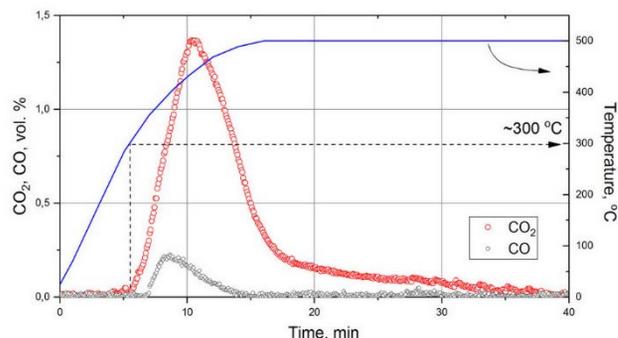


Fig. 5 Changes in CO₂ and CO concentration during thermal cleaning of chips in the air

As presented in the Figure 5, the carbon dioxide concentration in gases increases at a temperature of about 300 °C and after several minutes reaches its maximum value of 1.42 vol%. The presence of carbon dioxide is associated with the burning process (oxidation) of organic impurities present on the surface of chips. The impurities include cooling and lubricating emulsions based on mineral oils, used in sawing processes (and also in cutting, drilling, grinding, threading, etc.). Higher CO₂ concentrations should be expected for larger masses subjected to the thermal cleaning process. In turn, the temporary increase in carbon monoxide concentration (up to 0.5 vol%) begins at a temperature of about 350 °C. It could be the result of incomplete combustion of organic components. With an excess of oxygen in the system, however, there is a rapid decrease in CO concentration and further increase in CO₂ content. When argon was used as a protective atmosphere, no increase in the concentration of any of the gases was recorded.

3.3. Melting

Melting experiments for materials compacted under different pressures were carried out in three variants using:

- crude chips (not subjected to cleaning process),
- chips thermally cleaned in the air,
- chips thermally cleaned in a protective atmosphere of inert gas (argon).

When compacts made of chips not subjected to any thermal cleaning were melted, as soon as the pellets were placed in molten salt, a combustion reaction started, producing flame and smoke. After several seconds, the flame went out, which probably marked the end of the reaction of combustion of the flammable fractions (Figure 6). After this time, the salts were observed to take on a dark grey, nearly black colour.

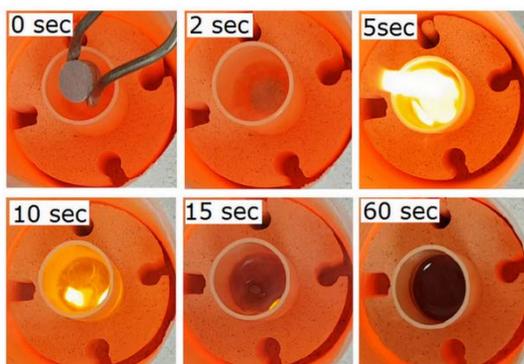


Fig. 6 Initial stages of the compacts melting (crude chips)

After solidification and cooling, manual crushing of the sample was difficult. The salts were hard and when they were dissolved in water, the metal surface was rough and lustreless; in the case of samples compacted at a high pressure, the coagulated metal was not spherical in shape.

In the case of thermally pre-cleaned chips, the flame did not appear, thus indicating the sufficiently full removal of flammable fractions in the thermal cleaning process. After placing the pellets

in molten salt and reaching the melting point, their disintegration was observed, followed by the appearance of small metallic droplets. The observed disintegration of the pellets was probably associated with the change in metal density during the solid-liquid phase transition and loosening of the compact structure. The change in the density during phase transition is approximately 15% [14], which means that it was also possible for the molten salt to penetrate inside the pellet and absorb the impurities. Schematically, Figure 7 shows the compact melting process comprising:

- heating of compact (Figure 7a)
- melting, loosening of the compact structure, penetration of molten salt and absorption of impurities (Figure 7b)
- sedimentation and coalescence of droplets (Figure 7c).

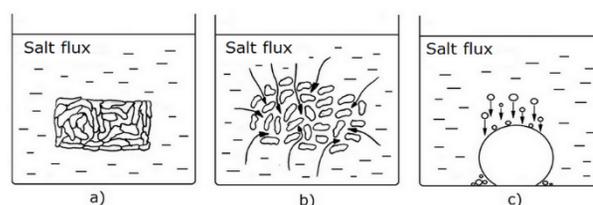


Fig. 7 Stages of the compacts melting process: a) heating, b) disintegration, salt penetration, beginning of coalescence, c) sedimentation and coalescence

Figure 8 shows the appearance of metallic fractions melted under selected conditions.

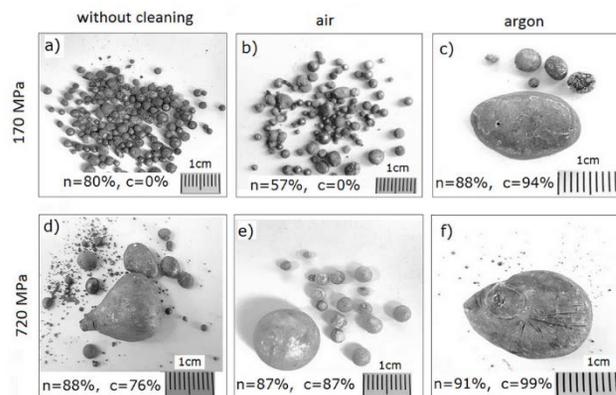


Fig. 8 The appearance of metal after melting for the two extreme cases of compacting pressures applied (170 and 720 MPa)

Figures 9 and 10 illustrate the results of calculations of the metal recovery yield and the degree of coalescence as a function of compacting pressure for compacts melted without cleaning (crude chips), and for chips cleaned in the air and in an atmosphere of argon.

Analyzing the results presented in Figure 9 it can be stated that the highest influence of pressing pressure on the metal recovery yield was obtained when the chips were subjected to cleaning in the air. With the lowest pressure of 170 MPa, the recovery yield was only 57%.

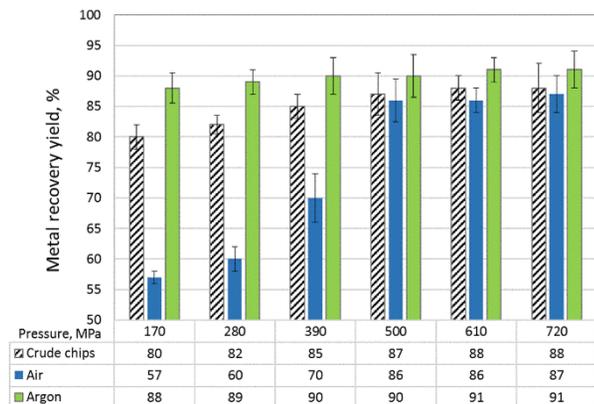


Fig. 9. Metal recovery yield as a function of compacting pressure

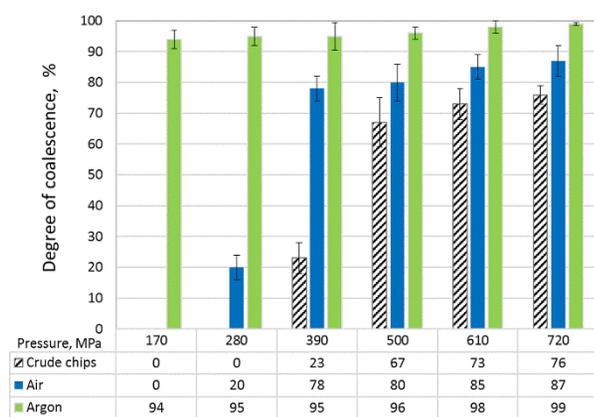


Fig. 10. Degree of coalescence as a function of compacting pressure

The increase in compacting pressure caused a clear improvement in the metal recovery yield (up to 88% at 500 MPa). It should also be noted that after melting, the solidified salts were light grey in colour and their disintegration was relatively easy. The obtained metal had a metallic lustre and the shape of most obtained precipitates was nearly spherical. At the lowest compacting pressure, the metal coalescence was not observed and none of the metallic precipitates had a diameter larger than 3 mm. At higher compacting pressures, the coalescence was increasing, reaching its maximum value of $c = 87\%$ at a pressure of 700 MPa (Figure 10). Quite surprising are the high recovery yields obtained during remelting of chips that have not undergone any cleaning process. Yet, compared to the above mentioned thermal cleaning in the air, this can be explained by the fact that during cleaning, the chips are oxidized with oxygen present in the atmosphere. In contrast, compared to chips without cleaning, the coalescence has increased quite significantly because of the improved salt ability to remove the Al_2O_3 film.

Regarding the optimal values of both metal recovery yield and its coalescence, the most effective thermal cleaning process has proved to be oxygen-free heating. Chips cleaned in this way could be compacted at low pressures (170÷390 MPa) with high recovery yield of 88÷90% and coalescence degree of 94÷95%. The use of an argon protective atmosphere produced metal that lacked both metallic lustre and spherical shape, contrary to the

case when an oxidizing atmosphere (air) was present during cleaning. The salts after solidification were hard to break. This suggests that during the thermal cleaning process without oxygen, the decomposition of hydrocarbons took place, but residual products of this decomposition could remain on the surface of the chips and passed to molten salt during melting.

Considering the achieved results and observations, an experiment was performed in which thermal cleaning was carried out in two stages. In the first stage, an oxygen-free atmosphere was used to break down the hydrocarbon compounds. In the second stage, air was introduced into the system to remove the flammable residues of thermal decomposition that may have remained on the chip surface. In the second stage, to reduce the oxidation rate of aluminium chips, the temperature was lowered to 350 °C. After cleaning process, the chips were consolidated at a pressure of 170 MPa and melted according to the procedure applied in previous experiments. As a result of this experiment, metal with a spherical shape and a clean, shiny surface was obtained. Salts were not difficult to crush. The calculated metal recovery yield was 94%, while the degree of coalescence was 100%, and these were the highest values of all obtained in the present research. The appearance of the obtained metal and its chemical composition is shown in Figure 11.



Fig. 11 The appearance of the metal after two-stages cleaning of chips and melting and its chemical composition

The most serious disadvantages of this process when carried out under laboratory conditions include the demand for large amounts of salt to ensure a sufficiently high degree of metal coalescence and recovery yield. In this work, recovery yield means the total amount of metal obtained in relation to the mass of the charge (melted compacts). Under industrial conditions, the actual recovery yield is strongly associated with coalescence, because small metallic liquid droplets suspended in molten salt, which do not undergo coalescence and cannot reach the metallic phase at the bottom of the furnace during the entire melting process will cause metal losses. Therefore, in salt melting techniques, the viscosity and density of salts are very important, as results from the well-known Stokes law (Equation (3)).

$$V = \frac{2r^2(\rho_m - \rho_s)g}{9\eta} \quad (3)$$

Where: V -settling velocity ($m \cdot s^{-1}$), r -droplet radius (m), ρ_m -density of the metal ($kg \cdot m^{-3}$), ρ_s -density of the salt ($kg \cdot m^{-3}$), g -gravitational acceleration ($m \cdot s^{-2}$), η -salt viscosity ($kg \cdot m^{-1} \cdot s^{-1}$)
In industrial processes, with each melt, both density and viscosity of the salts increase due to the growing degree of saturation with alumina (and other impurities). Then the salt loses its ability to

coalesce metal and the sedimentation of smaller metallic droplets takes a longer time. When this happens, the salt should be replaced to reduce metal losses. When melting aluminium scrap with a large surface area in relation to volume (foils, chips, filings), it is necessary to use significant amounts of salt, which results in a large amount of the generated waste (salt slag). The solution for metal recovery in the melting process proposed in this research work requires further studies to optimize the process in terms of the amount of the salt used and waste reduction to a minimum. These studies are currently at the stage of development and elaboration of guidelines.

4. Conclusions

The described research was carried out on aluminium scrap, which is currently not subjected to recycling processes by traditional melting methods with the use of salt flux. The laboratory results allowed obtaining high levels of both metal recovery yield and degree of coalescence. However, to obtain the results so promising it was necessary to:

- perform preliminary thermal cleaning operations,
- prepare the material for melting by consolidation,
- apply appropriate parameters of the melting process.

As a result of the conducted tests, it was found that the optimal process of the thermal removal of organic contaminants is a two-stage process with the initial decomposition of hydrocarbons without access of oxygen, followed by oxidation of flammable fractions in the air. Reducing the temperature in the second stage to 350 °C allows reducing the metal oxidation rate and is also beneficial for the safe handling of fine aluminium stocking. Studying the effect of compacting pressure on chips cleaned in an argon atmosphere, it was found that the pressure of 170 MPa was quite sufficient.

The undeniable advantages of the proposed process include:

- high metal recovery yield (up to 94%),
- high degree of coalescence (up to 100%),
- the possibility of metal refining and adjustment of chemical composition,
- obtaining a commercial product with the desired composition.

Acknowledgment

The financial support from the Polish Ministry of Science and Higher Education contract No. 16.16.180.006 is gratefully acknowledged.

References

- [1] Boin, U. & Bertram, M. (2005). Melting Standardized Aluminum Scrap: A Mass Balance Model for Europe. *Journal of Metals*. 7, 26-33. DOI: 10.1007/s11837-005-0164-4.
- [2] Rojas-Díaz, L.M., Verano-Jiménez, L.E., Muñoz-García, E., Esguerra-Arce, J. & Esguerra-Arce, A. (2020). Production and characterization of aluminum powder derived from mechanical saw chips and its processing through powder metallurgy. *Powder Technology*. 360, 301-311. DOI: 10.1016/j.powtec.2019.10.028.
- [3] Kondej, D. & Gawęda, E. (2006). Explosion of metal dust on the example of dust. *Bezpieczeństwo Pracy*. 10, 12-15. (in Polish).
- [4] Wan, B., Chen, W., Lu, T., Liu, F., Jiang, Z. & Mao, M. (2017). Review of solid state recycling of aluminum chips. *Resources, Conservation & Recycling*. 125, 37-47. DOI: 10.1016/j.resconrec.2017.06.004.
- [5] Tahmasbi, K. & Mahmoodi, M. (2018). Evaluation of microstructure and mechanical properties of aluminum AA7022 produced by friction stir extrusion. *Journal of Manufacturing Processes*. 32, 151-159. DOI: 10.1016/j.jmapro.2018.02.008.
- [6] Abd El Aal, M., Taha, M.A., Selmy, A.I., El-Gohry, A.M. & Kim, H.S. (2019). Solid state recycling of aluminium AA6061 alloy chips by hot extrusion. *Materials Research Express*. 6(3), 036525. DOI: 10.1088/2053-1591/aaf6e7.
- [7] Chiba, R. & Yoshimura, M. (2015). Solid-state recycling of aluminium alloy swarf into c-channel by hot extrusion. *Journal of Manufacturing Processes*. 17, 1-8. DOI: 10.1016/j.jmapro.2014.10.002.
- [8] Zhang, T., Ji, Z. & Wu, W. (2011). Effect of extrusion ratio on mechanical and corrosion properties of AZ31B alloys prepared by a solid recycling process, *Materials & Designs*. 32, 2742-2748. DOI: 10.1016/j.matdes.2011.01.012.
- [9] Chiba, R., Nakamura, T. & Kuroda, M. (2011). Solid-state recycling of aluminium alloy swarf through cold profile extrusion and cold rolling. *Journal of Materials Processing Technology*. 211, 1878-1887. DOI: 10.1016/j.jmatprotec.2011.06.010.
- [10] Haase, M. & Tekkaya, A.E. (2015). Cold extrusion of hot extruded aluminum chips. *Journal of Materials Processing Technology*. 217, 356-367. DOI: 10.1016/j.jmatprotec.2014.11.028.
- [11] Gronostajski, J.Z., Kaczmar, J.W., Marciniak, H. & Matuszak, A. (1998). Production of composites from Al and AlMg2 alloy chips. *Journal of Materials Processing Technology*. 300, 37-41. DOI: 10.1016/S0924-0136(97)00390-7.
- [12] Da Costa, C.E., Zapata, W.C. & Parucker, M.L. (2003). Characterization of casting iron powder from recycled swarf. *Journal of Materials Processing Technology*. 143, 138-143. DOI: 10.1016/S0924-0136(03)00394-7.
- [13] Xiao, Y. & Reuter, M.A. (2002). Recycling of Distributed Aluminium Turning Scrap, *Minerals Engineering*, 15, 963-970. DOI: 10.1016/S0892-6875(02)00137-1.
- [14] Leitner, M., Leitner, T., Schmon, A., Aziz, K. & Pottlacher, G. (2017). Thermophysical Properties of Liquid Aluminum. *Metallurgical and Materials Transactions A: Physical Metallurgy and Materials Science*. 48, 1-10. DOI: 10.1007/s11661-017-4053-6.