

Table 3.1 Different types of scrap and potential processing method

Type of scrap	Potential processing method
Light mixed consumer scrap, end-of-life vehicles (ELVs)	Comminution with shredder, subsequent separation with air classifier, magnetic separator and handpicking
Waste of electric and electronic equipment (WEEE)	Comminution with hammer mill, subsequent separation with air classifier, magnetic separator and other equipment
Cable scrap	Comminution with rotor shears and granulators, subsequent separation with air tables and other equipment
Ash from waste incineration including ferrous and non-ferrous metals	Classifying with screens, comminution with shredder, subsequent separation of metals
Mixed stainless steel scrap	Comminution with hydraulic shear or shredder, subsequent separation of metals
Intermediate metal products from waste sorting plants	Comminution with hammer mill, subsequent separation with magnetic and eddy current separators and other equipment
Sheet metals and residues of stamping	Compaction with scrap press
Ferrous- and non-ferrous turnings	Comminution with turnings crusher, subsequent separation of cutting fluids with centrifuge, magnetic separator
Heavy scrap with wall thicknesses up to 150 mm	Comminution with hydraulic scrap shear, where necessary with subsequent screening of fines
Heavy scrap with wall thicknesses more than 150 mm	Comminution with flame cutting or blasting
Cast iron scrap	Comminution with vertical drop work

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3.1 Aluminium-Based Waste

In recent years, the processing of aluminium scrap (mainly chips and used drink cans) has attracted increasing attention. Aluminium scrap has a complex chemical composition based on aluminium (>90%). Magnesium, zinc, silicon, iron, etc. are the main impurities. Sources of impurities are the composition of the alloy for producing drink cans (mainly, Al-Mg alloy containing up to 3–4% Mg) and mechanical impurities that enter into the scrap due to inefficient sorting, classification and storage of the scrap (Gopienko 2019). Recycling of aluminium also leaves behind a solid waste (Shinzato and Hypolito 2005), which keeps this research field still active looking for more environmentally friendly alternatives.

Another Al-based material is aluminium dross, a by-product of the aluminium smelting process. This material can be mechanically recycled to separate the residual

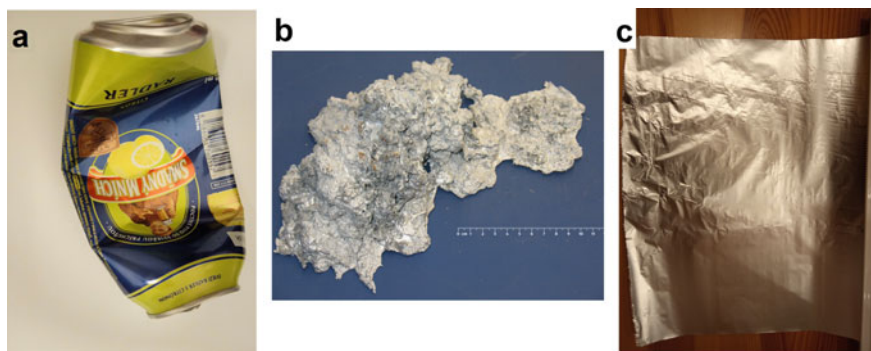


Fig. 3.1 Examples of aluminium waste which can be recycled using high-energy ball milling: **a** can, **b** dross and **c** foil

aluminium metal from the aluminium oxide (Mahinroosta and Allahverdi 2018; Meshram and Singh 2018).

However, as it will be demonstrated in this chapter, the most intensively studied aluminium waste with regards to the ball milling process are the aluminium foils. Aluminium foil is typically less than 150 μm thick. Foils are available in gauges as thin as 6.3 μm . Heavier foil gauges ($>17 \mu\text{m}$) provide an absolute barrier to gases and liquids (Kerry 2012), which is mainly applied in flexible packaging (Morris 2017). Upon termination of its use, recycling processes, including high-energy ball milling, can be applied.

The photographs of waste Al can, dross and foil can be seen in Fig. 3.1.

3.1.1 Aluminium Foil

Waste aluminium foil scrap was subjected to ball milling to recycle it into a powder suitable for the fingerprint detection in (Hong et al. 2000). Milling brought about reduction of particle size and a significant increase in specific surface area. Milling was realized under argon; however, 8% of oxygen was present in order to prevent explosion upon contact with air after milling. The changes in the morphology with milling are demonstrated in Fig. 3.2.

The effect of size of milling balls was also investigated. Larger balls created larger impact and the particle size was decreasing more rapidly in the first stages in this case (Fig. 3.3).

The effect of breaks between the milling cycles during the treatment was found to be beneficial in this case, as the cooling period provided a less ductile behaviour of the produced material. This is well-demonstrated by the comparison of SEM images of the aluminium flake powder treated under the same conditions with and without breaks (Fig. 3.4).

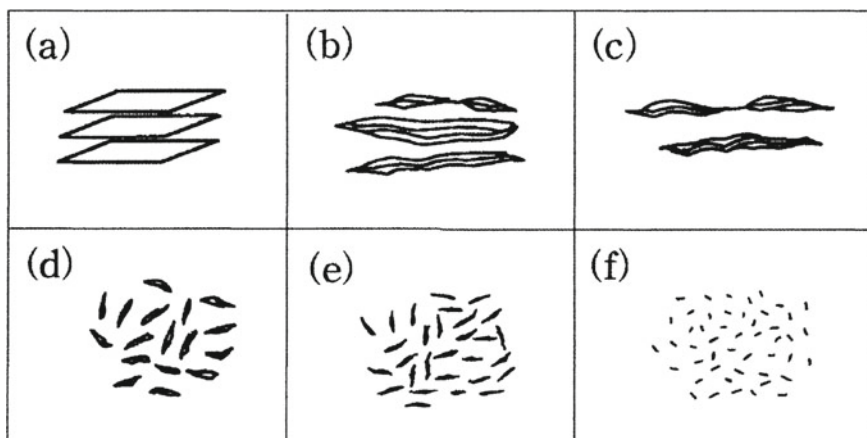


Fig. 3.2 Changes in morphology of aluminium flake from aluminium foil with the progress of milling procedure: **a** cut foil, **b** laminated and micro-forged foil, **c** a local crack in the foil, **d** coarse flake powder, **e** fine flake powder and **f** very fine flake powder. Reprinted from (Hong et al. 2000), Copyright (2000), with permission from Elsevier

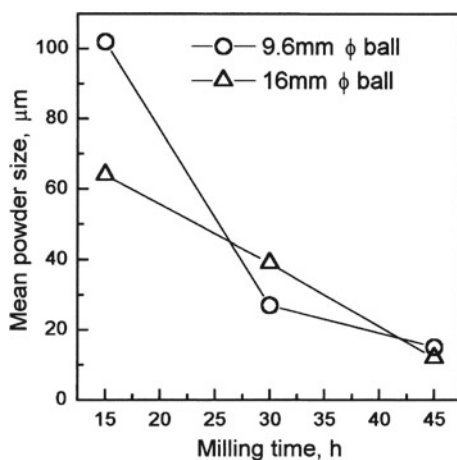


Fig. 3.3 Effect of the milling balls size on the mean powder particles size in the during ball milling of aluminium foil. Reprinted from (Hong et al. 2000). Copyright (2000), with permission from Elsevier

Also the effect of addition of various amounts of stearic acid was tested. It was found that the finest powder can be produced upon the introduction of 3% of stearic acid.

The potential application of the studied materials is in the detection of human fingerprints; however, it was found that too fine powder is not suitable because of not efficient adhesion on the fingerprint line.

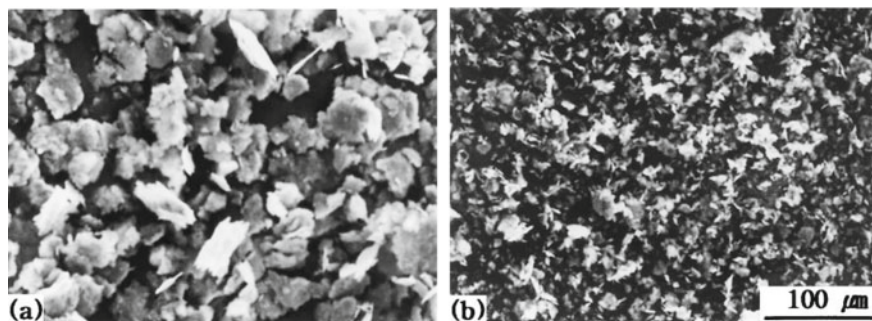


Fig. 3.4 SEM micrographs of ball milled aluminium powder with a different number of breaks: **a** 0 and **b** 3. The scale bar is most probably the same for both images but unfortunately, the authors did not provide the scale bar in part (a). Reprinted from (Hong et al. 2000). Copyright (2000), with permission from Elsevier

Quite similar topic is covered in (Hong and Kim 2001); however, this time the effect of the foil thickness is investigated. The utilization of thinner foils results in lower particle size at the end of the treatment. The addition of oleic acid as a grinding aid in different amounts resulted in the improvement of performance. The addition of 5% (the highest content tested) led to the best results. Again, the effect of milling balls was investigated, leading to a slightly lower particle size upon the use of larger balls (Fig. 3.5).

The targeted application of the prepared material was its use as a pigment for car paint. This ability was measured by checking the gloss. When the amount of the Al paste prepared from Al foil was up to 5%, the performance was improved, due to

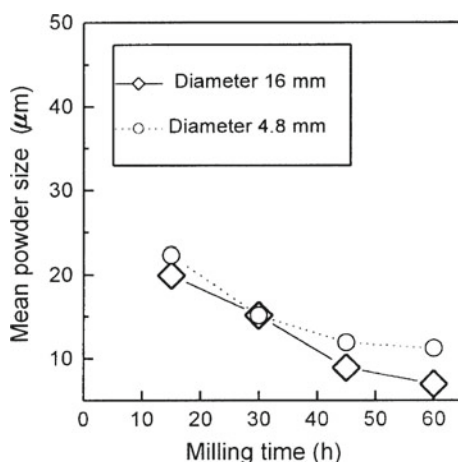


Fig. 3.5 Effect of milling balls size on the mean powder particles size during the wet ball milling of aluminium foil. Reprinted from (Hong and Kim 2001), Copyright (2001), with permission from Elsevier

high reflectivity of the produced powder. If more than 5% was introduced, the gloss decreased dramatically due to diffuse reflection of light, and the performance was even worse than for the aluminium paste-free paint.

Waste Al foil of different thickness was subjected to ball milling in (Swamy and Shafirovich 2013a). The design of the experiment was to use three 10 min cycles and to apply smaller milling balls in each subsequent cycle to ensure the most efficient particle size reduction. NaCl was used as an admixture, and subsequently, water splitting reaction producing hydrogen was observed. The effect of initial particle size and the temperature of the water splitting reaction was investigated in detail. The best results (93% reaction progress) have been achieved at 80 °C when performing the experiment with Al/NaCl mixture. The activation energy of water splitting reaction was calculated to be 53.3 kJ/mol. In comparison with previous studies, time of milling was reduced, and the process did not require any other additives like stearic or oleic acid.

The same methodology was used in a follow-up study (Swamy and Shafirovich 2014). The first step was ball milling of the Al scrap with NaCl. Also the pure Al powder was used. The produced powders were then extensively studied for the reaction with water (the effect of particle size and temperature was investigated), and it was found that they chemically split water and release hydrogen, on the contrary to the generally known phenomenon that Al cannot react with water due to its passivation. Boehmite (γ -AlO(OH)) was detected in the solid residue after the treatment at higher temperatures, whereas its combination with bayerite α -Al(OH)₃ was observed after processing at lower ones. As the authors performed the experiments at various temperatures, they were able to apply the Arrhenius plot and calculate the activation energy of this reaction (63 kJ/mol). Finally, the authors performed the combustion reaction with the ball-milled foil, so basically, the same reaction which was monitored in solution was ignited, and the explosive reaction with front propagation was observed. The content of Al in the sample had to be at least 40 wt% for the combustion reaction to start. The propagation of the reaction front can be well seen in Fig. 3.6. The reaction product was mainly Al₂O₃.

The authors were capable of turning waste Al foil into a very reactive material utilizable for various purposes.

3.1.2 Other Al-Based Waste

The cryo-milling, together with the processes of cold pressing and hot extrusion, was applied for the treatment of waste aluminium chips, which were co-milled with aluminium and fly ash, in order to create the composite material with good mechanical properties in (Vatansever et al. 2011). The focus was also on the influence of particle size of fly ash on the mechanical properties. In general, the coarser particles resulted in the better effect.

Aluminium dross was first sintered to produce α -alumina and subsequently ball milled in water both in the presence and the absence of surfactant sodium lauryl

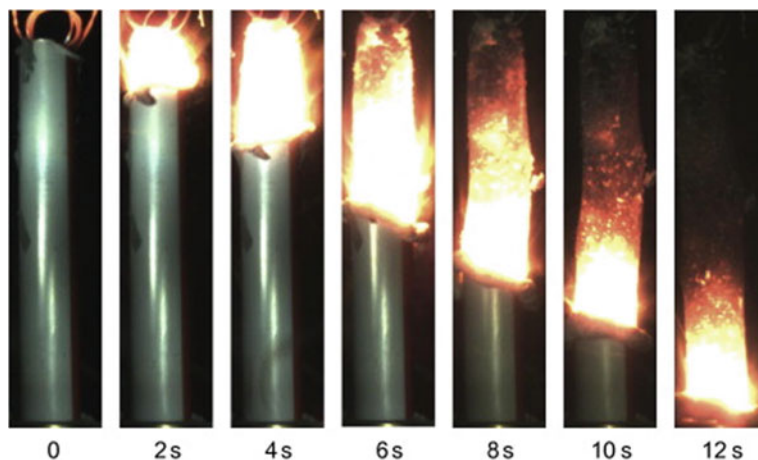


Fig. 3.6 Propagation of the combustion front over Al (obtained from ball-milled foil)/H₂O mixture at 40 wt% Al. Reprinted from (Swamy and Shafirovich 2014), Copyright (2014), with permission from Elsevier

sulphate (SLS) in (Meor et al. 2012). The presence of surfactant led to slightly smaller particle and crystallite size in comparison with surfactant-free milling.

Al-Si waste from hot dip aluminizing significantly contaminated by iron was used for mechanical machining and subsequently for spark plasma sintering in (Kučera and Dalibor 2018). When the ball milling process was included before the SPS treatment, the compressive strength was significantly increased; however, the plastic deformation was absent, and thus, low ductility was observed. The aim of the paper was to show that the waste material can be effectively turned into something useful by using mechanical machining, without utilizing the conventional casting technologies.

The mechanochemical treatment of Al waste cans for the production of hydrogen from water was pursued in (Ho and Huang 2016). In this study, the planetary ball milling, roll ball milling and hand grinding were compared. The comparative tests were performed with the commercial Al powder, and as planetary ball milling has shown to be the most effective method, this was used for the treatment of waste cans. The milling was conducted in the presence of NaCl. The specific surface area analysis (both S_{BET} and N_2 adsorption isotherms) documenting the effect of activation is provided in the study. The planetary ball milling yielded the S_{BET} value $1.7 \text{ m}^2/\text{g}$ for milled Al cans, which was almost two times lower than in the case of planetary ball-milled Al powder (in that case, the S_{BET} value $3.18 \text{ m}^2/\text{g}$ was evidenced) (Fig. 3.7). The material treated by other methods showed very small values. The presence of the hysteresis loops in the isotherms of planetary milled samples proves the presence of mesopores.

To demonstrate the effect of hydrogen generation properties of waste Al cans, Fig. 3.8 is provided. It can be seen that complete yield can be achieved in all cases (the

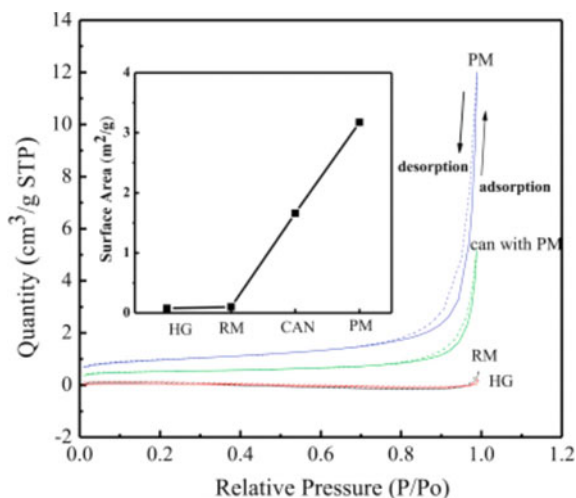


Fig. 3.7 Nitrogen adsorption-desorption isotherms of Al powder and Al can treated by various mechanical milling methods (PM—planetary ball milling, RM—roll ball milling, HG—hand grinding), specific surface area values are given in inset. Reprinted from (Ho and Huang 2016), Copyright (2016), with permission from Elsevier

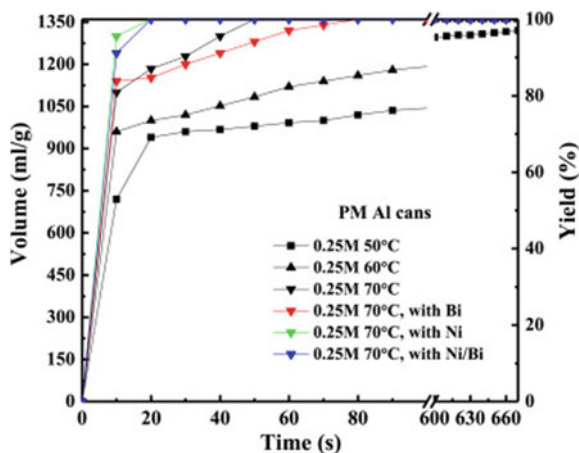


Fig. 3.8 Hydrogen generation ability of the ball-milled Al cans: effect of temperature and additives. Reprinted from (Ho and Huang 2016), Copyright (2016), with permission from Elsevier

authors studied various parameters—NaOH concentration, temperature and addition of nickel and bismuth powders).

It was found that waste Al scrap combined with Ni and/or Bi in NaCl mixtures and exposed to planetary ball milling could effectively react with water in mild alkaline solution at 70 °C with initial hydrogen generation rate 30 ml s⁻¹ g⁻¹ and complete

hydrogen release. The alkaline conditions need to be mild, as the corrosion process takes place at higher concentrations of NaOH.

Aluminium buffing (finishing process during which cloth wheels with compound applied are used) dust was co-milled with kaolin in different ratios and subsequently sintered at high temperature in order to prepare mullite ($3\text{Al}_2\text{O}_3 \times 2\text{SiO}_2$), improve the mechanical properties and use low-cost raw materials in (Kongkajun et al. 2019). The optimum composition was 60% dust, and 40% kaolin, as the highest bulk density and bending strength, being 2.71 g/cm^3 and 60 MPa, respectively, was achieved. Mullite was detected as a major phase in the XRD pattern of this sample.

In a study (Kirsever et al. 2015), ball milling was applied for the treatment of secondary aluminium production waste with the aim to produce mullite refractory ceramics. The waste material was co-milled with kaoline and quartz, and the effect of subsequent sintering time and temperature on the bulk density, apparent porosity and crystallization of produced mullite was investigated. The desired phase was successfully formed, and the best results were obtained upon the application of the longest sintering times and the highest temperatures.

The AA2024 (Al-based) alloy chips were milled in the presence of stearic acid as process control agent (PCA) in (Rofman et al. 2019). The PCA was added at a different time during milling (at the start, after 10 min or after 30 min). The overall milling time was 100 min, and the experiment without PCA was also performed. The morphology of the produced powders can be seen in Fig. 3.9.

When the PCA was not present, quite large agglomerates were formed (Fig. 3.9a–c). The early addition of PCA resulted in prolonging the first stage of particle size reduction (Fig. 3.9d–f), which is expressed by the formation of smaller particles on the larger ones. The powder with smaller amount of defects, flake-like structure and the lowest bulk density was formed upon the addition of PCA after 30 min (Fig. 3.9g–j). This is the most suitable option for the particular task. If PCA is present from the start (Fig. 3.9k–m), some particles remain unmilled, and the morphology of the produced powder is inhomogeneous.

The XRD patterns did not show any significant differences, and mainly, reflections corresponding to Al, with trace amounts of its alloys with Cu and Mg and Al_2O_3 , were observed. At the end, the hardness was investigated, showing that milling brought about an improvement.

Further reading on mechanochemical treatment of aluminium-based metallic waste: (Itkin 1986; Fair et al. 1987; Tachi et al. 1996; Antsiferov et al. 2002; Hong and Kim 2002; Dorofeev et al. 2003; Araujo and Tenorio 2005; Coelho et al. 2008; Susniak et al. 2013; Swamy and Shafirovich 2013b; Coelho et al. 2014; Jafari et al. 2014; Kubota and Watanabe 2014; Antolak-Dudka et al. 2016; Uzun and Durmus 2016; Kadir et al. 2017; Kučera et al. 2017; Oliveira and Coelho 2017; Yao et al. 2017; Gatamorta et al. 2018; Nguyen et al. 2018; Guerrero-Ortiz et al. 2019; Katundi et al. 2019; Lopez et al. 2019; Nguyen and Lee 2019a, b; Yusssoff et al. 2019).

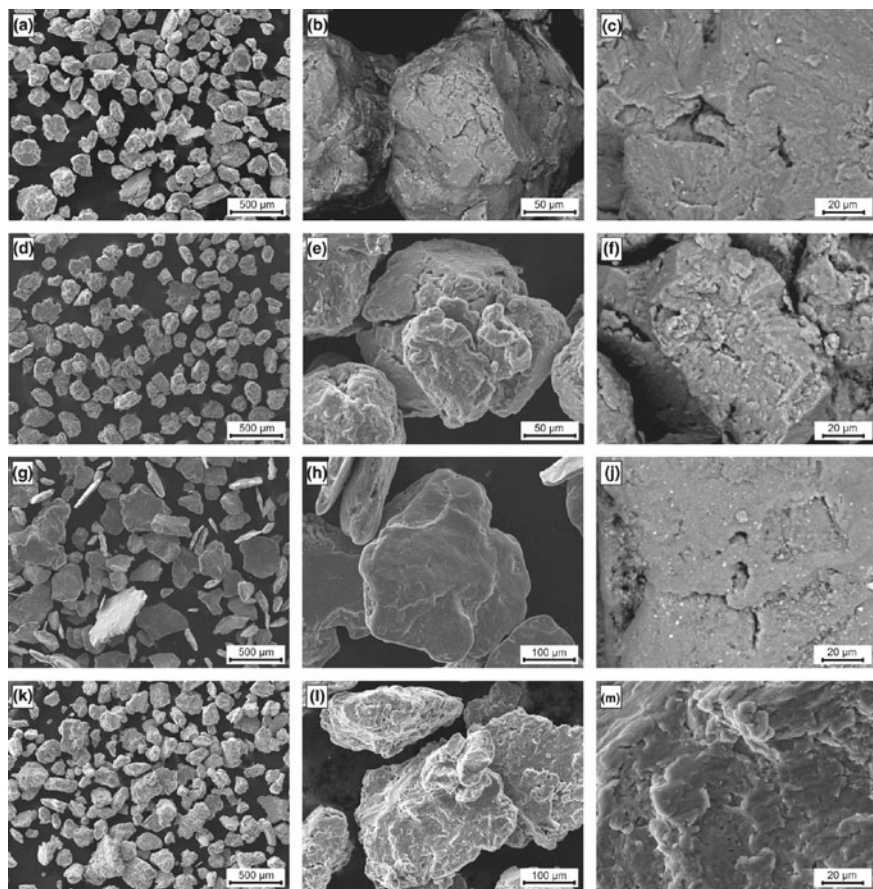


Fig. 3.9 SEM micrographs of powders taken at different magnifications for the following milling regimes: **a–c** 100 min (regime 1), **d–f** 10 min + PCA + 90 min (regime 2), **g, h, j** 30 min + PCA + 70 min (regime 3), **k–m** PCA + 100 min (regime 4). Reprinted by permission from Springer Nature Customer Service Centre GmbH: Springer Nature (Rofman et al. 2019), Copyright (2019)

3.2 Magnesium-Based Waste

Metallic waste based on magnesium most often concerns magnesium-based alloy chips.

Figen et al. (2015) utilized Mg waste for the hydrogen release application. Ball milling was applied for different times, and the physicochemical properties of the waste were investigated. The optimum milling time was found to be 15 h. This sample was then used for hydrogen generation tests. In pure water, no hydrogen formation was observed, whereas upon the addition of activator (various metal chlorides), the hydrogen release was significant. The best results were obtained for NiCl_2 and MnCl_2 .