Conventional recycling techniques generate hazardous residue that usually requires disposal at a high cost. Aluminium slags contain MgAl\(_2\)O\(_4\), Al\(_2\)O\(_3\)-FeO, calcium oxides, AlN, quartz (SiO\(_2\)), α-Al\(_2\)O\(_3\), periclase (MgO), spinel (Mg, Si)Al\(_2\)O\(_4\), chlorides (AlCl\(_3\), NaCl, KCl), fluorides (CaF\(_2\), NaF, AlF\(_3\), Na\(_3\)AlF\(_6\), etc.), carbides (Al\(_4\)C\(_3\)), sulphides (AlS\(_2\), FeSO\(_4\)), phosphors, impurities, apart from metallic aluminium (between 80% and 20%). By washing them with hot water the AlN compound can be transformed into Al(OH)\(_3\), which, in reaction with Na and K leads to the possibility of using aluminium white slag to obtain a refractory material - High-alumina refractory (HAR), with the main crystalline phase Al\(_2\)O\(_3\), and traces of MgAl\(_2\)O\(_4\), CaAl\(_2\)O\(_4\), by replacing the materials currently used. They can be used in the production of ceramics, cement, in the construction of furnaces used in the metallurgy of non-ferrous metals, the machine building industry and the defence industry, extending also in space and nuclear engineering [5, 6, 11].

The production of α-alumina has also been studied to avoid environmental pollution and to obtain a material with special properties. The main advantages of this new material are corrosion resistance, thermal shock resistance, thermal stability and good refractory properties. Another great advantage is the lack of the need to store it, thus avoiding the pollution of the groundwater [7].

Experimental part

The raw material used in the experiments is aluminium chips, unprocessed, in accordance with national and international standards. This material is classified as conforming SR EN 13920-12 or 13, equivalent to ISRI TEENS (fig. 1) or TELIC (fig. 2) notations and consists of aluminium borings and turnings of one or two or more alloys (TELIC - the material must be clean, uncorroded aluminium borings and turnings of two or more alloys and subject to deductions for fines in excess of 3% through a 20 mesh screen and dirt, free iron, oil, moisture and all other non-metallic elements), or derived from two or more alloys (TELIC - the material must be clean, uncorroded aluminium borings and turnings of two or more alloys and subject to deductions for fines in excess of 3% through a 20 mesh screen and dirt, free iron, oil, moisture and all other non-metallic elements) [18].

This type of material does not always meet moisture or impurity requirements. This paper proposes a high humidity aluminium metallic scraps processing technology, with low values in terms of combustion losses-taking into account the dimensions of the particles.

In this study, it is intended to reintroduce into the industrial circuit small metallic waste (scraps) with high humidity in order to obtain a secondary standardized alloy. The removal of impurities from the melt will be done through fluxing treatment.
The aluminium scraps used in the experiments were analysed by diffraction (fig. 3, 4) to highlight its composition. Since the humidity in the material is very high, the results obtained (in percent) are not conclusive.

By combustion of methane gas in room-type furnaces, the flue gases come in direct contact with the raw material for preheating, heating and melting. Following the reactions that take place [16] mainly, the following reaction products are produced: CO, CO₂, H₂ and H₂O. These gases, together with combustion oxygen, interact with the materials that form the charge, leading to the formation of a significant amount of slag, i.e. significant losses through oxidation.

In this article, the authors propose the processing of aluminium alloy castings to obtain low-temperature secondary alloy EN AB 46100 to reduce batch/load oxidation.

The choice of temperature was made based on the data from speciality literature (table 1) [17] but also of its own experiments.

### Table 1

| Alloy   | Si     | Cu     | Fe      | Mg      | Zn      | Rest. total | Al      | T Eutectic, °C |
|---------|--------|--------|---------|---------|---------|-------------|---------|---------------|
| AA 319.0| 5.5 – 6.5% | 3.0 – 4.0% | <= 1.0% | <= 0.1% | <= 1.0% | <= 1.60% | 85.8 – 89.9% | 562.3 (±2.3) |
| AA 332.0| 8.8 – 10.5% | 2.0 – 4.0% | <= 1.2% | <= 0.50% | <= 1.0% | <= 0.50% | 80.1 – 81.8% | 577.4 (±6)   |
| AA 333.0| 8.0 – 10%   | 3.0 – 4.0% | <= 1.0% | <= 0.05% | <= 1.0% | <= 0.50% | 81.8 – 89%  | 560.5 (±4)   |
| AA 383.0| 9.3 – 11.5% | 3.0 – 4.0% | <= 1.3% | <= 0.10% | <= 3.0% | <= 0.50% | 79.7 – 58.5% | 566.5 (±2.2) |
| AA 384.0| 10.8 – 12%  | 3.0 – 4.5% | <= 1.3% | <= 0.10% | <= 3.0% | <= 0.50% | 77.3 – 56.5% | 561.3 (±2.2) |
Based on the data in table 1 but also on our own experiments (EN AB 46100, 10.75% Si, 1.81% Cu, 1.34% Zn, 0.93% Fe, Teut = 568°C) it has been chosen that the working temperature, the temperature of the semisolid/pasty metal material in the furnace, should fall within the limits of 580 ÷ 620°C.

The experiment took place at SC AS Metal SRL, on a 16-tonne furnace equipped with the oxy-fuel system. Flue gas samples were taken at different points in the process with DELTA 2000-IV apparatus, as can be seen from table 2.

Low-temperature processing reduces losses of oxidation for both aluminium and other metallic elements in the scraps composition by incorporating it into the semi-solid/pasty melt. The subsequent overheating of the melt leads to an advanced assimilation of the scraps into the molten metal mass.

After the loading of each batch, the volatiles and the moisture in the chips/scraps evaporated after the contact with the hot bath and the remainder of the material was homogenized with the melt resulting in a viscous bath having a temperature of about 620°C.

| T-Gas | 783.1 | 574.2 | 483.2 | 680.4 | 580.1 | 690.7 | 760.3 | 787.2 | 770 | 821.6°C |
|-------|-------|-------|-------|-------|-------|-------|-------|-------|-----|--------|
| T-Amb | 38    | 32.4  | 37.6  | 39.1  | 37.9  | 31.4  | 37.4  | 38.1  | 30.9| 31.7°C |
| O2    | 5.7   | 16.4  | 20.4  | 15.1  | 19.4  | 18.1  | 15.1  | 10.1  | 21  | 4.7%   |
| CO2   | 8.9   | 2.7   | 0.3   | 3.4   | 0.9   | 1.7   | 3.4   | 6.3   | 0   | 9.5%   |
| Losses| 37.7  | 70.1  | 99.9  | 75.5  | 99.9  | 98.9  | 85.2  | 50.7  | -  | 37.3%  |
| Effic | 62.3  | 20.9  | 0.1   | 24.5  | 0.1   | 0.1   | 14.8  | 49.3  | -  | 62.2%  |

| CO/m³ | 2     | 1255  | 286   | 687   | 923   | 586   | 299   | 656   | 210| 839mg |
| NO/m³ | 9     | 3     | 0     | 4     | 0     | 0     | 4     | 5     | 7  | 8mg |
| NOx/m³| 14    | 4     | 0     | 6     | 0     | 0     | 6     | 8     | 10 | 12mg |
| SO2/m³| 0     | 2257  | 206   | 1396  | 1973  | 549   | 189   | 569   | 149| 194mg |
| Stage | 1     | 2     | 3     | 4     | 5     | 6     | 7     | 8     | 9  | 10 |

Remarks:
1. Burners on + closed door before loading;
2. Burners on + open door + loading;
3. Burners off + closed door after loading;
4. Burners on + open door + mixing;
5. Burners off + closed door after loading;
6. Burners on + open door + mixing;
7. Burners on + closed door after loading.
8. Burners on + closed door after loading;
9. Burners on + additional oxygen + closed door;
10. Burners on + closed door.

Table 2
THE CHEMICAL COMPOSITION OF THE FLUE GASES DURING THE EXPERIMENTS

Result and discussions
From the thermodynamic studies of the reactions that can occur between the metal bath/chips and the reaction products between methane gas and oxygen, given the chemical composition of the secondary alloy studied, we have selected the following reactions as very probable.

\[
\begin{align*}
2\text{Al} + 3\text{H}_2\text{O}(g) &= \text{Al}_2\text{O}_3 + 3\text{H}_2(g) \quad (1) \\
2\text{Al} + 3\text{CO}_2(g) &= \text{Al}_2\text{O}_3 + 3\text{CO}(g) \quad (2) \\
2\text{Al} + 1.5\text{O}_2(g) &= \text{Al}_2\text{O}_3 \\n2\text{Mg} + \text{O}_2(g) &= 2\text{MgO} \quad (3) \\
2\text{Mn} + \text{O}_2(g) &= 2\text{MnO} \quad (4) \\
2\text{Mg} + \text{O}_2(g) &= 2\text{MgO} \\
2\text{Al} + 1.5\text{O}_2(g) &= \text{Al}_2\text{O}_3
\end{align*}
\]

Another category of reactions that may occur are those with the formation of complex compounds, between the aluminum oxides and the metal oxides in groups 1 and 2 of the Mendeleev Table (spinel), as can be deduced from the electron microscopy analysis and the EDS analysis presented in figure 5.

Fig. 5. Electron microscopy analysis (a) and EDS analysis with the chemical composition of the filiform compounds (b) and fragmented gray compounds (c)
2Al₂O₃ + 2Mg + O₂(g) = 2MgAl₂O₄(ia)   (6)
Ca + 2Al + 2O₂(g) = CaAl₂O₄(ia)   (7)
Ca + 2Al + 4CO₂(g) = CaAl₂O₄(ia) + 4CO(g)   (8)
Mg + 2Al + 4CO₂(g) = MgAl₂O₄(ia) + 4CO(g)   (9)

**Activation energies of the reactions**

The dependencies of the speed constants of the temperature reactions (1) ÷ (5) are represented in figures 6-10 and can be calculated with Arrhenius’s equation:

\[ K = A \exp\left(-\frac{Q}{RT}\right) \]  (10)

where:
- \( A \) represents the frequency factor;
- \( Q \) is the activation energy of the reaction, kJ/mol;
- \( R \) is the universal gas constant;
- \( T \) is the absolute temperature, K.

By logarithm, it results:

\[ \ln K = \ln A + \left(\frac{1}{T}\right)(-Q/R) \]  (11)

The variation of the speed constant parameters in relation to temperature for each reaction is shown in tables (3-7).

### Table 3

| T, K    | ΔG, kJ | k      | ln k   | 1/T, K⁻¹ | 1/T*10⁴, K⁻¹ |
|---------|--------|--------|--------|-----------|--------------|
| 823.15K | -110.404 | 2.692E+051 | 118.422 | 0.00121485 | 1.21485      |
| 843.15K | -107.409 | 1.054E+050 | 115.186 | 0.00115603 | 1.18603      |
| 863.15K | -104.428 | 4.843E+048 | 112.102 | 0.00113585 | 1.15855      |
| 883.15K | -101.401 | 2.535E+047 | 109.159 | 0.00111531 | 1.13231      |
| 903.15K | -98.505  | 1.535E+046 | 106.348 | 0.00110724 | 1.10724      |
| 923.15K | -795.561 | 1.045E+045 | 103.690 | 0.00108325 | 1.08325      |
| 943.15K | -792.402 | 7.752E+043 | 101.059 | 0.00106028 | 1.06028      |
| 963.15K | -789.203 | 6.234E+042 | 98.539  | 0.00103826 | 1.03826      |
| 983.15K | -786.535 | 5.562E+041 | 96.122  | 0.00101714 | 1.01714      |

### Table 4

| T, K    | ΔG, kJ | k      | ln k   | 1/T, K⁻¹ | 1/T*10⁴, K⁻¹ |
|---------|--------|--------|--------|-----------|--------------|
| 823.15K | -823.859 | 6.023E+049 | 114.622 | 0.00121485 | 1.21485      |
| 843.15K | -823.864 | 3.464E+048 | 111.767 | 0.00115603 | 1.18603      |
| 863.15K | -823.948 | 2.274E+047 | 109.043 | 0.00113585 | 1.15855      |
| 883.15K | -824.181 | 1.688E+046 | 106.443 | 0.00111531 | 1.13231      |
| 903.15K | -824.105 | 1.406E+045 | 103.957 | 0.00110724 | 1.10724      |
| 923.15K | -824.212 | 1.304E+044 | 101.759 | 0.00108325 | 1.08325      |
| 943.15K | -845.717 | 1.299E+043 | 99.273  | 0.00106028 | 1.06028      |
| 963.15K | -845.760 | 1.383E+042 | 97.033  | 0.00103826 | 1.03826      |
| 983.15K | -845.803 | 1.613E+041 | 94.884  | 0.00101714 | 1.01714      |

![Fig. 6. Dependence of the speed constants of the temperature reaction 1 for the two intervals: a) 823.15 - 903.15 K; b) 903.15 - 983.15 K](image_a)

![Fig. 7. Dependence of the speed constants of the temperature reaction 2 for the two intervals: a) 823.15 - 903.15 K; b) 903.15 - 983.15 K](image_b)
**Table 5**

VARIATION OF THERMODYNAMIC PARAMETERS BY TEMPERATURE FOR REACTION 3

| T, K | ΔG, kJ | k   | ln k | 1/T, K⁻¹ | 1/T×10⁵, K⁻¹ |
|------|--------|-----|------|-----------|---------------|
| 823.150 | -1417.438 | 8.99E+089 | 207.126 | 0.00121485 | 1.21485       |
| 843.150 | -1411.220 | 2.72E+087  | 201.326 | 0.0018803 | 1.18603       |
| 863.150 | -1405.006 | 1.07E+085  | 195.795 | 0.0015855 | 1.15855       |
| 883.150 | -1398.794 | 3.49E+082  | 190.315 | 0.0013231 | 1.13231       |
| 903.150 | -1392.585 | 5.55E+080  | 185.469 | 0.0010724 | 1.10724       |
| 923.150 | -1386.378 | 2.82E+078  | 180.642 | 0.0010628 | 1.06628       |
| 943.150 | -1379.947 | 2.70E+076  | 175.992 | 0.0010628 | 1.06628       |
| 963.150 | -1373.286 | 3.04E+074  | 171.505 | 0.0010826 | 1.03826       |
| 983.150 | -1366.629 | 4.12E+072  | 167.202 | 0.0010714 | 1.01714       |

**Table 6**

VARIATION OF THERMODYNAMIC PARAMETERS BY TEMPERATURE FOR REACTION 4

| T, K | ΔG, kJ | k   | ln k | 1/T, K⁻¹ | 1/T×10⁵, K⁻¹ |
|------|--------|-----|------|-----------|---------------|
| 823.150 | -1025.971 | 1.290E+065 | 149.922 | 0.00121485 | 1.21485       |
| 843.150 | -1021.719 | 2.007E+063 | 145.760 | 0.0018803 | 1.18603       |
| 863.150 | -1017.469 | 3.790E+061 | 141.790 | 0.0015855 | 1.15855       |
| 883.150 | -1013.220 | 5.56E+059  | 138.000 | 0.0013231 | 1.13231       |
| 903.150 | -1008.873 | 2.290E+058 | 134.279 | 0.0010724 | 1.10724       |
| 923.150 | -1004.723 | 7.102E+056 | 130.914 | 0.0010826 | 1.08326       |
| 943.150 | -1000.109 | 2.476E+055 | 127.549 | 0.0010628 | 1.06628       |
| 963.150 | -995.493  | 9.845E+053 | 124.324 | 0.0010826 | 1.03826       |
| 983.150 | -990.877  | 4.462E+052 | 121.230 | 0.0010714 | 1.01714       |

**Fig. 8.** Dependence of the speed constants of the temperature reaction 3 for the two intervals: a) 823.15 - 903.15 K; b) 903.15 - 983.15 K

**Fig. 9.** Dependence of the speed constants of the temperature reaction 4 for the two intervals: a) 823.15 - 903.15 K; b) 903.15 - 983.15 K
For reactions (1) ÷ (5), for temperature ranges, 823.15 - 903.15 K (550 - 630°C) and 903.15 - 983.15 K (630 - 710°C), result in the following values for the frequency factors (A) and activation energies (Q) (table 8).

Table 7
VARIATION OF THERMODYNAMIC PARAMETERS BY TEMPERATURE FOR REACTION 5

| T, K    | ΔG, kJ  | k   | ln k  | 1/T, K⁻¹ | 1/T×10⁸, K⁻¹ |
|---------|---------|-----|-------|-----------|--------------|
| 823.15  | -548.504| 1.452E+04| 94.779| 0.00121485| 1.21485      |
| 843.15  | -545.702| 1.013E+04| 92.117| 0.00118603| 1.18603      |
| 863.15  | -542.800| 8.001E+03| 89.578| 0.00115855| 1.15855      |
| 883.15  | -539.393| 7.088E+03| 87.154| 0.00113331| 1.13331      |
| 903.15  | -536.998| 6.991E+03| 84.838| 0.00110724| 1.10724      |
| 923.15  | -534.097| 7.624E+03| 82.622| 0.00108125| 1.08125      |
| 943.15  | -531.197| 8.125E+03| 80.500| 0.00106028| 1.06028      |
| 963.15  | -528.296| 1.159E+03| 78.466| 0.00103826| 1.03826      |
| 983.15  | -525.375| 1.609E+03| 76.513| 0.00101714| 1.01714      |

For reactions (1) ÷ (5), for temperature ranges, 823.15 - 903.15 K (550 - 630°C) and 903.15 - 983.15 K (630 - 710°C), result in the following values for the frequency factors (A) and activation energies (Q) (table 8).

Table 8
VARIATION OF ACTIVATION ENERGIES (Q) FOR THE REACTIONS (1) ÷ (5)

| Reaction | Temperature, K | ln A   | A     | Q/R | Q, kJ/mol |
|----------|----------------|--------|-------|-----|-----------|
| 1        | 823.15 - 903.15| 112.2  | 4.720283| -17.89| 0.148746  |
| 2        | 903.15 - 983.15| 113.3  | 4.731002| -19.35| 0.160958  |
| 3        | 823.15 - 903.15| 99.1   | 4.798129| -5.779| 0.045094  |
| 4        | 903.15 - 983.15| 100.7  | 4.812145| -7.581| 0.073032  |
| 5        | 823.15 - 903.15| 201.2  | 5.204399| -37.26| 0.316030  |
| 6        | 903.15 - 983.15| 202.8  | 5.212220| -39.08| 0.327764  |
| 7        | 823.15 - 903.15| 144.4  | 4.972587| -25.55| 0.212435  |
| 8        | 903.15 - 983.15| 146.0  | 4.983596| -27.29| 0.226302  |

For reactions (1) ÷ (5), values of free enthalpy (Gibbs energy) have very high values in absolute value, which means that all these reactions take place from left to right (for example, at a temperature of 610°C / 883.15 K: ΔG₁ = - 801.461 kJ, ΔG₂ = - 824.018 kJ and ΔG₃ = - 1398.794 kJ). The reaction activation energy (Q) exhibits higher values for the 630 ÷ 710°C / 903.15 - 983.15 K temperature range, than the 550 ÷ 630°C / 823.15 - 903.15 K interval. The phenomenon that occurs and leads to an increase in activation energy is oxidation of the scrap surface, a phenomenon which subsequently leads to an increase in the amount of slag resulting in the production of secondary alloys with aluminium base, using small waste.

Conclusions
The processing of small metallic waste at high temperatures leads to significant losses of both aluminum as well as the metals that are part of the secondary alloys. The losses are even higher as the quality of the materials used is lower.

The proposed technology consists of processing the small waste at low temperatures (580 ÷ 620°C / 853.15 - 893.15 K for the EN AB 46100 alloy), temperatures near the eutectic temperature of the said alloy.

Using an intermediate step in the technological process -oxygen only feeds, stage after loading the furnace with a new amount of waste, leads to the reduction of natural gas consumption by burning volatile substances from pre-heating waste composition.

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