Technical Sciences
Academy of Romania
www.jesi.astr.ro

**Journal of Engineering Sciences and Innovation**
Volume 6, Issue 2 / 2021, pp. 137-146

**B. Chemical Engineering, Materials Science and Engineering**

*Received* ***14 January 2021*** *Accepted* ***17 May 2021***
*Received in revised from* ***3 February 2021***

# Superior recovery of ferrous waste

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**Abstract.** Our experimental research has confirmed many practical results regarding the possibilities of ferrous waste recovery and has generated new perspectives for their use. It turned out that through an adequate preparation of ferrous waste involving washing - calcination - fragmentation - magnetic and granulometric sorting - rigorous dosing of the reducer - with or without the addition of new components (alloying elements, fluxes, etc.), depending on the purpose pursued, by carrying out closed, opened or virtual metallothermic reactions, pure technical iron, ferroalloys, alloy steels, additives used for non-removable joints by welding (welding aluminothermy) or powdery active components (virtual thermitic mixtures) used in thermochemical treatments can be obtained.

**Keywords**: ferrous waste; “closed” metallothermia; “opened” metallothermia; “virtual thermitic mixture”; experimental programming; active alliting components.

## 1. Introduction

Recycling of reusable metal materials is a must; in this way it ensures the drastic reduction of the consumption of natural resources, the protection of the environment and at the same time the availability of the areas that would otherwise be blocked to store them [1-7]. Many categories of waste cease to be considered waste after undergoing a succession of specific processing. The criteria for determining the conditions under which certain types of scrap cease to be waste are defined in Regulation (EU) No 182/2011. Council Regulation (European Commission) No 333/2011 in accordance with Directive 2008/98 / EC of the European Parliament and of the Council [9]. The new directive specifies that a certain material ceases to be considered waste when it can be used normally, has

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undergone a processing operation (even summary), there is a constant market and a demand for that material, it meets certain technical requirements (it no longer contains liquids-oils, paints, nor it - waste nor the containers in which it was stored), legislative and standards, it has no negative effects on people or the environment. Residues of iron or steel resulting from the recovery operation must in turn contain less than 2% sterile mass, not contain an excess of iron oxides, oil or oil emulsions, lubricants or greases, radioactive elements, or dangerous substances.[9]. The steel industry is one of the most key areas in terms of recycling possibilities. Steel production in 2019 globally was 1869 million tons, of which 170 million was EU steel production. The steel industry can become an example of good practice in the circular economy - waste from the steel industry is recyclable and most often after pre-processing, it goes back to the manufacturing process of cast iron and steel, respectively. The main solid wastes resulting from the production of cast iron and steel are furnace and converter sludge (depending on the source between 30 and 53% iron), dust from electro filters (from electric arc furnaces), slag from steelworks (contain between 12 and 30% iron), barks with oxide impurities resulting from the cleaning of cast iron and steel pots (65 ÷ 75% iron), or those determined by the presence of splashes. In addition to these types of ferrous waste, the main sources of iron are scales from forging and rolling mills, slag from the production of ferromanganese, red sludge from the extraction of alumina from red bauxite), pyrite ash resulting from the process of obtaining sulfuric acid (have over 50% iron) and others. According to estimates by a group of researchers from ICEM SA-Romania [8], made in the first years of the first decade of the 21st century, the amount of furnace and converter sludge stored in the dumps in Galați and the Călan Iron and Steel Plant exceeded 8 million tons, the scales coming from the rolling and forging sections represented 3-4% of the steel production, the big inconvenience related to this last category of waste being the large amount of oils it contains (1.5-2.5%, reaching some cases at 10%), and the amount of slag accumulated at that time at ARCELOR MITAL was ~ 75mil.tons. Regarding the amount of red sludge stored in waterproof basins in Oradea and Tulcea, Romania, the information from the same source indicated a value of over 30 million tons at that time. Of particular interest is the ferrous waste in the historical dumps that does not meet the conditions to be considered scrap, so it requires complex but justified processing, to be used as input for iron or steel recovery operations, or to obtain in some cases another destination (obtaining mixtures of iron oxides or complex allied oxides used in “closed”, “open” metallothermia or „virtual” metallothermia. From the point of view of the European List of wastes, contained in Directive CE2000 / 532 and GD 856/2002, part of the analyzed waste is considered non-hazardous (e.g., scales, furnace, and steelworks sludge, etc.), instead another hazardous part (e.g., dust from electro filters), the dangerous character being determined by the zinc content (over 1%).

## 2. Methods used in research, materials and equipment

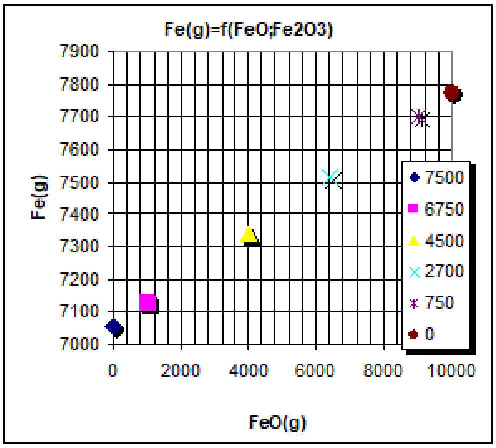
The research had a double approach, an analytical one, through experimental programming, starting from the possible thermodynamically reactions of aluminothermic reduction of iron oxides, simple or in different combinations and another experimental one, to confirm or refute the analytical conclusions. For the experimental part were used iron oxides $Fe_2O_3$ and $Fe_3O_4$ obtained by processing the scales from the rolling / forging sections and FeO resulting from the reduction with CO of $Fe_2O_3$, respectively aluminum powder with medium particle sizes within the limits of 150-500μm, resulting by air spraying of aluminum melt (ALCOA process). These approaches have tried, on the one hand, to estimate the efficiency of iron extraction by closed aluminothermy (system in which heat losses are rigorously controlled and limited) from of iron oxides, respectively the amount of heat released by aluminothermically reduction in an opened system (practical variant in some cases for making aluminothermic welds, for example and not only) of iron oxides. The thermal effects of the reactions were determined experimentally using thermitic kits (iron oxide-reducer-aluminum powder mixtures, well mixed in bitronconic mixers) with a total mass of 200g. The yields of iron extraction from the aluminothermically reduction reactions of iron oxides from processed scales and the amounts of heat related to these reactions were reported per 10 kg of iron oxide mixtures, for each variant taken into analysis (theoretical and experimental). ***Note***. The amount of aluminum reducer was determined according to the type of reaction in the analysis, respectively the amount of iron oxides, so that the stoichiometry of the reactions is observed. In order for the reaction not to be explosive and to be controlled, amounts of inhibitor-fragments of OL37 wire were added, calculated so that the temperature does not exceed the value of 3273K, regardless of the composition of the thermitic mixture analyzed / tested. Another direction of use of ferrous waste, respectively of iron oxides resulting from their primary processing (washing-calcination-grinding-magnetic and granulometric sorting, etc.), was the one related to „virtual” metallothermia - a term introduced by the authors to define the behavior of mixtures composed of iron oxides-aluminum-multiferroic compounds of the $FeAlO_3$ type with a perovskite-type structure, resulting by mechanical alloying, during heating for thermochemical processing. It was found that such mixtures are able under strictly specified conditions to generate a considerable thermal effect, but also to be active sources of aluminum supply, able to saturate the surfaces of metal products, to increase the resistance to oxidation at high temperatures (800 ÷ 900°C ), corrosion resistance and erosion, respectively.

## 3. Results. Interpreters

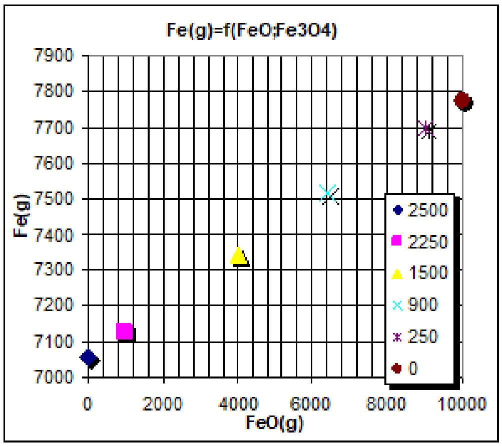
The results of theoretical research on the thermodynamics of the reduction of iron oxides with aluminum [11] led to the conclusion that all iron oxides are reduced relatively easily, the enthalpies of free reaction being negative (exergonic reactions), and the trend of reactions it is all the more pronounced as the mixtures contain more types of iron oxides . For example, the free enthalpy of individual reactions to reduce iron oxides FeO, $Fe_2O_3$ or $Fe_3O_4$, calculated at 1273K, are in the range of values ~ -730 ÷ -3000KJ / mol, at the upper limit being the value corresponding to the reduction of magnetite, but the enthalpy of the aluminothermic reduction reaction of the FeO-$Fe_2O_3$-$Fe_3O_4$ oxide mixture reaches the same temperature of -5531.4KJ / mol. In the same value ratio are found the thermal effects of these aluminothermic reduction reactions (strongly exothermic reactions): in the range -893 ÷ -3500KJ / mol for single oxides (at the lower limit are found FeO and $Fe_2O_3$, and at the upper $Fe_3O_4$), reaching ~ -6200KJ / mol for the oxides mixture. Research in the field of „closed" aluminothermy aimed at maximizing the efficiency of iron extraction from its oxides [11]. Analytically it was determined (multiple regression analysis; passive experiment [10]) and experimentally confirmed that the extraction efficiency of iron from its oxide mixtures, FeO + $Fe_3O_4$ + $Fe_2O_3$ increases with the increase of the proportion of ferrous oxide in the mixture (fig.1). Moreover, a closer analysis shows that ferric oxide also has a special role on the extraction efficiency of iron, so that the role of ferrous oxide in the mixture can be compensated by changing the proportion of magnetite, or the mixture of magnetite and hematite.

From the point of view of the amount of heat released during the aluminothermic reduction reaction of iron oxides (under the conditions of „open" aluminothermy) (fig. 2), the situation is exactly the opposite, the highest amount of heat being recorded in the case of aluminothermic reduction of oxides mixtures containing as small proportions of FeO synthetic oxide as possible [11].

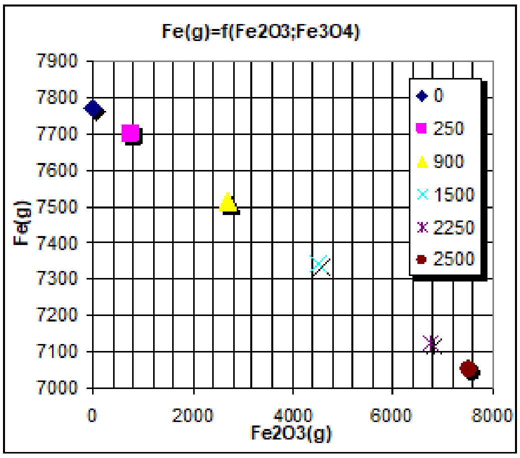
The conclusion can be anticipated if we consider the relatively low thermal effect of the aluminothermic reduction reaction of ferrous oxide, so that an increase in its proportion in the iron oxides mixture is expected to decrease the overall thermal effect of the reaction, so the total amount of heat. Since one of the applications of open aluminothermy is aluminothermic welding, and it requires heat not only to release iron / steel from oxides, but also sufficient heating of the metal elements to be assembled so that they are partially melted, it is particularly important to adjust the proportion oxides from mixtures of ferro- oxides. Mixtures of iron oxides powders (recovered from waste from various sources) with aluminum, obtained by mechanical alloying in high energy ball mills, are a special raw material for the initiation of „virtual" aluminothermia. Moreover, these mixtures obtained by mechanical alloying represent „virtual thermitic mixtures", which under certain strictly specified conditions can provide heat due to reactions between components and also active aluminum capable of superficially saturating the surfaces of metallic products with which it comes into contact (aliting), giving them resistance to oxidation in the field of high temperatures, resistance to corrosion and erosion.




***$Fe_3O_4$=100- Σ($FeO$+$Fe_2O_3$)***

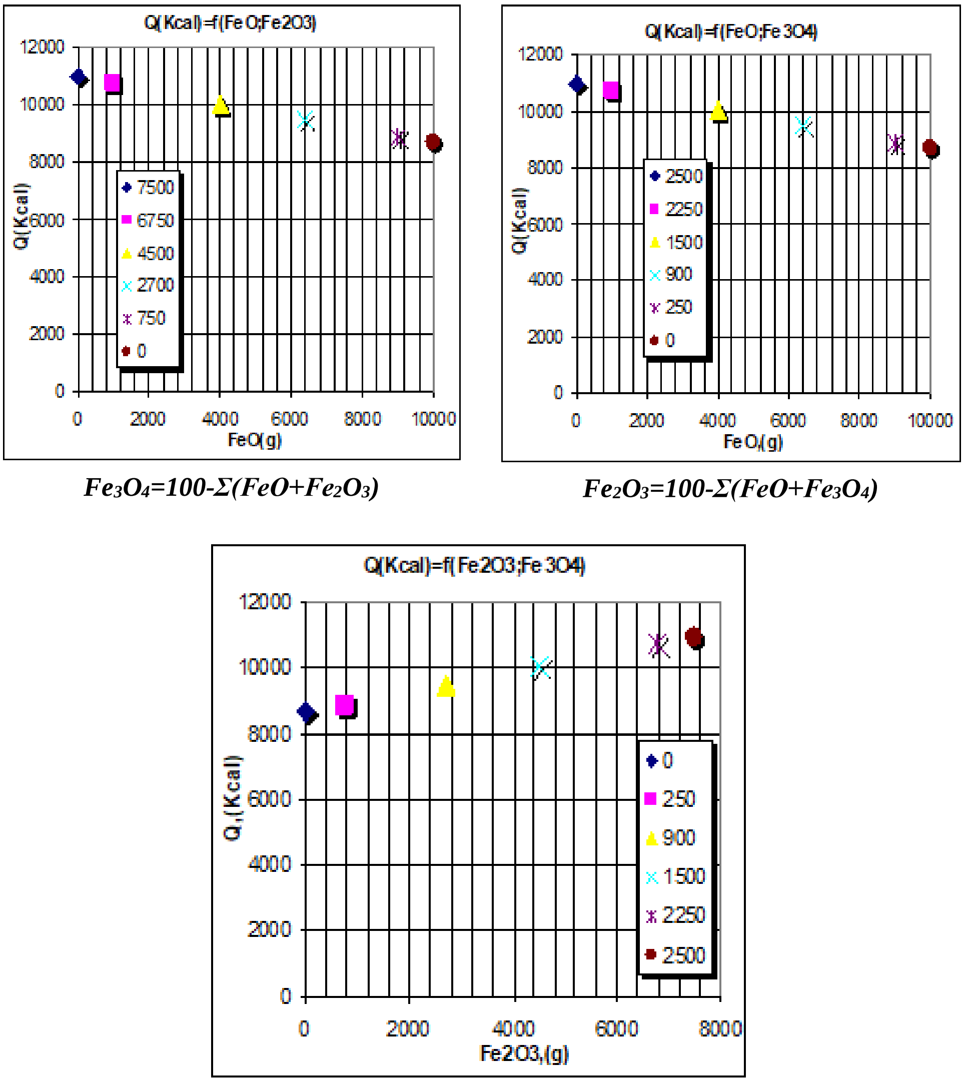



***$Fe_2O_3$=100- Σ($FeO$+$Fe_3O_4$)***




***$FeO$=100- Σ($Fe_2O_3$+$Fe_3O_4$)***

Fig. 1. Dependence of the amount of iron, resulting from the aluminothermic reduction of the mixture of iron oxides (10Kg), of the type and proportion of iron oxides in the mixture.



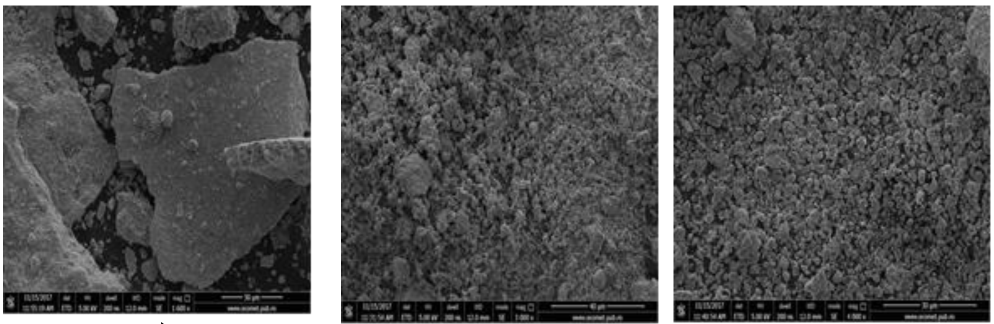

***$Fe_3O_4$=100-Σ($FeO$+$Fe_2O_3$)***

***$Fe_2O_3$=100-Σ($FeO$+$Fe_3O_4$)***

***$FeO$=100-Σ($Fe_2O_3$+$Fe_3O_4$)***

Fig. 2. Dependence of the amount of heat released by the aluminothermic reduction reaction of a thermitic mixtures containing 10Kg of iron oxides, of the type and proportion of iron oxides in the mixture.

Experimentally, the scales resulting from the forging of the carbon steel semi-finisheds, after degreasing, washing (fig. 3, a) and preliminary grinding (fig. 3, b), were mixed with aluminum powder in echimasic proportions and subsequently ground (mechanically alloyed) in high energy ball mills (~ 1kJ / min) for 30 hours (fig. 3, c). The result was a powders mixture in which by X-ray diffraction (Fig. 4) identified the presence of all iron oxides-FeO, $Fe_3O_4$, $Fe_2O_3$, together with aluminum and an iron oxialuminide, $AlFeO_3$ (iron and aluminum oxide, type $Al_2O_3$ • $Fe_2O_3$), multiferroic, with a perowskit structure. In conclusion, theoretically, all the necessary conditions have been created to trigger an aluminothermic reaction during heating, to perform a certain type of thermochemical treatment (in this case aliting), because by mechanical alloying the powdery mixture contains in addition to iron oxides and aluminum, free and in the multiferoic compound $FeAlO_3$. The effects of the initiation of the aluminothermic reaction during heating to achieve the aliting process are reflected in the substantial increase in temperature and thus to the acceleration of the reactions in the environment through which aluminum will be obtained in the active state, as well as the acceleration of the adsorption and diffusion processes. Experimental tests [12] performed on pure technical iron matrices in powdery solid medium in which there are iron oxides, the multiferoic compound $AlFeO_3$, together with free aluminum (Fig. 5), led to the conclusion that the value of aluminum concentration. in the surface layers increased very rapidly to ~ 33% mass (in 4 hours at 900°C). The rate of formation of the diffusion layer under the conditions of initiating the aluminothermic reaction between the components of the powder mixture obtained by mechanical alloying is ~ 30% higher compared to that recorded by aliting in conventional powdery media, under the same temperature and time conditions.



**a)** **b)** **c)**

Fig. 3. Electron microscopy images of the initial carbon steel scales (a) and after grinding in high energy ball mills, 3 hours (b) and after mechanical alloying, together with aluminum (echimasic proportions), in ball mills with high energy ~10J / rot, 102rot / min, 30 hours (c).

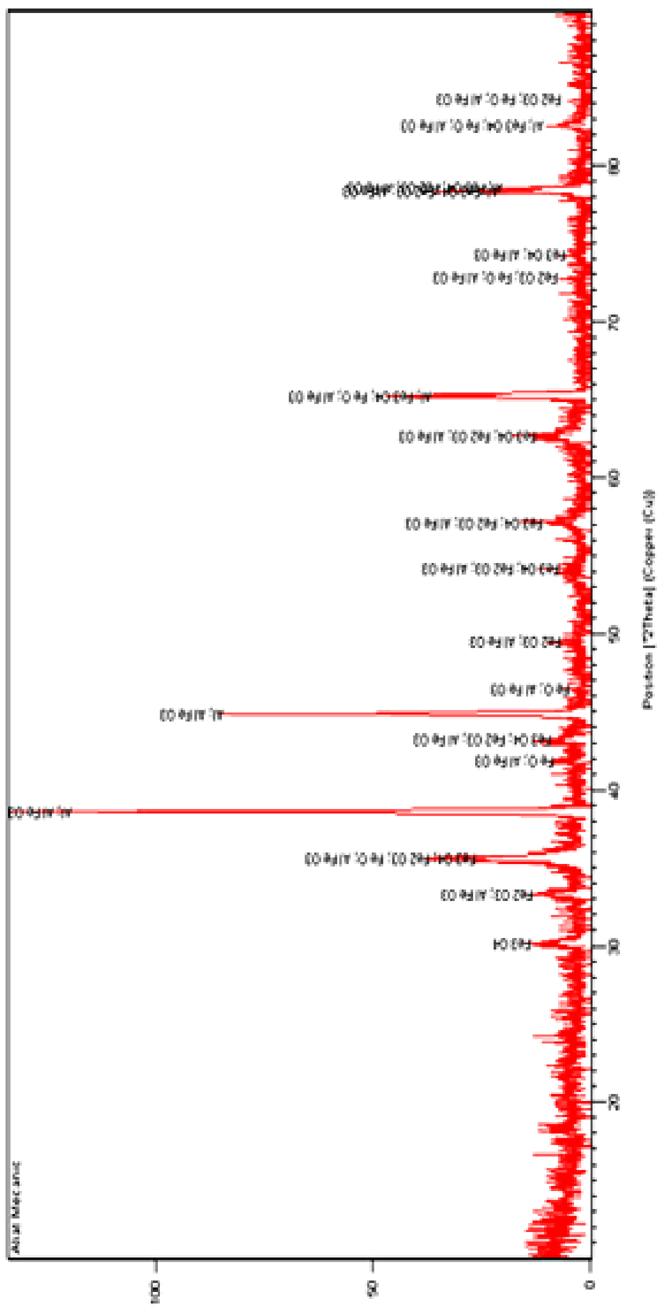
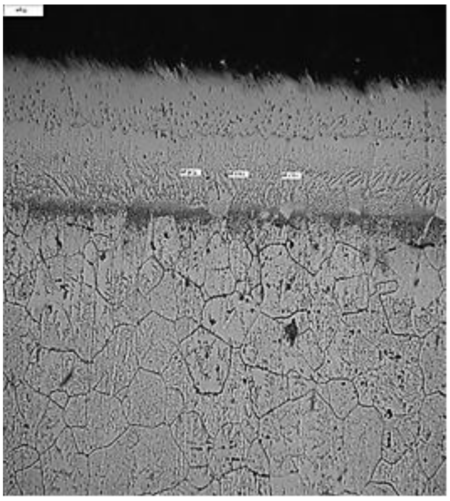
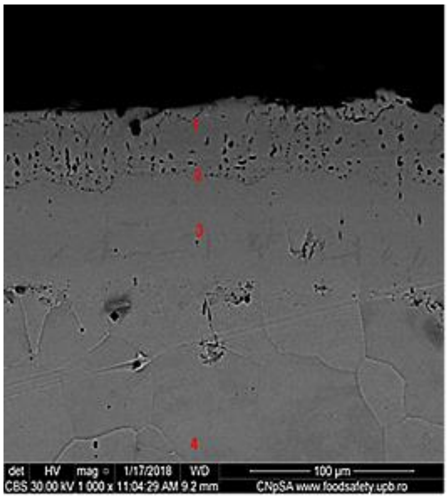


Fig. 4. Phase composition of mechanically alloyed Fe-Al powder, 30 hours, in high energy ball mills.



a)




b)

Fig. 5. Images of optical (a) and electronical microscopy (b) of the alited layers obtained on Fe-ARMCO matrices, under the following conditions: T = 900°C / 4 hours isothermal maintenance in solid powdery media with the composition: 50% mixture (50% ferrous waste + 50% aluminum powder, obtained by mechanical alloying 30 hours), 48% $Al_2O_3$ and 2% $NH_4Cl$.

The results of quantitative chemical microanalyses performed on the alited layers in environments containing the active component obtained by mechanical alloying of ferrous waste with aluminum, confirm the existence of a gradient of iron aluminides, in the surface area of the layer being present aluminides with moderate aluminum content, type.

FeAl, and in the deeper areas the aluminides with high concentrations of iron, of the $AlFe_3$ type.

## 4.Conclusions

Theoretical and experimental research focused on ferrous waste, obtained especially from the rolling, or forging of low-carbon or low-alloyed steels, have shown that they can be a particularly valuable source for obtaining new steels, by „closed metallothermy”, for the production of thermitic kits intended for use to achieve non-removable joints by “open metallothermy” or as a source of active elements in the practice of thermochemical treatments (cementation with aluminum-aliting) by „virtual metallothermy” The analyzed categories of „raw materials” - scales of low-carbon or low-alloyed steel from rolling or forging operations, in accordance with Directive 2008/98 / EC of the European Parliament and of the Council do not fulfill the conditions imposed for its immediately utilization, and consequently, before utilization must be subjected to a series of preliminary processing steps, including degreasing, washing, calcination, fragmentation, magnetic and granulometric sorting, etc.

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