

Pack-Aliting in Thermitic Powder Mixture Obtained by Mechanical Alloying

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The paper deals with the effects of the structural state modification of the main pulverulent component used for the alloying of metallic products made of steels, cast iron or nonferrous alloys, on the layers kinetics formation. The aliting process is most often done in a powdery mixtures, composed of three components: the active component providing aluminum, a neutral one with the role of dispersing the others, also having the role of blocking the sintering tendency and a halide as an activator, by cleaning the metal surfaces to be saturated. The aim of the paper is to present the ways to ensure the kinetics of the aliting layer formation, while reducing the heat treatment temperature. These could be accomplished by replacing the aluminum or ferroaluminum powder with equimassic amounts mixture of thermitic powders, consisting of ferrous oxides and aluminum powders, mechanically alloyed in high energy ball mills. Thus, it is possible to produce the aluminothermic reduction reaction in the component obtained by mechanical alloying at the same time generating notable thermal effects.

Keywords: pack-aliting, mechanical aliting, ferrous oxides waste, aluminothermic reduction

Pack-aliting (aluminizing) process in metallic powders is one of the most convenient and commonly used solutions for increasing the heat resistance, corrosion and erosion characteristics of metallic products made of steels, cast irons, refractory alloys, nonferrous metals and alloys [1-4]. Conventional, the metallic powders used at aliting it is composed of: aluminium or ferroaluminum powder as active component, aluminum oxide (Al_2O_3) as neutral one and a surface cleaner & activator of reaction, respectively a halide (NH_4Cl) in order to bring the aluminum in the active state [1-4]. The aliting temperature for steel products are in the range of 950 ÷ 1050 °C (from very thin parts to 1.5 mm thickness, the temperature drops in the range 850 ÷ 860 °C), lowering below these limits resulting in a drastic decrease in the kinetics of the layer formation [1-4]. The tendency of the aluminum powder to adhere to the surface to be processed, leads to the degradation of its quality, as well as to the increase of its concentration in the superficial areas of the layer. Hence, the need for an annealing, with direct effect on the reduction/removal of the layer brittleness. Thus, it resulted in its replacement with a ferroaluminium, namely mixtures of iron and aluminum powders [5].

The neutral component is no longer necessary unless the aliting layer is subject to very high quality conditions, in which case 20-40 % alumina/kaolin is added. The results confirmed the concentrations to be achieved in the layer as well as a low level of adhesion. The kinetics of the alloying process can be accelerated and the aluminum concentration control in the superficial layer of the aliting layer becomes more accurate, if the active component of the medium is a mixture of submicron ferrous and aluminium waste powders, obtained by mechanical alloying in high energy ball mills [6,7]. Iron oxide wastes are the result of hot processing of semi-finished (slabs, billets, stocks, slugs, blocks, blanks, etc), low carbon or low alloy steels [8].

The use of such submicron mixture of powders obtained by mechanical alloying has been the research subject, assuming that the energy input from the aluminothermic reduction reaction will be large enough to allow the reduction of the alloying temperature while maintaining a high level of kinetics layer formation. Concurrent by the blocking of the adhesion formation tendency on the surface subjected to the thermochemical processing and the control of the aluminum concentration within the acceptable limits (20 ÷ 30 %) are ensured.

Experimental part

The platelets scraps (fig. 1a) having millimeter average dimensions were initially fragmented into ball mills for 2-3 h (fig. 1b), at mill rates of about 80 % of critical speed (102 rpm for a 2.5 l mill), after which they were mixed with aluminum grain powder (<100 μm) and subsequently being subjected to mechanical milling in ball mills with energies of about 10 J/rot at approximate to 85% of the critical rotation speed for 30h. A submicron alloy powder resulted (fig. 2), with the phases composition shown in figure 3.

The ball mill used for mechanical fragmentation and alloying, having a volume of 2.5 L is equipped with 4.5 kg of tungsten carbides balls (Widia), so that the value of the ratio between the mass of the grinding bodies and the mass of the mixture of powders to be processed is about 11.0, thus there is a certainty of fragmentation and concurrently intense mechanical alloying.

The phase composition analysis of the mechanically alloyed mix powder (fig. 3) shows the presence of all iron oxides FeO , Fe_3O_4 , Fe_2O_3 , Al and AlFeO_3 (double iron oxide and aluminum type $\text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$) compound with a perovskite, multiferroic structure [9].

So, all conditions are created for initiating an aluminothermic reaction among the components of the powder produced by the mechanical alloying, a process with direct implications on the temperature of the system and therefore the kinetics of the reactions underlying the

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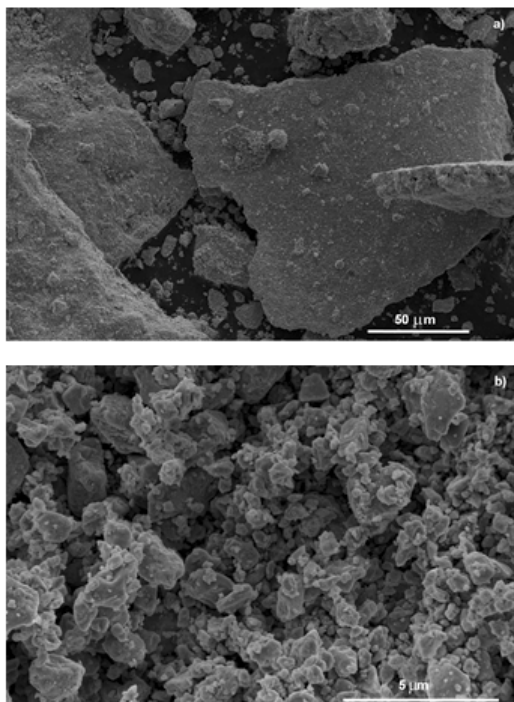


Fig. 1 SEM images (SE) of: a) initial platelet scrap; b) fragmented scrap after 3h of grinding

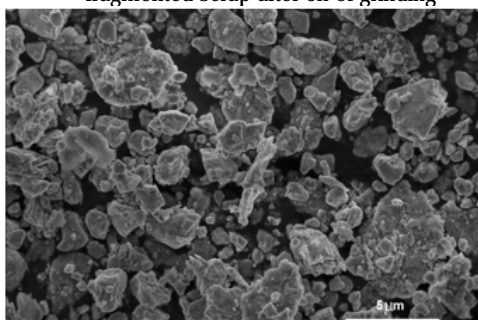


Fig. 2 SEM image (SE) of Fe-Al mechanically alloyed powder for 30h in high energy balls mill superficial saturation with aluminum. The mixture of the three submicron pulverulent components was carried out in a bitronconic mixer/homogenizer, in air atmosphere.

Thermo-chemical processing was performed on pure technical iron (Fe-ARMCO), at 800 ÷ 900 °C/ 4h, followed by cooling in the furnace up to 450 °C and subsequently in air. The samples were maintained throughout processing in steel containers, packed in the submicronic mixture powder (50 wt%) to which 48 wt.% Al₂O₃ powder and 2 wt.% NH₄Cl were added. During the thermochemical processing the temperature was automatically monitored.

According to Fe-Al binary phase diagram, five types of intermetallic compounds (Fe₃Al, FeAl, FeAl₂, Fe₂Al₅ and FeAl₃) might be formed during pack-aliting in thermitic powder mixture obtained by mechanical alloying [10].

The investigation of the results was carried out by: optical microscopy-OM (imaging analysis system equipped with a ReichertUnivar microscope and OmniMet Enterprise software from BUEHLER), SEM/EDS microscopy (Quanta™ SEM Inspect F50) and X-ray diffraction-XRD (PANalytical X'Pert Pro Multipurpose Diffractometer).

Results and discussions

The main goals of the experimental research were to prove that the waste resulting from the thermal and plastic processing of low-carbon, low or medium alloyed carbon steel semi-finished products can be used as raw materials in the processing of the active components of the pulverulent solid media used for aliting heat treatment,

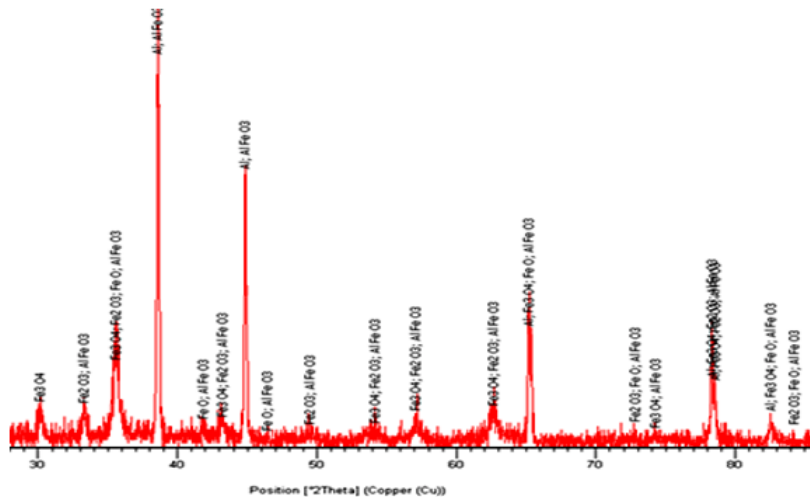


Fig. 3 Phase composition spectra of Fe-Al mechanically alloyed powder in a high energy ball mill for 30h

resulting in strict control of environmental reactivity during thermo-chemical heat treatment. The main effect on controlling the concentration gradient of aluminum in the layer thickness. At the same time, it was demonstrated that a thermitic medium has been created, having a notable thermal effect generator with direct consequences on the temperature level at which the aliting process can be carried out. It is particularly important that the thermitic medium is uniformly distributed in the powdered alloy mixture (the mixture is homogeneous and isotropic) in this way it becomes possible to avoid the sintering of the components of the environment (especially of the thermally agglomerated ones) and the formation of uniform thickness layers with predicted chemical composition and phase gradient.

As can be seen in figure 4, aliting in pulverulent solid media containing 50 wt% of thermitic active component, at temperatures below the optimum range indicated for steel products (950 ÷ 1050 °C) [2-4], ensures a particularly active environment, the kinetics of formation and growth of the layers being superior [3-5], the maximum concentration of aluminum in the layer being in the 33-35 wt% range. The advance/growth rate of the layer under

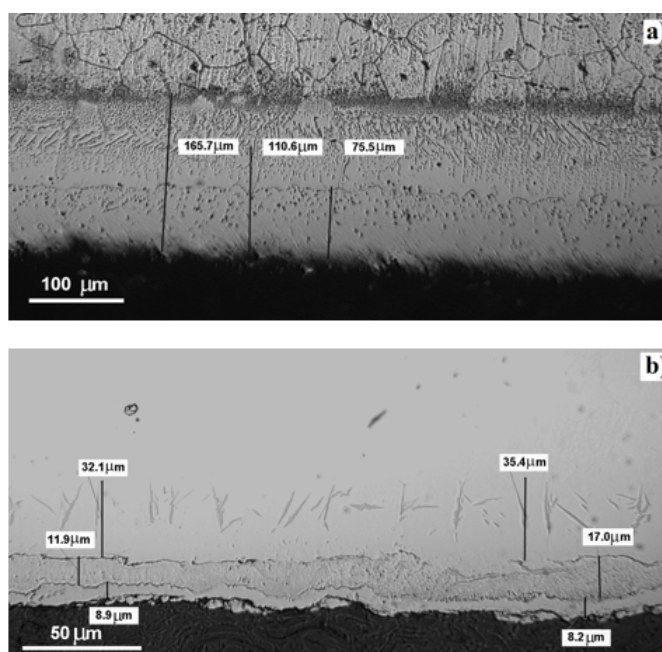
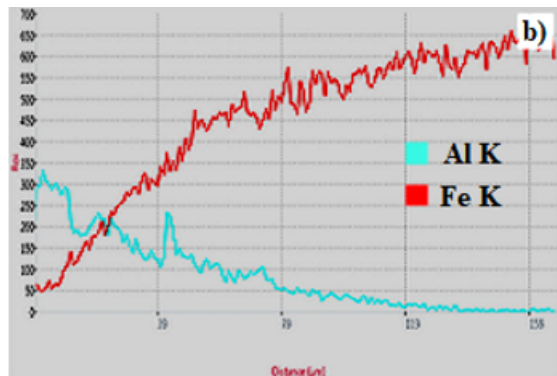
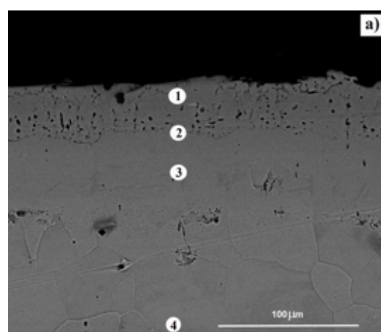


Fig. 4 Microscopy images of aliting layer obtained on Fe-ARMCO at 900 °C / 4h / furnace up to 450 °C / air and the elemental composition of the marked areas

these conditions is about 32 μm/h (at about 165 μm total thickness layer, as it shown in figure 4. a), compared to 25 ÷ 30 μm/h (at 100 ÷ 120 μm, total thickness layer), under the same processing conditions (in terms of thermal and temporal parameters), but in conventional media containing 99.5 wt.% ferroaluminum and 0.5 wt.% NH₄Cl [3.4].

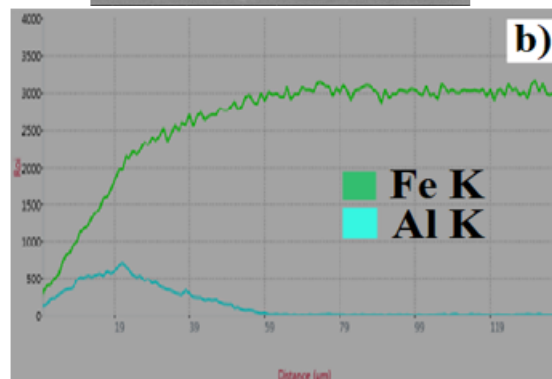
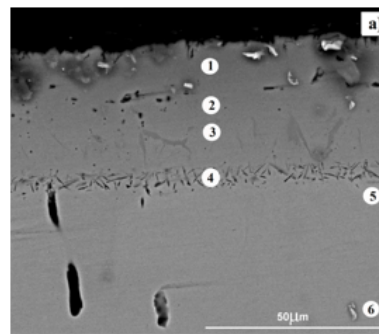
Quantitative elemental analysis (EDS) performed on the aliting samples, in the new active medium with thermic properties, confirmed the claim that the maximum concentration of aluminum in the alloyed layer is close to the optimal value (in terms of the admitted fragility level) and the presence of aluminum gradient concentration in these areas [11-13].

The decrease on the thermochemical processing temperature obviously leads to a decrease in the speed of formation and growth of the aliting layer (fig. 5), the growth rate recorded in this case decreasing to about 12 μm/h (about 61 μm layer thickness, as it shown in fig. 4. b), and the maximum concentration of aluminum in the layer increasing up to 35 wt.% (fig. 5 - Zone 1). The slight increase



Zone	Element	wt.%	at.%
1 - (FeAl ₂ , Fe ₂ Al ₅ , FeAl ₃)	Al	33.32	50.85
	Fe	66.68	49.15
2 - (FeAl)	Al	21.07	35.59
	Fe	78.93	64.41
3 - (Fe ₃ Al)	Al	11.62	21.39
	Fe	88.38	78.61
4 - (ARMCO)	Al	0.00	0.00
	Fe	100	100

Fig. 5 Cross-sectional SEM (a), EDS profiles (b) and analysis (c), of the layer formed by pack-aliting on Fe-ARMCO substrate at 900 °C / 4h / furnace up to 450 °C / air.



Zone	Element	wt.%	at.%
1 - (FeAl ₂ , Fe ₂ Al ₅ , FeAl ₃)	Al	35.77	53.01
	Fe	64.73	46.99
2 - (FeAl)	Al	21.95	36.79
	Fe	78.05	63.21
3 - (Fe ₃ Al)	Al	13.12	23.81
	Fe	86.88	76.19
4 - (α-Fe _(Al) , Fe ₃ Al)	Al	8.72	16.5
	Fe	91.28	83.5
5 - α-Fe _(Al)	Al	0.35	0.72
	Fe	99.65	99.28
6 - (ARMCO)	Al	0.00	0.00
	Fe	100	100

Fig. 6 Cross-sectional SEM (a), EDS profiles (b) and analysis (c), of the layer formed by pack-aliting on Fe-ARMCO substrate at 800 °C / 4h / furnace up to 450 °C / air

of the aluminum concentration in the superficial areas of the aliting layer is dictated by the diminishing of the diffusion coefficient of this element in the metal matrix with the decrease of the aliting temperature (from 900 °C to 800 °C). The results of the elemental microanalyses performed on the marked areas (fig. 6 - table c)) confirm the existence of a gradient of the iron aluminides, on the depth of the layer. Thus, aluminides with moderate Fe content (FeAl type) predominate at the surface. Along with sectioning, predominate those with a higher Fe content (Fe₃Al type).

The most probable mechanisms by which the active aluminum is formed remain the same as in the case of alloying in pulverulent solid medium containing

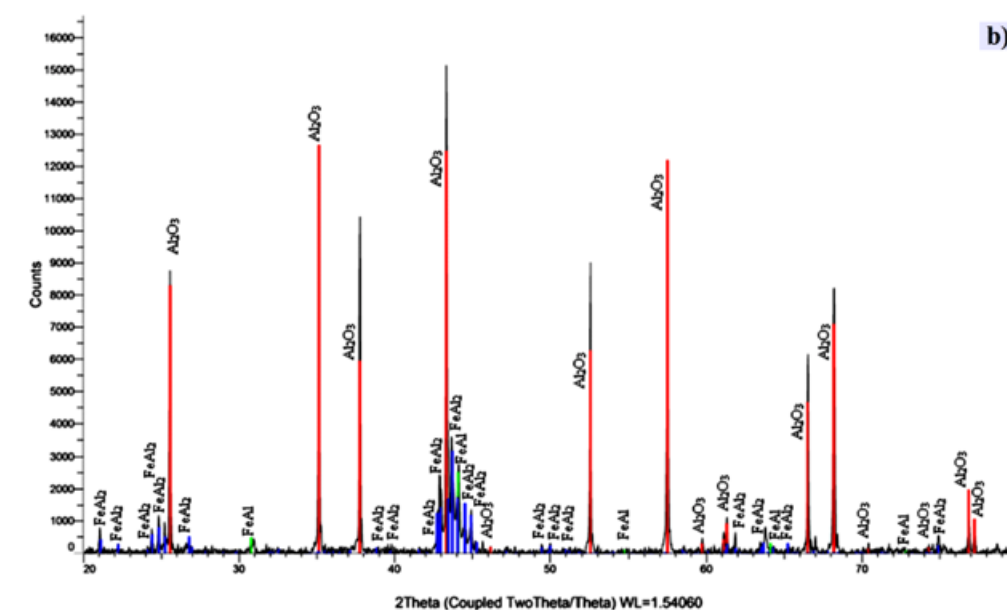
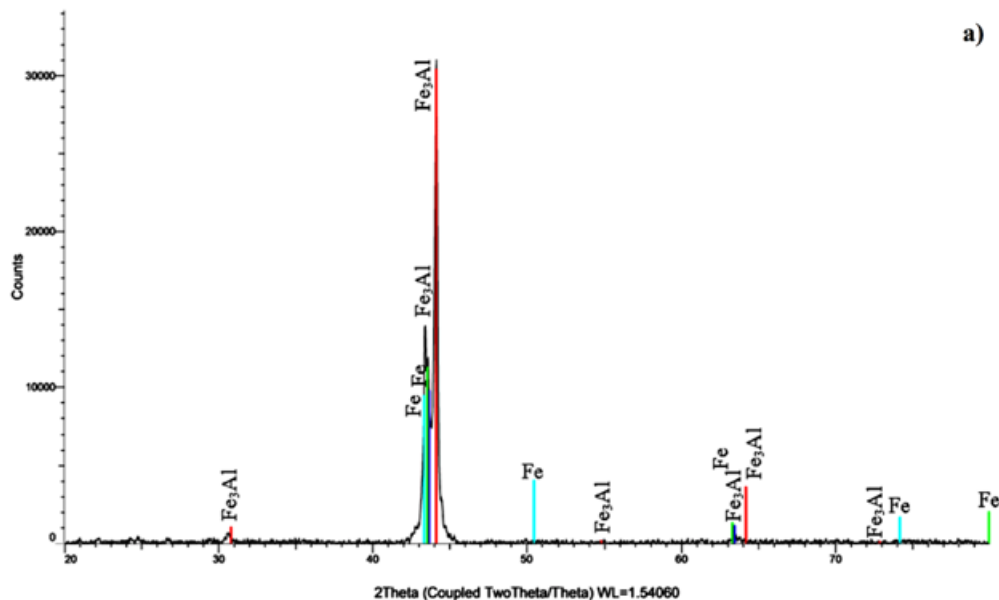


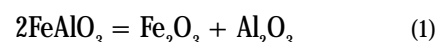
Fig. 7 X-ray patterns of reaction products resulting from the reduction of the aluminothermic reaction: a) useful fraction; b) slag

ferroaluminum. The phase composition of the ferroaluminum powder has been found to be very close to that of the equimassic mixture of iron powders and aluminum, thermally processed at temperatures associated with aliting regimes.

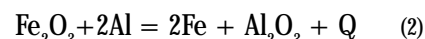
In the early moments of the process (before the initiation of the aluminothermic reaction), aluminum chloride (AlCl_3) is formed as a result of the direct reaction between hydrochloric acid vapours (resulting from the thermal decomposition of ammonium chloride), and the remaining aluminum which did not interact with the iron during mechanical alloying (fig. 4), or with aluminum on the Fe_xAl intermetallic compounds surface.

Subsequently, in the presence of aluminum, or through a disproportionation reaction of aluminum chloride (AlCl_3), the formation of aluminium sub-chloride (AlCl) occurs and is adsorbed on the surface of the metal matrix subjected to thermochemical processing by autoreducing and releasing the saturation aluminum surface. The iron aluminides stability is particularly high [14], but at the temperature generated by the aluminothermic reaction (upwards of 2400°C) [15], it is very likely to melt them and thus facilitate the chemical reaction of the AlCl formation.

On the other hand, the complex intermetallic compound (FeAlO_3) can decompose into constituent oxides, Fe_2O_3 and Al_2O_3 , according to the reaction:



In this way, it contributes to the general temperature increase of the system by direct participation in the aluminothermic reduction reaction, according to the reaction:

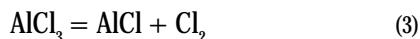


The Gibbs free energy for this reaction is $-795,5 \text{ KJ/mol}$ at 800°C and respectively $-787,3 \text{ KJ/mol}$ at 900°C , having an enthalpy of $-884,9 \text{ KJ/mol}$ at 800°C and respectively $-883,8 \text{ KJ/mol}$ at 900°C [16].

X-ray diffraction studies performed on equimassic compositions made of ferrous and aluminum scraps, obtained by mechanical alloying and in which the metallothermic reaction was initiated, confirm the hypothesis that the entire amount of aluminum (fig. 7) will be found after the initiation of the aluminothermic reaction in Fe_3Al type iron aluminides localized in the useful fraction of the reaction products (fig. 7a), respectively FeAl and FeAl_2 (together with Al_2O_3) in the resulting slag (fig. 7b).

In this case, the main aluminum source generating both AlCl_3 (in the presence of HCl vapours) and AlCl , after the initiation of the aluminothermic reduction reaction among the components of the compound obtained by mechanical alloying, is the aluminum bonded to the iron aluminides.

AlCl can also be generated by the disproportionation reaction of aluminum chloride, according to the reaction:



Conclusions

Experimental research has highlighted that the waste resulting from the thermal and plastic processing of low-carbon, low or medium alloyed carbon steel semi-finished products can be used as raw materials in the process of producing the active components of the pulverulent solid media used for aliting heat treatment.

The mechanical alloying of ferrous scalings powders with aluminum powders results in a submicron powder with a great potential in the aliting process. Its use as an active component in a mixture with a neutral component and a reactive activator or activator of the surfaces to be saturated allows an intensification of the kinetics of saturation and a more rigorous control of the potential of the aliting medium so that the aluminum concentration in the superficial layers rising close to an optimum value.

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