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SUPERIOR VALORISATION OF THE ALUMINIUM SCRAPS FOR OBTAINING COMPLEX ALUMINIUM MASTER ALLOYS USED IN ADVANCED REFINING OF THE STEELS

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ABSTRACT

The research about aluminium scraps valorisation to obtain master alloys with reactive elements (Al, Mn, Si) used for special steels refining is presented in this paper. By this way the recycling of aluminium scraps leads to increase the recovery ratio of aluminium as scraps into new materials with added value. These are FeAl, FeMnAl, FeMnSiAl. A new technology for obtaining these materials was proposed. This solution was established to ensure reproducible results, the steadfastness of the chemical composition of alloys, a maximum recovery ratio of elements and low energy consumption.

KEYWORDS: aluminium scraps, valorisation, complex alloys, reactive elements

1. Introduction

No other metallic material is discussed at the moment more critically than aluminium. The discussion about the position of this metal within an economy which aims at sustainable development is conducted strongly controversially. The adversaries of aluminium name the production of the metal “one of the environmentally most harmful activities of mankind”, whereas the preopponents denote aluminium “the green metal” [1, 2, 3]. These controversial points of view are based mainly on different parts of the life-cycle of aluminium. For correctly position of this metal in accordance with sustainable development, it is necessary to extend the view to the whole life-cycle with a correct evaluation of the efficiency of the recycling-loop for aluminium. The aim of a recycling with orientation towards sustainability has to keep aluminium produced with high energy input in the material cycle as long as possible.

The recycling loop for aluminium divided in two different loops (a closed-loop and an open-loop) is shown in Figure 1 [4].

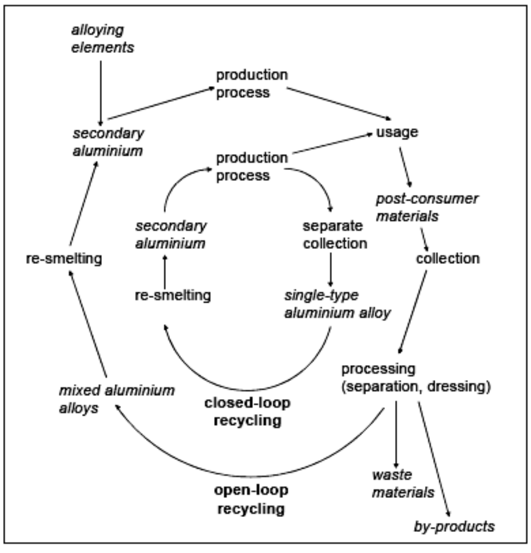

Fig. 1. *Recycling loop for aluminium [4]*

Theoretically, aluminium can be recycled for an unlimited number of times without loosing its chemical and physical properties. For this it is essential to find the best solution to improve the quality of recycling in accordance with economic factor and environmental protection. The choice of the optimum solutions for secondary aluminium industry can be in accordance with superior utilisation of the aluminium scraps for obtaining of the new materials with added value [5].

The present work is focused on the metallic scraps for input materials used for obtaining complex alloys for advanced steels refining. It is known, the aluminium is used for refining steels. The main problem of aluminium as a deoxidizer is the control of steadfastness of the refining process. The low density of aluminium, comparable with density steel slag, determines its float up and interaction with oxidizing atmosphere. The utilization yield and recovery ratio of aluminium for refining action are low and variable. In respect to aluminium the positive effect of complex refining alloys is explained by the effect of the alloying on the aluminium deoxidizers properties (in special for density and thermodynamic properties).

Recent literature has shown once again that effects obtained from the combined addition of two or more refining elements as complex deoxidisers are often greater than the added effects of the individual elements. In this case, the use of the aluminium alloyed with reactive elements is more effective than the singular elements addition.

If alloying elements are simultaneous present in deoxidisers with determined chemical composition in accordance with the utilisation purpose, the refining capability of each element is increased because the complex non-metallic inclusions are formed and, the thermodynamic activity of each element that is present in these deoxidizing products is lower than their activity in the pure oxide. In this way, at equilibrium for a stable temperature, the oxygen content of the molten steel is lower [6, 7].

The same type of synergetic effect has long been recognized with regard to the combined role of aluminium, silicon, manganese, calcium and barium in the steels refining.

The increasing demands for products specification makes any non-metallic inclusions present in steel an important issue during the steelmaking process. There is a way to reduce the disadvantageous effects of non-metallic inclusions on the steel properties. The modification of inclusions create excellent conditions for its floating up and dissolving in the slag by the change in chemical composition of non-metallic inclusions during the steelmaking process. This can be achieved by steel treatment with deoxidisers with controlled chemical composition. An overview on world-wide steelmaking gives for deoxidizing practice the following alloys FeAl, FeMnAl, FeMnSiAl, FeMnSiAlCa, FeMnSiAlCaBa, Table 1 [8].

Table 1. *Complex aluminium deoxidisers for steel refining*

Alloy	**Chemical composition,** %wt			
	Al	Mn	Si	Fe
FeAl40	20-40	-	-	balance
FeMnAl15	10-20	45-75	-	balance
FeMnSiAl	~10	40-60	15-20	balance

The obtaining of complex aluminium alloys can satisfy the physical and chemical properties in respect to optimal development of the processes. The alloys making technology must be flexible in accordance with the conditions of the each producer able to assure the alloys necessary by quantities. For this reason these technologies must have reproducible results, to ensure steadfastness for chemical composition, maximum recovery ratio of the elements and, low energy consumption and raw materials. This paper presents the research for establishing the technology for obtaining the complex aluminium alloys utilised in the refining processes for the steels. The particularity of this method is the use of recyclable input materials and the flow of input materials for alloys making technology.

2. Experimental details

The induction furnace with crucible is utilised for obtaining master alloys. Its characteristic properties are the following: 50Hz low frequency; 100kg capacity; neutral lining.

The input materials used were the aluminium scraps and pieces of steel sheets with 0.15%C, 0.48%Mn, 0.20%Si, 0.022%S, 0.028%P. Also, the ferromanganese (minimum 80.00%Mn, maximum 0.5%C, 2%Si, 0.03%S, 0.3%P) and silico-manganese (60-65%Mn, 10-26%Si) are utilised for FeMnAl, FeMnSiAl alloys. The chemical composition of complex aluminium alloys obtained is given in Table 2.

Table 2.*Chemical composition of complex aluminium alloys*

Alloy	**Casting temperature**	**Chemical composition**				**Recovery ratio of element**		
	[^{0}C]	[%wt]				[%]		
		Mn	Al	Si	Fe	Mn	Al	Si
FeAl	1230	-	40.81	-	balance	-	89.25	-
	1230	-	39.88	-	balance	-	86.33	-
FeAlMn	1490	55.23	10.34	-	balance	88.73	90.78	-
	1520	60.61	15.15	-	balance	87.68	87.97	-
FeAlMnSi	1470	40.76	10.02	20.59	balance	97.21	90.34	85.45
	1490	40.80	9.95	20.83	balance	95.07	86.92	84.87

Figures 2-4 showed the microstructure of FeAl, FeMnAl, FeMnSiAl alloys.

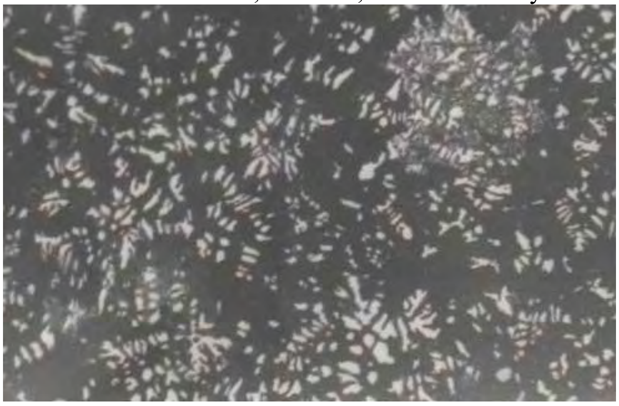

Fig. 2. *Microstructure of FeAl alloy (X160)*

Fig. 3. *Microstructure of FeAlMn alloy (X160)*

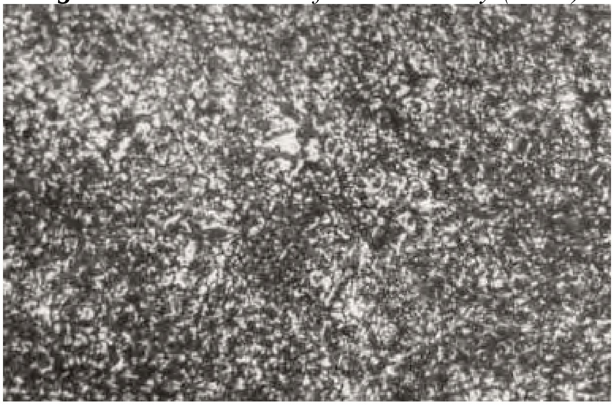

Fig. 4. *Microstructure of FeAlMnSi alloy*

Priorly, was obtained the starting ingot by melting of the aluminium scraps into the crucible of the reverberatory furnace. This starting aluminium ingot was melted into crucible induction furnace. Pieces of steel sheets scraps were added into aluminium melted that was superheated to750^0C. The gradual dissolution of the preheated steel scraps (at 150 – 200^0C) was realised for range of temperature 750 – 1250^0C. The alloy making continues with the FeMn or SiMn addition and with the temperature increase to about 1500^0C. For degassing argon was blown into the melting charge. Technical parameters of the degassing process are: the flow of inert gas 0.3 – 0.5daN/cm^2; the gas quantity is two-three times more than the melting volume.

To prevent the interaction between aluminium and oxygen the following protection flux was utilised: 40% NaCl, 20% Na_2SO_4, 25% CaF_2, 5% Na_3AlF_6, 5% $CaCO_3$, 5% Na_2SiF_6. If the aluminium scraps as ingot were used to begin melting, the quantity added was 2…3% from treated alloy weight (2/3 of quantity was added into input material and 1/3 on the melting surface). If aluminium scraps used were non-processed the quantity was increased with 5…10%.

3. Results and discussions

The quality of the maste alloys is mainly influenced by the physical and chemical processes that are developed during the obtaining of the alloys. For determining the flow of the input components must be taken into account the fact that between aluminium and iron there is a large mutual solubility. There are the solutions with low melted temperatures, Figure 5. For this reason, the aluminium scraps were melted firstly and then steel scraps were dissolved into aluminium melted. For obtaining the FeAlMn alloys or FeAlMnSi, the FeMn or SiMn was also added. The flow of the input materials and the using of the aluminium scraps processed as a hot starting aluminium ingot lead to reducing of the energy consumption.

The alloys obtained were compact, gaseous inclusions are not present. Mainly, interactions between elements and oxygen or water vapour can occur during the process. The protection flux and degassing ensure the avoidance of reactions between elements and oxygen and also the dissolution of the gases. Due to the great thermodynamically activity of aluminium in respect to the oxygen, a compact oxide film (Al_2O_3) can be formed at the surface of the aluminium melted.

The presence of aluminium into bath protects all other elements as iron, silicon, manganese for interaction with oxygen. Even if another element was initially oxidised, the regeneration occurs at increasing of the temperature ($MeO + Al \rightarrow Me + Al_2O_3$ where Me = Fe, Mn, Si). The element returns from slag into melting bath.

The knowledge about phase equilibrium is essential as application of aluminum based alloys. The microstructures presented in Figure 2-4 are in accordance with the equilibrium diagrams. For the Fe-Al alloys, the binary phase diagram is shown in Figure 5. In the composition range from 0 to about 54 at.% Al four solid phases exist. The solid solubility of Al in f.c.c. γ-Fe is limited to 1.3 at.%. In contrast, in disordered b.c.c. α-Fe (A2) up to 45 at.% Al can be dissolved depending on temperature. Between 0 and 54 at.% Al two ordered compounds exist. $D0_3$-ordered Fe_3Al is stable at compositions around 27 at.% Al below 552°C and B2-ordered FeAl (α_2) occurs between 23 and 54 at.% Al again depending on temperature. In addition lines are shown for the Curie temperature (T_c), for the different modifications of FeAl (α_2) and the area in which the so-called ‘K-state’ is observed.

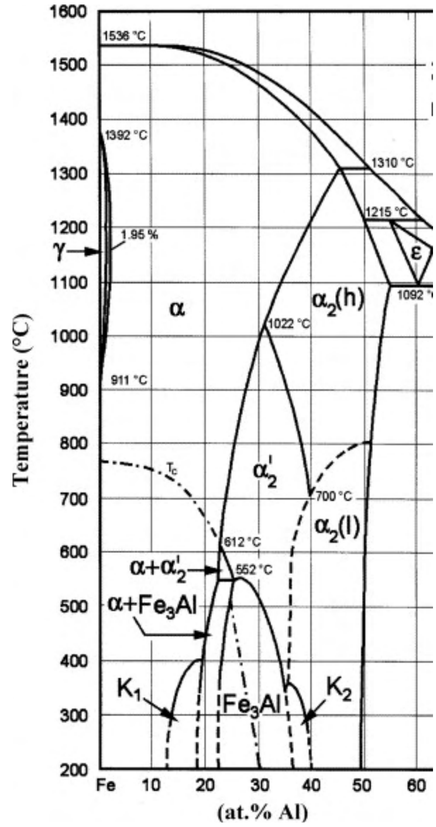

Fig. 5. *Fe-rich part of the Fe–Al system [9, 10]*

For alloys to about 30%Al, the structural researches of this alloys show the presence of the joint region $\alpha+\beta_2$ (β_2 is α_{2n} phase) that has at the boundaries the ordered phases α and β_2. For the alloys obtained, α solid solution, ε + ξ eutectoid and, the ξ compound with dendrite form are present.

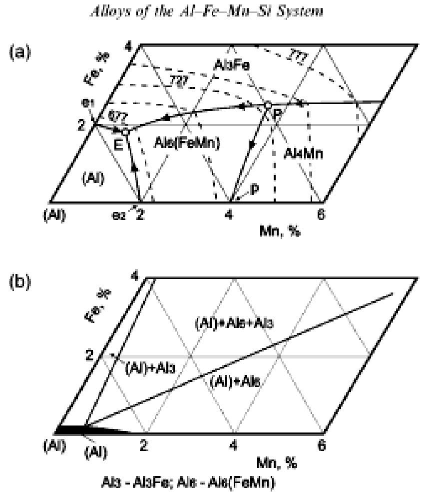

Fig. 6. *Phase diagram of Al-Fe-Mn system: (a) liquidus and (b) isothermal section at 627^{0}C [11].*

The phases in specific Fe-Al-Mn systems are not yet clear. For the aluminium corner of the Al-Fe-Mn ternary system, only two phases - Al_3Fe and $Al_6(FeMn)$ – can be in equilibrium with (Al), Figure 6 and Table 3 [11].

Manganese substitutes the iron in the Al_6Mn phase, up to $Al_{12}FeMn$ 12.85%Fe, 12.64%Mn). The limit solubility of manganese in Al_3Fe compounds to the formula $Al_3Fe_{0.88}Mn_{0.12}$ (4-5% Mn). The phase $Al_6(FeMn)$ has an orthorhombic crystal structure (which is isomorphic to the Al_6Fe and Al_6Mn phases). For FeAlMn alloy with about 20% Mn at high temperature between 1400 and 1500K, the binary structure $\alpha+\gamma$ is formed. Below 1150K the k phase appears (Fe_3AlC_x) and, the structure $\alpha+\gamma+\kappa$ is formed.

Table 3. *Invariant reactions in ternary alloys of Al-Fe-Mn system [11]*

Reaction	**Point in Figure 6.a**	**Temperature**	**Concentrations in liquid phase**	
			Mn	**Fe**
		$[^0C]$	[%]	
$L+Al_3Fe+Al_4Mn \rightarrow Al_6(FeMn)$	E	727	3.45	2.5
$L \rightarrow (Al)+ Al_3Fe+ Al_6(FeMn)$	P	654	0.75	1.75

The eutectoid transformation $\gamma \rightarrow \alpha+\kappa$ is developed and, κ is ordered at the boundaries of α and γ grains. In accordance with carbon content, the temperature of the eutectoid transformation is modified: for ~1% C at 1150K, the eutectoid transformation is passed at grain boundaries; at 1025K it is developed into γ phase grains; at 900K, eutectoid transformation is strong and the structure has α phase and some γ residual (it is disposed at grain boundaries and dispersed in the grains); below 900K is enhanced the separation of the κ phase that is concentrated at grain boundary of γ phase and dispersed into these grains and, simultaneous increased the α phase quantity, Figure 7.

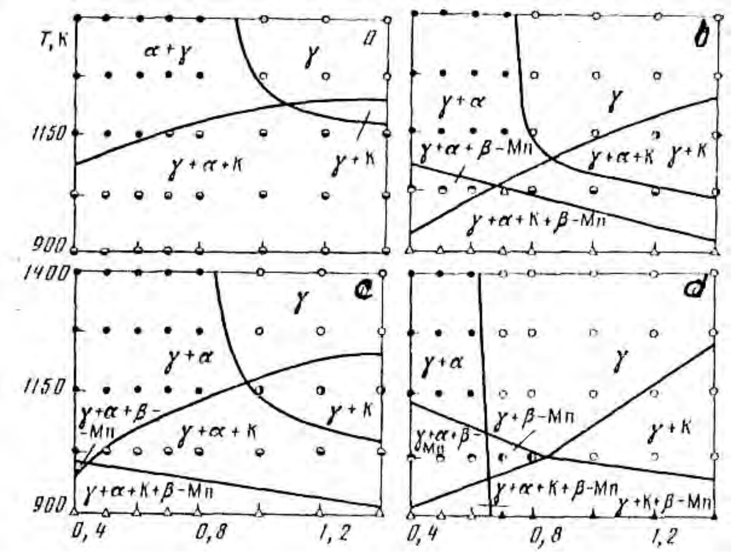

Fig. 7. *Section of the Fe-Mn-Al system (10%Al) for different concentrations of manganese: a. 20%, b. 25%, c. 30%, d. 35% [12]*

Up to 25 at.% Mn for alloy, the domain of the γ phase increases and, simultaneously the $\alpha+\gamma$ domain is decreased. Concomitantly the temperature for κ phase is decreased. Specificalfor these alloys is the presence of β_{Mn} phase. Between 1400…1025K, the structure has two phases $\alpha+\gamma$. At decreasing of the temperature about 900K, the structure passes into $\alpha+\gamma+\kappa+\beta_{Mn}$. κ phase is formed at grain boundary of $\alpha+\gamma$ phases and, β_{Mn} on the α grains surface, this is in accordance with the decreasing of the manganese solubility into α in respect to γ phase. The decreasing of the temperature leads to reduce manganese solubility and it is separated as free phase. The carbon content variation leads to decrease of the β_{Mn} phase and increase of the κ phase. For the alloys with 30% Mn, the γ domain is increased in respect to $\alpha + \gamma$ domain. The temperature for the κ phase separation is decreased and this for β_{Mn} phase separation is increased. The structure has 6 domains: γ, $\alpha+\gamma$, $\gamma+\kappa$, $\alpha+\gamma+\kappa$, $\alpha+\gamma$, $\alpha+\gamma+\beta_{Mn}$, $\alpha+\gamma+\kappa+\beta_{Mn}$. To alloys with 35% Mn has 7 domains: γ, $\alpha+\gamma$, $\gamma+\kappa$, $\gamma+\beta_{Mn}$, $\alpha+\gamma+\beta_{Mn}$, $\gamma+\kappa+\beta_{Mn}$ $\alpha+\gamma+\kappa+\beta_{Mn}$.

The equilibrium diagram of the Fe-Al, Fe-Mn and Al-Mn binary system correlated with the information previously presented shows the phases for the Fe-Mn-Al alloy obtained: solid solution, β_{Mn} + κ eutectoid and, ξ compound with dendritical form, Figure 3. For the FeAlMnSi alloys, the structure is formed by α solid solution and free silicon and iron. Also, the complex phases Fe_5Si_3, $Al_5Mn_{12}Si_7$ and, Al_4Si_2Fe are present in the structure of the alloy (Figure 8) [13].

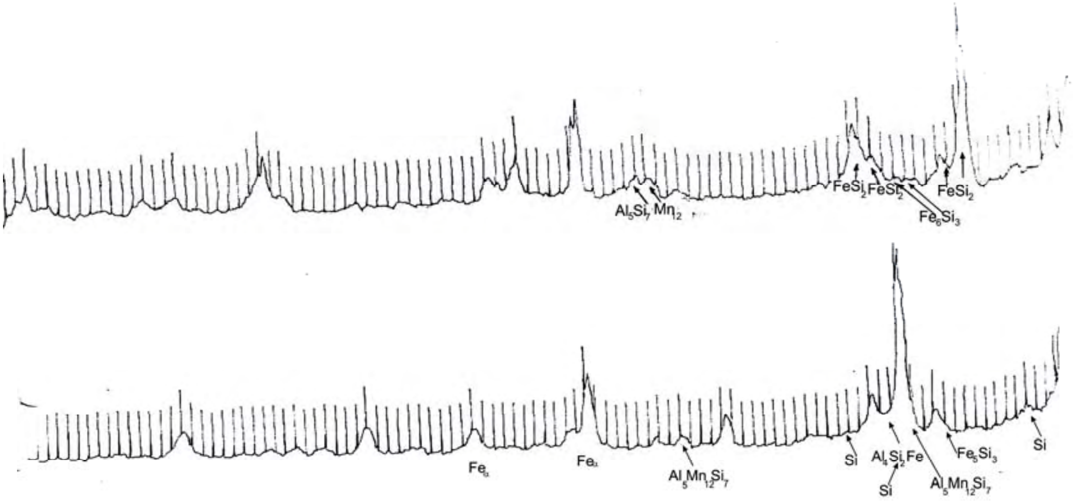

***Fig. 8.** Diffraction analysis of the FeAlSiMn alloy*

4. Conclusions

A solution is proposed for superior recycling of the aluminium and steel scraps. Improving of the quality of the recycling will become more important for the market of the aluminium scraps and for its users. For steel industry, the utilisation of the complex deoxidisers based aluminium is enabling the removal and improvement of the composition and morphology of inclusions and, to modify the physical and chemical properties of the treated steels. For greater recovery ratio of elements into master alloys obtained by scraps the order of the input materials into crucible furnace is very important. The technology studied ensures the maximum recovery ratio and the reduction of the energy and raw materials consumption.

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