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SCRAP QUALITY AND METALLURGICAL EFFECTS ASSOCIATED WITH COPPER AND TIN AS TRAMP ELEMENTS IN THE CASTING STEELS

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ABSTRACT

The complex property requirements for steels make it essential that there is a thorough understanding of the influence of tramp elements on their properties. Surface aspects, metallurgical structure, mechanical properties (toughness, tensile strength hardness ...) and weldability are some examples of requirements for quality steels in correlation with these residual elements. An increased content of residual elements such as Cu, Ni, Sb, Sn, As… may deteriorate the final properties of steels.

These elements are introduced to steel using steel scrap in the steelmaking process. The recycled scrap can contain considerable quantities of impurities. For this reason the control of ferrous scrap is necessary in order to preserve the recycling rate at the current high level without sacrificing steel quality.

In this paper we discuss about copper and tin as particularly tramp elements in respect to their influence on the properties of the engineering steels and structure. For a lot of casting steels, we analyze these residual elements in respect to the tolerable contents. The possible synergic relations between other elements and these impurities are also considered. The sources and the effects of the residual elements were discussed as far as possible, in order to obtain accurate answers for practical situations.

KEYWORDS: tramp elements, copper, tin, scrap recycling, steel casts

1. General consideration

Copper and tin in steel are harmful to steel properties and for this reason these are called tramp elements.

The main source of copper and tin in the steelmaking processes is represented by metallic scraps.

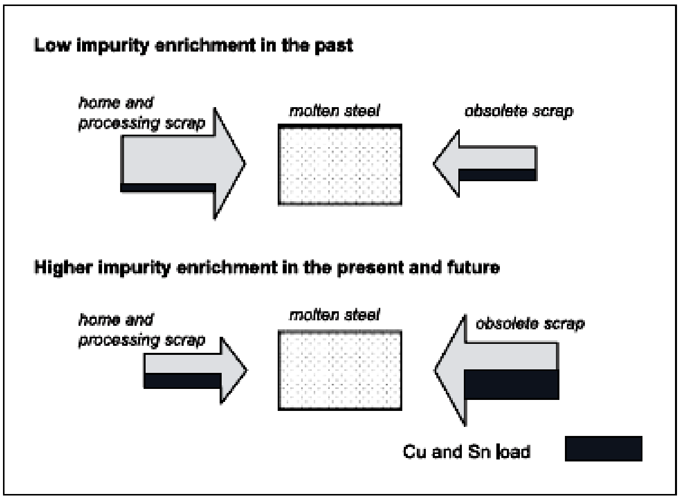

Fig.1. *Development of scrap material flow [1].*

Scrap becomes for the steel industry the single largest source of raw material because it is economically advantageous to recycle old steel into new steel. The impurity content largely determines the value of these resources.

Due to the disposal of a large amount of copper-containing steel scraps, the amount of copper-containing steel scraps is increasing day by day. Tin content in the steel circle increases at the same time. The development of material flow is schematically given in Figure 1.

Recently, the quantity of steel scraps such as waste automobiles and electronic appliances that contain copper wires, tin galvanized plate and other materials has spectacularly increased.

Moreover, over time they became part of the waste recycling cycle for the steel production without purification treatments. As result to these scraps recycling, the tramp elements accumulation in the scraps continuously increases. Also, in the steels that used these ferrous scraps, the content of these elements increases. Figure 2 shows the evolution of the copper content for the scrap and for the steels. This is the result of combining the technical information on the present purity of the scrap with an econometrical modelling.

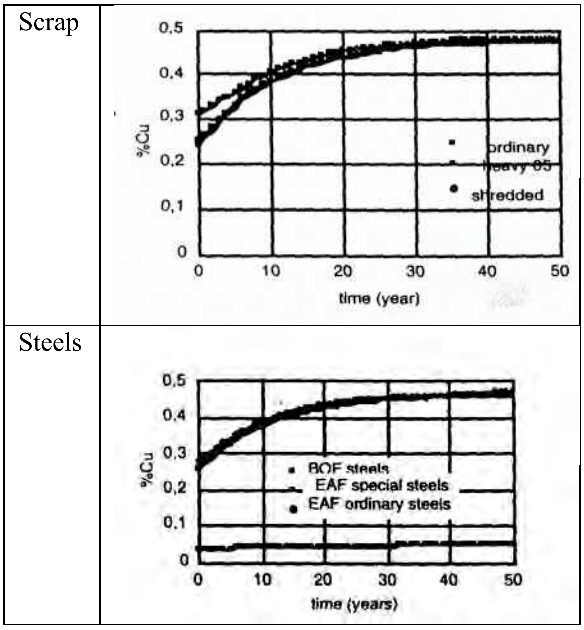

Fig. 2. *Evolution of scrap and steel quality at the time scale ranges over 50 years, 1995-2050 [2].*

Also, Figure 3 shows the results of projections of the level of copper and tin in obsolete scrap from 1985 until 2015 which are calculated in the case of Japan.

On the average, the copper level is expected to increase by 50 % over a 20-year period of time and the same conclusion applies to tin.

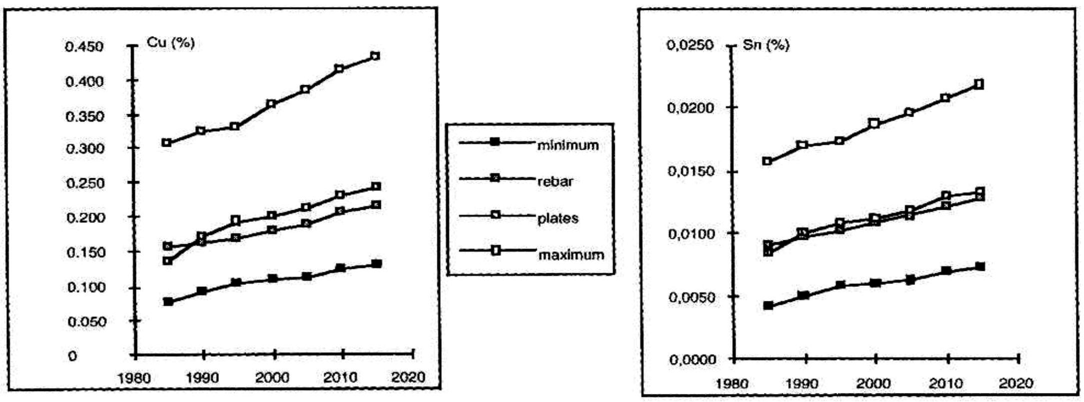

Fig.3. *Cu and Sn long term evolution in EAF steels as a result of tramp elements accumulation in the scrap deposit [3].*

The tendency of this evolution shows that the pollution of the scrap is inevitable. The steel quality is affected if the methods to remove copper and tin as tramp elements were not applied. The control and removal of copper and tin are necessary in order to preserve the steel recycling rate at the current high level without sacrificing steel quality. The methods for the purification of the scraps must be in accordance with the quality of the recycled scraps and the steelmaking process.

The techniques for eliminating the tramp elements can be divided into three groups: pretreatment of scrap by mechanical and chemical methods at different temperatures; elimination of the tramp elements during the preheating; elimination of the tramp elements on scrap melt or liquid steel. For the quality of the steels, the quality of scrap metal is an essential factor.

The input tramp elements reporting to the steel product must be severely restricted-especially for tin, copper, and zinc. This is essential because scrap, compared to other products, has specific characteristics. It has an unstable origin because it comes from a harvesting activity among a large number of producers, having very different structures, generally unknown to the consumer. Scrap is not a result of an industrial process [4].

On basis of the classical Quality Assurance Systems were established and imposed the scrap specifications.

The Romanian standard in relation with the quality of the steel scraps is SR 6058-1 from April 1999 „Ferrous materials for remelting" [5].

In the international standards, scrap quality is defined quite simply by two families of parameters, physical and chemical. The geometry and size of the scrap define the class of physical parameters. More important are the chemical parameters which are defined in terms of iron and tramp elements contents.

The value for the maximum allowable contents of tramp elements in recycled scrap is essential for the standard specifications. In the new European scrape code, impurity levels are specified for the different scrap families. The measurable criteria are used there for defining the residual elements like Cu, Ni, Cr, Mo, Sn. The limit value for copper that is established by European Steel Scrap Specification is ≤ 0.25 %wt for category E3 scrap and ≤ 0.4 %wt for category E1 scrap. More content (≤ 0.5 %wt) is specified for incinerated shredded scraps (category E46 scrap). Also the limit values for tin content are the following: ≤ 0.010 %wt for obsolete scraps (category E3 scrap) and ≤ 0.070 %wt for category E46 scrap [6]. There are two forms of copper that is present in the scraps: the copper as parts mixed with steel scrap and copper in the dissolved state. The contamination of the scraps with copper parts are specific for the obsolete scrap. The content of tramp elements in these scrap varies in a large scale, Table 1.

Table 1. *Typical composition of the obsolete scrap from varied source, %wt [7]*

Source	Shredded scrap	Urban incinerator	Cryo shredded
Cu	0.230-0.430	0.304-0.980	0.169-0.275
Sn	0.027-0.042	0.032-0.140	0.022-0.033

Usually, the obsolete scrap consists of iron and steel products discarded after the end of their service life. After their processing by shredding, a mix of steel and copper parts results. The presence of the copper in the metallic feeds of the steelmaking process is determined by incomplete separation of the components according to their nature. The second main source of copper is the scraps formed by high copper containing steels. In this case the copper is dissolved in the solid solution with the steel.

The sources of tin in the steelmaking processes are the coated components of the scrap. Tin is present as thin layers on the surface of the scraps such as beverage, cans and other packages.

2. Experimental method and materials

The variation of copper and tin content of the cast steel was studied. The samples were from varied steel grades used for the castings production at a Romanian steel foundry. An electric arc furnace is used for the steels making. In this paper we discuss about copper and tin as particularly tramp elements in respect to their influence on the properties of the steels. For a number of cast steels we analyze the content of these residual elements in respect to the tolerable contents. The possible synergic relations between other elements and these impurities are also considered. The sources and the effects of the residual elements were discussed as far as possible, in order to obtain accurate answers for practical situations.

3. Results and discussions

The copper and tin are tramp elements for the steels analyzed. These are not alloying elements. The level of copper and tin into cast steels was presented by graphs. The frequencies of the measured copper and tin contents are given in Figure 4.

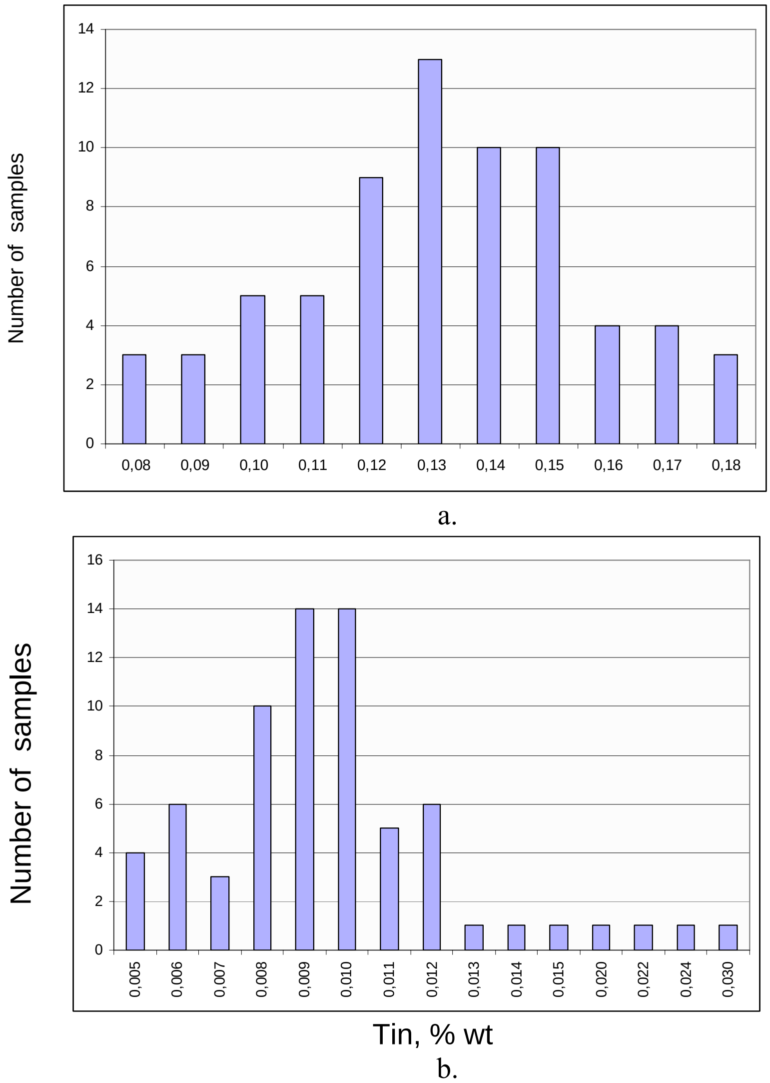

Fig. 4. *Tramp elements content of the cast steels: a. copper; b. tin.*

The origin of copper and tin in the steel samples are the scraps used into feeds for the steelmaking processes. In our cases, all feeds are composed of similar ferrous scrap. In the scrap yard of the foundry the scraps are not stocked or sorted after their composition. Also, it is not evaluated the steel scrap quality before feeding in the furnace. Only at the end of the melting period the chemical composition of the melting bath is determined. In this case, we can estimate that the quality of the ferrous scraps used as feeds for the steelmaking processes is comparable. As result, the copper and tin content for the steels analyzed varied in small scales. These are 0.08-0.18% for copper and 0.005-0.030% for tin.

Copper is wholly transferred to steel from scrap. Practically, copper is not found in steelmaking slag. The melting temperature of pure copper is much lower in comparison with steel (1083^{0}C). At typical steelmaking temperature which is over 1600^{0}C, the solubility of copper in the steel melt is practically unlimited. In comparison with iron, copper is characterized by a lower oxygen affinity. Accordingly, it is not removed by oxidation and transferred to the slag. Also, no essential copper content was found in the steelmaking dust. Unlike copper, tin is partially transferred to steel from scrap. Practically, tin is distributed between steel and dust. The melting temperature of tin is 232^{0}C. This is much lower in comparison with the temperature of the ferrous bath. In these conditions, most part of tin passes to the vapors form. This is found as oxides in the EAF dust. These are confirmed by the higher levels of tin (about 0.2…0.3% Sn) of the dust emitted in steelmaking processes [8]. Like copper, the solubility of tin in the steel melt is practically unlimited. As a result of the lower oxygen affinity, tin dissolved in the ferrous melting is not oxidized and transferred to the slag.

This element is not found in steelmaking slag. The average content of tin which is calculated for the steel samples analyzed is 0.01166%.

The values of copper and tin content must be discussed in relation to their influence on the properties and structure of the steels.

Copper and tin, like other residuals and alloying elements, can develop influence on metallurgical structure of the steels. In accordance with the type of the steel grade the elements develop varied micro- and macrosegregations: to grain boundaries, on free surface and to interfaces. As result of the structural modifications the copper and tin in steel are detrimental to various steel properties and these are tramp elements in relation to recycling steels. The effect of the contamination of the melt with tramp elements can be cumulative and irreversible. They can directly influence the mechanical properties of steel products.

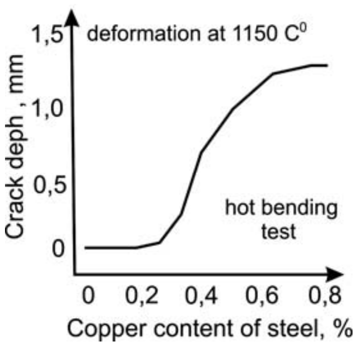

Fig. 5. *Relation between copper content and crack depth.*

The addition of some amounts of copper to iron based alloys during the smelting process is a well-known method of increasing their strength.

Upon heat treatment a fine structure of Cu precipitates in the iron matrix increased the strength of the alloy. Also copper contributes to the increasing of the corrosion resistance.

It is well known that small additions of alloying elements such as copper, chromium, nickel, phosphorus, and silicon lead to the development of adherent and protective rust on the steel during long-term atmospheric exposure.

However, copper is a key element related to surface defects which can appear during casting or hot rolling [1, 7]. The addition of copper to the steel cannot exceed 0.2% because it promotes cracking during the hot working process, Figure 5.

The surface cracks are in relation with the liquid phase that is formed at the grain boundaries above a certain temperature. With respect to its role in causing hot shortness (caused by a loss of hot ductility in the temperature range 1100-1300^{0}C), copper content should be kept below ≈0.1 %wt [1]. These conditions are in accordance with the solubility limit of copper in austenite or ferrite, Figure 6.

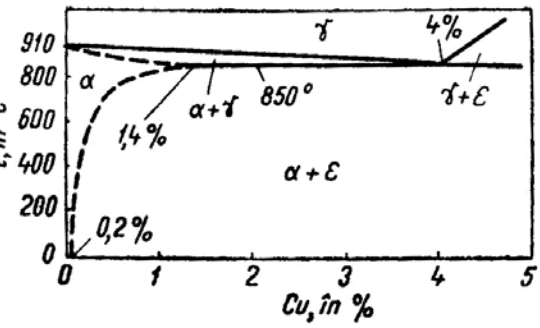

Fig. 6. *Diagram of the Fe-Cu binary system.*

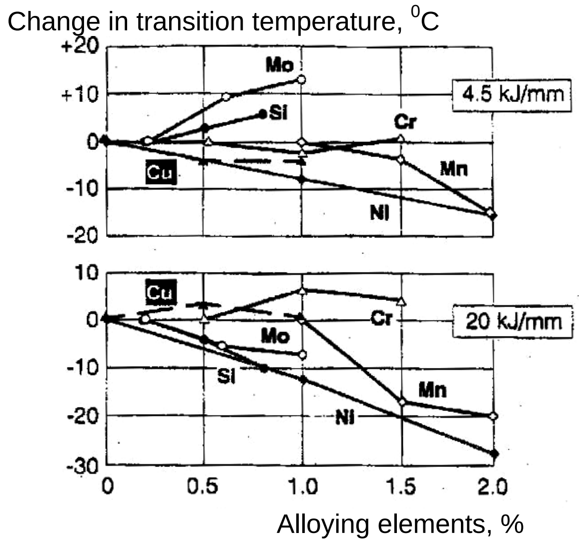

Fig. 7. *Effect of some elements on the transition temperature at fusion line for two different welding procedures.*

Copper has influences on the properties of the welded joints. This element impairs the toughness in heat affected zone or weld metal, Figure 7. Segregation of tin at grain boundaries has a more detrimental impact [7].

The copper, in the analyzed steel, does not exceed 0.2%: the maximum content is 0.18% and the average value is 0.1317%.

Sometimes, few fine cracking appeared on the surface of the steel castings in the critical zones at higher copper content and at the application of some thermal treatments.

The association of the elements in steel modifies the effect of copper: some elements amplify and others reduce or neutralize the negative effect of copper.

This is considered a synergism effect and is illustrated by empirical expressions called „copper equivalent" Cu_{eq}=%Cu+10%Sb+5%Sn+2%As-%Ni. The synergism effect of copper and tin on the hot shortness (by lowering the melting point of the Cu-Sn enriched zones) can be expressed by following equivalence: 0.4% Cu in steel exerts the same influence as the sum Σ(0.3%Cu+0.02%Sn).

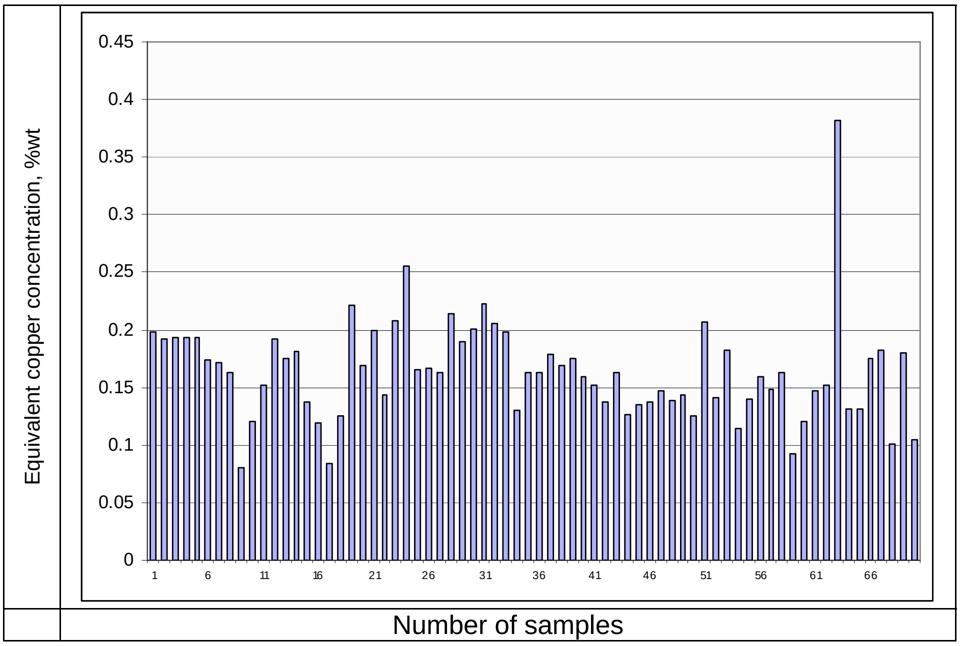

Fig. 8. *Variation of the equivalent copper of the steel samples.*

Also the sum Σ(%Cu + %Cr + %Ni + %Mo) must be considered and restricted for the casting and hot rolling of the steels: to maximum 0.13% for bar steel and 0.80% for thin sheet. We calculated the „copper equivalent" for the steels samples. The evolution of the „copper equivalent" for the steels samples is given in Figure 8. The values of the equivalent copper for the steels samples do not exceed 0.4%. At these values the probability to promote cracking on casts surface is lower.

4. Conclusions

The copper and tin content for the steels analyzed is within the tolerable limits. Only three samples have the copper content near the maximum value which is restricted for prevention of the surface defects. The tin content is lower than the admissible limit value in accordance with the steel quality. For the preservation of the steel quality we recommended the utilization of the scrap with controllable quality. Especially the restrictions for the copper and tin are necessary. This is imperiously necessary because the scraps originated in various and uncontrolled suppliers. It is necessary to apply the advanced method to control the quality of the scrap. Also, the methods for the preparation and the pretreatment of the scrap must be applied.

References

[1]. Savov, L, Volkova, E., Janke, D. *RMZ-Materials and Geoenvironment,* Vol.50, No.3, pp.627-640, 2003.

[2]. Birat, J.P., Huin, D., Le Coq, X., Roth, J.L., Lemiere, F., *La Revue de Metallurgie-CIT*, April 1995, pp.477-486

[3]. Sato, S., Takeuchi, M., Mizukami, Y., Birat, J.P., *La Revue de Metallurgie-CIT*, April 1996, pp.473-483

[4]. Wulff, S.W., *La Revue de Metallurgie-CIT*, Oct 1998, pp.1202-1208

[5]. *** „*Ferrous materials for remelting*" ASRO-Romanian Stadard SR 6058-1, April 1999

[6]. Baillet, G., Birat, J.P., Bobrie, M., *La Revue de Metallurgie-CIT*, Nov. 1996, pp.1185-1200

[7]. Marique, C., *La Revue de Metallurgie-CIT,* Nov. 1996, pp.1378-1385

[8]. Ciocan, A., *Valorificarea deşeurilor metalurgice. Procese şi tehnologii,* Galaţi University Press, 2008.