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Role of carbon in the melting copper processes

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Abstract

In the descriptions of technological processes melting and refining dominates principle of separate character behavior copper alloys in proportion to melting another alloys. Even, as in case of ferrous metals, about similar affinity to undesirable factors. The assumption of these opinions is the pose for main cause dissolubility of carbon in copper alloys and low relation as additional cause in majority these alloys poses as to oxygen. It results from this the row of conception as well as admitting to receive oxidative and the reducing conditions. Carbon in second method complies in direct contact with metal solution mainly. With analysis of thermodynamical factors it results that proprieties of copper and majority of her alloys responsiveness from oxygen at an angle of do not it run away from ferrous metals. The differences result with reason different range of temperatures of processing in liquid state mainly. In the work show, that opinions the leaning on it dissolubilities of carbon can be recognized (and only in approximation) only for copper about large purity. They do not concern it her mostly multiple alloys, at which the majority of alloy additions marks with possibility of creating carbides. Equally important the possibility of creating of carbides of accidental dirts is. The author's investigations show as on presence the even significant contents of carbon in some metallic phaze. The introduced in work analyses' and results of industrial tests investigations arrangement authorize acknowledgeable the reduction conditions diffusive the slag refinement from production the carbon - the nitrogen - the oxygen the for most rational. According to passed by author of model they come the perishable carbides from with easiness subject the dissociation in non - metallic electrolyte, contributively to actuation reductive influence. Introduced and investigation own arguments authorize to conclusion that the technological process of fusion of copper alloys does not it be to characterize in relation with separate guilds to different alloys and should to be to hold on valid in steel - makes principles.

Keywords: Carbon, Copper alloy

1. Introduction

The paper presents the analysis of metallurgical problems of copper refining. Slag extraction is commonly used in casting processes of copper melting in Polish foundry. According to the W. Nernst [1] principle of two non-mixing liquids a balance of concentrations takes place in liquid slag and refining copper. In this way non-metallic inclusions occurring in the refined copper are quickly extracted. However, there is a considerable discrepancy in the literature as far as the slag structure and its interactions with the refined metal.

The metallurgical processes taking place in real conditions involve interaction between metal atmosphere, liquid slag and liquid metal as well as non-metallic inclusions. Each of the mentioned above composites of the melting system has different properties. Their mutual interaction influence the change of the properties of the whole system. The analysis of metallurgical processes is usually limited to the chemical composition analysis of the slag formed in a result of the reduction process. However, no structure investigations have been attempted until now.

The thermodynamic analysis and laboratory investigations [2-4] have suggested that the aluminium silicate slag in reduction conditions are worth being given a special consideration. Considerable intensification of the reduction processes during introducing the carbide into the slag has been observed [3,5]. It has been reflected by the value of the reduction indicator. The intensification of the reduction processes proves that not only products of dissociation of carbides and reduced metal oxides are observed but also non-metallic inclusions. Authors [6] showed that the products can be analysed with the use of an electron microscope.

In the descriptions of technological melting and refining processes dominates principle of separate character behavior copper alloys in proportion to melting another alloys. It it was recognised generally [8-11], that carbon does not dissolve in copper. Develop this assumption on the copper alloys, which the majority of alloy component (Ni, Mn, Fe, Si, the Al) is the carbide elements. It concerns the additions and dirts also, mainly from secondary processing of scrap-metals

The presence of vestigial volumes of carbon in copper were confirmed experimentally [12,13]. In copper alloys the influence of carbon was been possible to find indirect proofs analysing the mechanical proprieties. Author's tests and numerous industrial investigations [14-18] shew even presence the significant contents of carbon in some metallic phaze. The microanalyses' of silicon bronze confirmed the clear contents of carbon [14], mainly by smelting in graphite crucibles. Was successful detectable contents of this element even to establish in copper industrial alloys with the tin, zinc, and lead [15].

2. Analysis of problem

It it was one should was accept in copper alloys the attendance of carbon in ionized form $[C_2^{2-}]$ – Table 1. According to molecular theory figure such determines in solution carbides.

The form of carbon as ion $[C^{2-}]$ it is however difficult acceptable, because element this having the building $1s^2 2 s^2 2p^2$ can create in solutions following ions mainly:

$$[C^-] \rightarrow [C^{2+}] + 3e \qquad (1)$$

$$\text{or} \quad \rightarrow [C^{4+}] + 5e \qquad (2)$$

Little probable are yet ion arrangements $\{C^+\} + 2e \rightarrow \langle C\rangle + 1e$ or $\rightarrow \{C^{4-}\} - 3e$. The latter possibility is inadmissible in slag because carbon would have to appear in configuration of helium. However the course of last reaction is the description of forming to soot black, there are observed on surface of crucible near mirror of refined metal, near at hand. Such figure of carbon can influence spot the atmospheres of fusion exclusively.

It thermodynamical analyses' for collected in table 1 carbides were moved from select oxides of copper alloys component (tab.2)

Table 1.
The thermodynamic analysis of the carbides possible [17, 18]

Element		Carbide		Gibbs energy	ΔG_T^o [J/mol]	
.	T_{melt} [K]		T_{melt} [K]	$\Delta G_T^o = f(T)$	1200, [K] (930°C)	1500, [K] (1230°C)
Al	933	Al_3C_2	1700	ΔG^o=-63330+22,7·T	-35700	-33900
		Al_4C_3	2000	ΔG^o=-21200+ 7,7· T	-14039	-11729
B	2303	$B_{12}C_3$ (B_4C)	2400	ΔG^o=-9920+ 1,33· T	-12750	-12500
		$B_{13}C_2$	2000		-8683	-82841
Ba	983	BaC_2	>1200	ΔG^o=-21400+ 0,5· T	-20935	-20785
Ca	1112	CaC_2	2570	ΔG^o=-14400 - 6,3· T	-22100	-22900
Ce	1583	Ce_2C_3	>1200	ΔG^o=-45000 - 3,5· T	-48255	-49305
		CeC_2	2500	ΔG^o=-14400-6,45· T	-26415	-28365
Fe	1809	Fe_3C	>1140	ΔG^o =2685 + 2,63· T	+5130,9	+591,9
Mn	1517	Mn_3C	1300	ΔG^o=-3330 - 0,26· T	-3572	-3649,8
		Mn_7C_3	1600	ΔG^o= -30500+5,0· T	-25850	-24350
Si	1685	SiC	1800	ΔG^o=-17460+1,83·T	-15758	-15209
Ti	1943	TiC	3450	ΔG^o=-44160+ 3,0· T	-4950	-40050
Zr	2125	ZrC	3800	ΔG^o=-47000+ 2,2· T	-44960	-44294

Over presented analyses' found affirmance in founders' opinions many times. It was affirmed the difficulties of procurance from alloys with the silicon, nickel, alluminium whether the iron the casts without gas blisters. Exchanged alloy additions create carbides. The increased content of carbon be moved also the porosity in melting of alloys with different additions (tab. 2).

Table 2.
The Results of the chemical analysis and the mechanical properties of the B555, B101 alloys

Alloy	Kind of crucible	[O] [ppm]	Porosity [%]	[C] [ppm]
B555 CuSn5Zn5Pb5	ceramic	12	1,1	0-10
	graphite	49	1,8	--
B101 CuSn10P	ceramic	10	0,7	0-10
	graphite	86	3,2	10-20

If more rathe desoxygenation such alloys did not accomplished deep, then reaction had to set (5). Numerous blisters were in cast effect. In the melting atmosphere the wide part of CO/CO_2 and the vapors of the component alloy (M') or their oxides (M'O) was observed . The author's test and industrial investigations shown the significant contents of carbon in some metallic phaze. The microanalyses' of silicon bronze confirmed clear contents of carbon, mainly near smelting in graphite crucibles (figure 1).

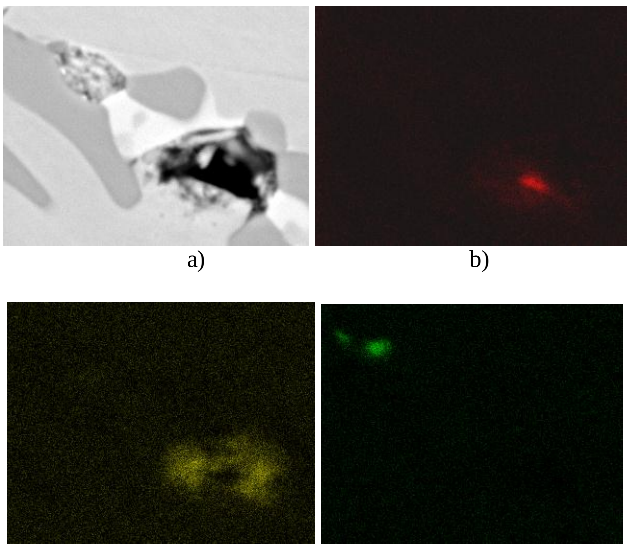

Fig. 1. Microanalysis of chosen components of bronze (a) the be drowned in graphite crucible BK331: b) - carbon, c) - silicon, d) - iron

In consequence after carbon dissolution in including oxygen alloy is possible setting reaction :

$$[C] + [O] = (CO) \quad (3)$$

It taking into account reactions 1 and 2, the figure of oxygen ions was put in to the liquid metals how $[O^{4+}]$ as well as $[O^{-}]$ [21]. It the possibility of setting reaction was put additionally (3). Because carbon (how in reaction 3) in solution of copper alloys come from carbides of alloy additions (mainly M'C), it can the total figure of ion reactions of carbon monoxides formation have figure:

$$[M'C] + [O] = [M'] + (CO) + 2e \quad (4)$$

With introduced reactions (3) and (4) it is possible to bring in, that possible is forming gas blisters - (CO). They can be one of main causes of casts porosity. According as with theory of segregation during solidification [19, 20] in layer diffusive comes to crossing of value of dissolubilities. It has similarly how in steel - makes in ingot moulds, this to lead to dissolved reaction carbon and oxygen (how at 4).

The oxygen can also react with the carbon in solid state, coming from for example from facings of stove. It melting near absence of oxygen in atmosphere such reaction were it been possible to record:

$$[O] + < C > = (CO) \quad (5)$$

In conditions of melting copper and her alloys (even with use of cover) the possibilities of direct desoxygenation solution of metal with the carbon are little effective (tabl.3,4)

Over presented analyses' found affirmance in founders' opinions many times. It was affirmed the difficulties of procurance from alloys with the silicon, nickel, alluminium whether the iron the casts without gas blisters. Exchanged alloy additions create carbides. The increased content of carbon be moved also the porosity in melting of alloys with different additions (tab. 3). If more rathe desoxygenation such alloys did not accomplished deep, then reaction had to set (5). Numerous blisters were in cast effect. In the melting atmosphere the wide part of CO/CO_2 and the vapors of the component alloy (M') or their oxides (M'O) was observed . The author's test and industrial investigations shew the significant contents of carbon in some metallic phaze [14-18]. The microanalyses' of silicon bronze confirmed clear contents of carbon, mainly near smelting in graphite crucibles.

It was it been possible like to expect the carburisations near usage the charcoal as components of saline refinig mixtures. It was presented in work [11]. To possibly also effect of gas porosity

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Table 3.
The thermodynamic analysis of the possible reactions the cooper alloys component oxides with the carbide. [10,11]

No	Equation of reaction	Calculated value ΔG^o	
		1200 K	1500 K
1	2	3	4
1.	$9C+2Al_2O_3 => Al_4C_3+6CO$	+ 869	+ 1223
2.	$3C+Al_2O_3=>3CO+Al.$	+ 710	+ 420
3.	$3C+Al_2O_3=>Al_2OC+2CO$	—	—
4.	$2C+2Al_2O_3=>Al_4O_4C+2CO$	—	—
5.	$7C+2B_2O_3=>B_4C+6CO$	+ 553	+ 810
6.	$3C+BaO_3=>2B+3CO$	+ 360	+180
7.	$3C+SiO_2=>SiC+2CO$	+ 169	+ 256
8.	$2C+SiO_2=>Si+2CO$	+ 350	+ 280
9.	$7C+7MnO=>MN_7C_3+4CO$	+ 1079	+ 1550
10.	$C+MnO=>Mn+CO$	+120	+ 40
11.	$3C+CaO=>CaC_2+CO$	+ 134	+ 205
12.	$C+CaO=>Ca+CO$	+ 300	+ 220
13.	$C+Na_2O=>2Na+CO$	+ 80	- 20

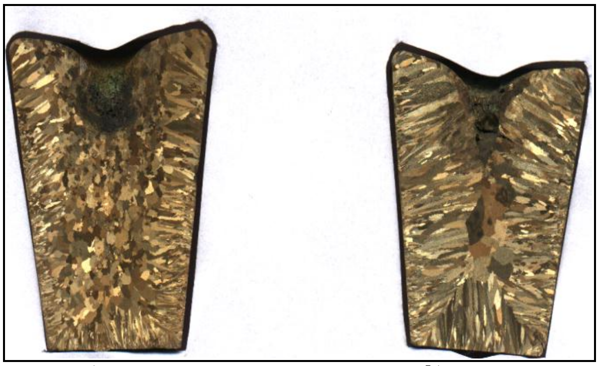
Table 4.
The Results of the chemical analysis and the mechanical properties of the B555, B101

Alloy	Kind of crucible	[O] [ppm]	[S] [ppm]	Porosity [%]	Loss of melting [%]	[C] [ppm]	Impact resistance [J]	Rm [Mpa]	A5 [%]
B555 CuSn5Zn5Pb5	ceramic	12	--	1,1	2,7	0-10	13,4	340	24
	graphite	49	--	1,8	3,7	--	--	--	19
B101 CuSn10P	ceramic	10	--	0,7	0,9	0-10	--	320	25
	graphite	86	--	3,2	2,7	10-20	24,0	256	--

On the basis of the thermo gravimetrical measurements an original methods, which modulates real conditions of reacting, was elaborated [1,9]. On the basis of this measurements system a method of interpretation the slag property was proposed. The method enables estimation of refining features of slag (S). In the experiments with derywatograph refined alloy is replaced with non-metallic inclusions (WN) in the melting pot. The inclusions are introduced into the slag in proportions which respond with the melting losses of the alloy. Al_2O_3 standard is proposed to be replaced with S+R (where R-reducer) refining sample. This made it possible to achieve thermal and mass effects concomitant with reduction reactions of WN which are is in the slag. The analysis of slag containing WN [4] allowed to establish the possible combinations of EW and r values together with a proposed explanation. On the basis of calculations it was also found that due to the differences in vaporisation or reaction with the atmosphere of compositions the simultaneous consideration of two values (r and EW) is necessary.

Proposed numerical indexes of EW and r are regarded as a measure of refining abilities of the whole system A-S-WN-R. It enabled optimisation of alternatives of WN interactions with carbides and carbide-originating metals in slag of various different chemical compounds.

It has been described the influences of same alloys compounds on the structure, properties and segregation effect of the ingot. The experiments on bronze melting with the slag refining proved



a) **b)**

Fig. 2. Probe - the macro (0,5x) of the industrial BK331 ingot before (a) and after (b) carbon-carbide slag (with the carbon powder)

that optimum is achieved. For example for silicon bronzes are selected refiner with calcium carbide, carbon and aluminium as the complex reagent (figure 2). The reducers of this kind not only make it possible to keep a constant deficit of impurities in the slag layer but also let carbon in the melting atmosphere. The efficiency of eliminating oxygen out of the melting atmosphere is much bigger – 10^{-6} –10^{-9} hPa oxygen partial pressure. The author slag constitution with the carbon reagents has been applied in metallurgical and foundry conduction.

The attendance of copper alloys additions (how Ni, Mn, Fe, Si, the Al, or impurities M') being creator the carbides makes up the principle it treatment the process of copper alloys melting how in steel manufacture (fig. 3).

It is allowed the different interpretation (less probable) - existence in such copper alloys only dissolved carbon. In result of attendance of iron, the silicon whether the aluminium (as well as the vestigial quantities of nickel) it is allowed the dissolubility of carbon and oxygen (without necessity of creating the compound's).

If so desoxygenation alloy does not it was accomplished deep, it has to set reaction (4) and then (5). Existence in cast plentiful of blisters is effect.

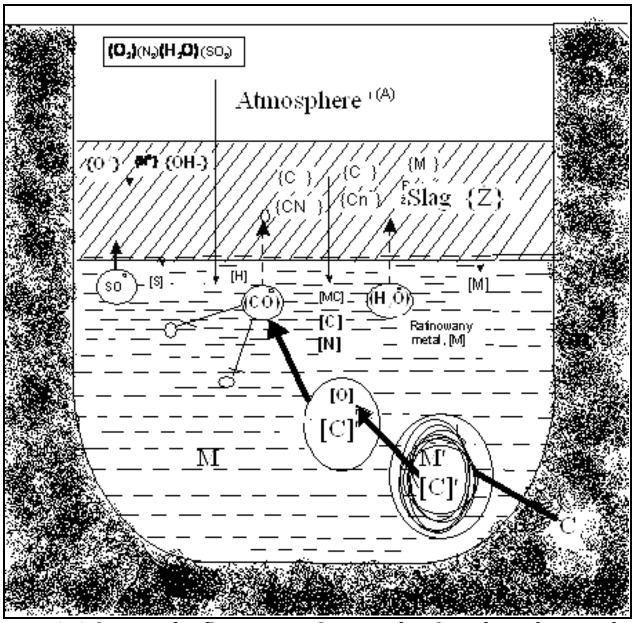


Fig.3 Schema of influences with part of carbon from facing of stove on the melting alloy

3. Summary and conclusions

The active components of melting atmosphere influence the processes taking place while slag refining An alternative for that methods is gas-slag refining in where the concentration of impurities extracted by the slag is obtained. Most of the experiments have shown that in this way is possible to achieve optimum economic and technological results.

On the basis of the analysis of the problem and the results of the author's research it is stated that the most promising are the reducing conditions of refining. In the previously works author has been presented scheme of interaction of chemical reagents in the melting copper conduction as: carbide compound, metal, cyjanamide or carbon. The paper presents the analysis of the ion reaction in to the slag during refining process with the metal carbide, oxygen, nitrogen and carbon. It proves that there is a big discrepancy in the opinions on the calcium and carbon role in the slag and their interaction with refined metal and the atmosphere of melting. Author shows on the most important role of the carbon $\{C^{2+}\}$ and $\{C^{4+}\}$ ions on the effectiveness of carbide slag metal extraction process.

It has been described the influences of same alloys compounds on the structure, properties and segregation effect of the ingot. The experiments on bronze melting with the slag refining proved that optimum is achieved. For example for silicon bronzes are selected refiner with calcium carbide, carbon and aluminium as the complex reagent. The reducers of this kind not only make it possible to keep a constant deficit of impurities in the slag layer but also let carbon in the melting atmosphere. The authors slag constitution with the carbon reagents has been applied in metallurgical and foundry conduction.

The analysis of responsiveness mechanism of interventions the non - metallic components in copper alloys fusion and spilling, of the forming of gas intruding it, leads to following conclusions:

- it is not proper the opinion about separate character of features of copper metallurgical alloys in relation to different alloys (mainly on the basis of iron, nickel or manganese),
- the presence of carbon in direct contact with majority of copper alloys, including particularly the solvent carbon components, it is invalid – lead to the cast porosity.

References

[1] W. Nernst, Nachrichten Geseltschafts Wissenschaft Góttinger Mathematik, B.1, (1906), p.13-24 (in German)
[2] J.O.M. Bockris, Trans. Faraday Soc., 52, (1956), p.17-21
[3] A. Bydałek, Chemii Process, No 10,(1971), p.27-30
[4] A. Yazawa, Y. Takedo, Metall. Review of MMIJ, vol.4, No.1, (1987), p.5358
[5] A.W. Bydalek, Journal of Therm. Analysis, vol.45, (1995), p.919-922
[6] A.W. Bydalek, W. Maziarz, Procedings IX Conf.of Electron Microscopy of Solids, 6-9 May 1996, Kraków-Zakopane, p.549-511
[7] A.W. Bydalek, M. Faryna, W. Maziarz, J. Morgiel, Procedings X Conf. of Electron Microscopy of Solids, 20-23 September 1999, Warszawa - Serock, p.303-306
[8] A. Krukowski, Podstawowe zagadnienia teorii procesów metalurgicznych,, PWN, Warszawa-Kraków ,1974 (in Polish)
[9] Mysik R.K., Porucznikow J.P., Cuchlew S.M.: Spilling under oxidative layer coppe, Cwet. Metałły, 11, (1989) 88-96 (in Russian)
[10] S. Rzadkosz, M. Kranz, P. Nowacki, M. Pękoś, The influence of interventions refining on structure and propriety of copper and her alloys, XXXII Konf. „Nowoczesne Technologie w Odlewnictwie", AGH Kraków (2008) 81-88 (in Polish)

[11] Z. Górny, J. Sobczak, Non-ferrous metals based novel maerials in foundry practice, ZA-PIS, Kraków, 2005 (in Polish)
[12] T. Nakamura, F.Noguchi, Y. Neda, Fire refinning of grude copper by alkaline cerbonate feluxes, Metal, vol.3, No 2, (1986) 102
[13] O. Kubaschewski, E. L. Evans, C. B. Alcock, Metallurgical Thermochemistry, Oxford, 1967
[14] K. Najman, W. Muszyński, A.W. Bydałek, The influence of refinement of bronze BK331 on his abrasion resistance, Archiwum Odlewnictwa, R. 4, nr 11, T. 2, (2004) 29--34 (in Polish)
[15] A. W. Bydałek, K. Najman, Fusion in reducing conditions silicon bronzes, Archiwum Odlewnictwa, R. 6, nr 22, (2006) 107—110 (in Polish)
[16] A. W. Bydałek, P. Schlafka, K. Najman, The results of copper alloys refining precesses in the reduction conditions, Archives of Foundry Engineering , Vol. 8, iss. 4, (2008) 219-223
[17] J. F. Elliot, M. Gleiser, Thermochemistry for Steelmaking, London, 1960
[18] A.W. Bydałek, The part of carbon in processes of extraction of slags during fusion of copper, Masinostroenie, nr 21, T. 2 (2005) 166-170 (in Russian)
[19] B. Chalmers, Principles of solidification, London, 1968
[20] K. Mamro, They steel deoxidation, Sląsk, Katowice, 1976 (in Polish)