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The analysis of carbon attendance in copper alloys as reason of gas porosity

A.W. Bydałek*
Polytechnic Institute, Public Higher Vocational School of J. A. Komeński in Leszno,
Al. Mickiewicza 5, 64-100 Leszno, Poland
*Corresponding author. E-mail address: abydalek@mckk.com.pl

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Abstract

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. 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, Porosity

1. Introduction

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 [1-4], 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 [5,6]. 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 [7-9] shew even presence the significant contents of carbon in some metallic phaze. The microanalyses' of silicon bronze confirmed the clear contents of carbon [7], 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 [8].

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:

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

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

Little probable are yet ion arrangements $\{C^{+}\} + 2e \rightarrow <C> + 1e$ 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 [10,11]

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

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 $[O^{-}]$. 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 [12,13] 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.2)

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 [7-9]. 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 [4]. To possibly also effect of gas porosity.

Table 2.
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 3**.**
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	--

3. Summary and conclusions

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.1,2).

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.

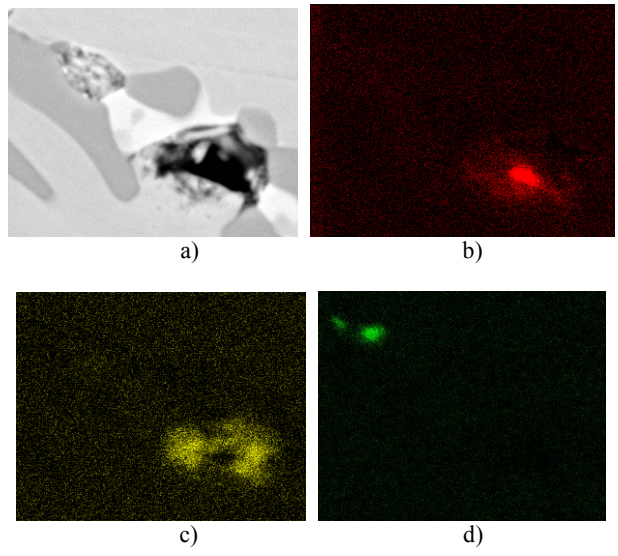

Fig. 1. Microanalysis of chosen components of bronze (a) the be drowned in graphite crucible BK331: b) - carbon, c) - silicon, d) - iron

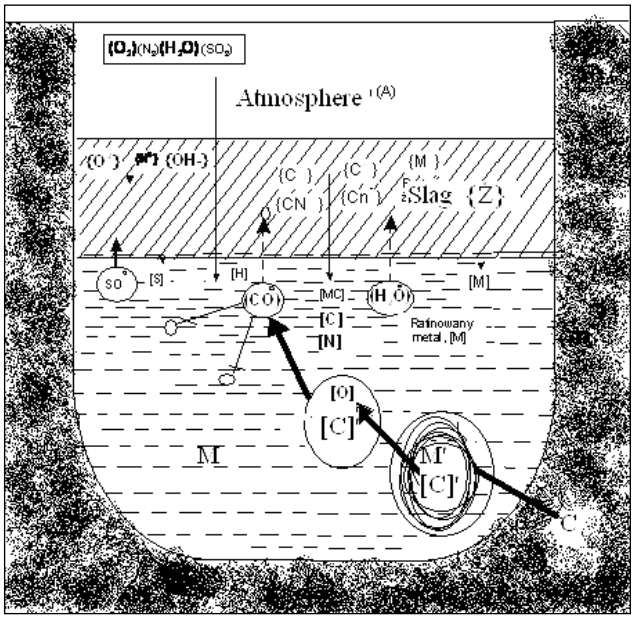

Fig. 2. Schema of influences with part of carbon from facing of stove on the melting alloy

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.

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