INTEGRATED EVALUATION OF EFFECT OF MAIN IMPURITIES ON WELDABILITY OF COPPER

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The wide application of commercial grades of copper, containing different impurities, in many fields of industry requires profound analysis of their influence on weldability. At the present work the integrated evaluation of effect of main impurities on copper susceptibility to formation of cracks and pores was made using electron-fractographic and X-ray analysis and also new methods, developed by the authors, for evaluation of tendency of copper to formation of solidification cracks. It is shown that simultaneous presence of different impurities in copper unlike the binary system of copper–impurity reduces its tendency to solidification crack formation. Content of 0.2 % Ni increases the crack resistance of copper. It was established that level of influence of low-melting impurities on crack formation in weld metal and near-weld zone depends on their distribution coefficient. It was for the first time established that low-melting surface-active impurities with a low distribution coefficient (K < 0.05) increase the tendency of welds to pore formation. The obtained results of investigations allow developing new consumables for welding of copper and its alloys. 15 Ref. 2 Tables, 3 Figures.

Keywords: copper, impurities, solidification cracks, pores, electron-fractographic and X-ray spectral analysis, distribution coefficient

The copper is widely applied in different fields of industry, including manufacture of welded assemblies and structures. The practical experience shows that copper in welding possesses an increased tendency to formation of cracks and pores [1–7]. Earlier, in collaboration with the Institute «Gidrotsvetmetobrabotka» (Moscow) the investigations of influence of harmful impurities on tendency to formation of cracks in weld metal on copper-impurity binary systems [7] were carried out. Some results of these investigations are presented in Figure 1.

In the present work the results of investigations of influence of different combinations of impurities (13 impurities within the limits of GOST 859–78 «Copper. Grades» for the copper M2) on tendency to formation of solidification cracks are given.

To carry out these investigations using method of mathematical planning of experiments the compositions of experimental melts of copper with different content of impurities were calculated. At the Institute «Gidrotsvetmetobrabotka» the ingots were melted, from which after

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Figure 1. Influence of impurities on crack formation in copper [7]

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	Content, wt.%										$K_{\rm cr}$, %, at $v_{\rm w}$, m/h					
Number of alloy	Bi	S	Pb	[0]	Р	Sb	As	Cd	Se	Те	Fe	Ni	Sn	14	8	6
201	0	0	0.005	0.01	0.01	0	0.01	0	0.005	0.005	0.05	0	0.05	27	14	6
202	0.002	0	0	0.01	0	0	0	0	0	0	0	0	0.05	21	9	5
203	0	0.005	0	0.01	0.01	0	0	0.01	0.005	0.005	0	0.2	0	23	8	0.5
204	0.002	0.005	0.005	0.01	0.01	0.005	0	0	0.005	0	0.05	0	0.05	41	20	11
205	0	0	0	0	0	0.005	0.01	0.01	0	0.005	0	0	0	26	12	8
206	0.002	0	0.005	0	0.01	0.005	0.01	0	0.005	0.005	0	0.2	0.05	42	22.5	0
207	0	0.005	0.005	0	0	0.005	0.01	0	0.005	0	0.05	0.2	0	31	0.5	0.5
208	0.002	0.005	0	0	0	0	0	0.01	0	0.005	0	0	0	42.5	3.5	2
209	0	0	0.005	0	0	0.005	0	0.01	0	0.005	0.05	0.2	0.05	31	6	6
210	0.002	0	0	0	0	0.005	0	0	0	0	0	0.2	0.05	29	7	6
211	0	0.005	0	0	0.01	0	0.01	0	0.005	0	0	0	0	41	14	6
212	0.002	0.005	0.005	0	0.01	0	0	0	0	0	0	0.2	0	23	5	0.5
213	0	0	0	0.01	0.01	0.005	0	0.01	0	0.005	0.05	0.2	0	27	0.5	0
214	0.002	0	0.005	0.01	0	0	0.01	0.01	0.005	0.005	0.05	0	0	44	4	5
215	0	0.005	0.005	0.01	0	0	0.01	0.01	0.005	0	0.05	0.2	0.05	51	9	0.5
216	0.002	0.005	0	0.01	0.01	0.005	0.01	0.01	0	0	0.05	0	0.05	44	16	13
41	Copper of grade M00 acc. to GOST 859–78									23	9	0.5				

Table 1. Calculation content of impurities and tendency of experimental melts of copper to crack formation

rolling into strips of 3 mm thickness the specimens of the type LTPM ($60 \times 25 \times 3$ mm) were cut out. According to the methods described in [7] the tendency of experimental melts of copper to formation of cracks in weld metal were evaluated. The chemical composition of experimental melts and results of tests are given in Table 1.

As is seen from the Table the mutual presence of different impurities in copper decreases its tendency to crack formation as compared to the copper-impurity binary systems [7]. It is especially noticeable on the example of melts 201, 202, 205, that, in our opinion, is connected with the formation of chemical compounds between the impurities (Bi₂O₃, Bi₂S₃, PbO, PbS, PbSe, PbTe, As₂Te₃, Cd₃As₂, CdSe, CdTe, Se₂Te₃, Sb₂Se₃) and, respectively, with decrease of their surface activity. The similar phenomenon is observed in welding of low-carbon steel, when introduction of oxygen into weld metal resulted in sulfur binding into low-melting oxysulfides, but here the surface activity of sulfur decreased and resistance to formation of solidification cracks increased. The presence of 0.2 % of nickel in copper (copper M2, M3 according to GOST 859–78) decreases considerably its tendency to crack formation (see Table 1, melts 203, 207, 212, 213) and its tendency to formation of solidification cracks is at the level of copper M00 (melt 41). In our opinion, this is also explained by the formation of chemical compounds of harmful impurities with nickel (NiO, NiSe, NiTe, NiSb, Ni₃P, NiBi).

To study the nature of crack formation, caused by harmful impurities, the electron fractographic and X-ray spectral analysis of structure and composition of crack surface was carried out. As is seen from Figure 2, a, cracks have an intercrystalline nature. At the surface of cracks in copper, containing harmful impurities (bismuth, sulfur, lead), the traces of liquid phase in the form of drop-like shaped branches, beads and dendrite crust are observed (Figure 2, b-d). In Figure 2, e the liquid interlayer, containing selenium is presented; in Figure 2, f the structure of crack surface on copper of grade M1 without introduction of any impurities is shown. The results of electron-fractographic analysis of crack surface evidences of crystallization nature of cracks forming in welding of copper.

X-ray spectral analysis of crack surface composition showed considerable (by one order and higher) enrichment of liquid interlayer with harmful impurities. It should be noted that the investigated low-melting impurities are the surface-active elements. This was shown by our calculations according to the criterion of Zhukovitsky ($\Delta \sigma = \sigma_{me} - \sigma_{im} >> 0$), and also experimental data [8–11] for some impurities (bismuth, lead, phosphorus, antimony). The mechanism of influence of harmful impurities on tendency to formation of solidification cracks, in our opinion, is connected with behavior of effect of adsorption decrease in ductility and strength (liquid-metal embrittlement) as a result of physical and chemical interaction of crystallizing liquid metal, enriched with harmful impurities with a solid phase. This is confirmed by an abrupt embrittlement action of molten bismuth in the contact with copper during tests at elevated temperatures. The same embrittlement effect is observed

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Figure 2. Typical intercrystalline character of cracks $(a - \times 100)$, structure of surface of cracks on copper, containing bismuth $(b - \times 1000)$, sulfur $(c - \times 600)$, lead $(d - \times 800)$, selenium $(e - \times 12000)$, and on copper M1 $(f - \times 800)$

at interaction of sulfur and other surface-active elements with nickel, copper and also alloy of nickel with copper [12].

To study the influence of some harmful impurities (bismuth, lead, phosphorus) on tendency of crack formation in the near-weld zone, the ingots of copper-impurity binary alloy with different content of mentioned impurities were melted in vacuum induction furnace at the E.O. Paton Electric Welding Institute. The alloys were preliminary rolled for strips of 5 mm thickness. The evaluation of experimental alloys was carried out according to the special methods developed by us [13] on «fish skeleton» specimens of a variable rigidity. The specimens were welded using tungsten electrode with partial penetration in argon at different energy inputs.

It is seen fom the test results (Table 2) that the most negative influence have bismuth and lead (cracks in near-weld zones are formed on cross and longitudinal notches) and phosphorus in the least degree, the negative influence of which begins to be revealed only at higher concentrations (>0.005 %). The correlation between the coefficient of impurity distribution and tendency to formation of near-weld cracks is observed, i.e. the lower it is, the more enriched will be grain boundaries with harmful impurity and, correspondingly, the tendency to crack formation will be higher.

Content of impurity, wt.%		Welding mode								
		$I_{\rm w} = 160$ A,	$v_{\rm w} = 17 \text{ m/h}$	$I_{\rm w} = 200$ A, a	$v_{\rm w} = 23 \text{ m/h}$	$I_{\rm w}=200$ A,	Κ			
		$n_{ m long}$	$a_{ m trans}$	$n_{ m long}$	$a_{ m trans}$	$n_{\rm long}$	$a_{ m trans}$			
Bi	0.001	+ + -		+		+ -	10 -	0.0001		
	0.004	+	13, 15	- +	15	+	- 13 -			
	0.1	+	10, 13, 15, 18	+	13, 15, 18	+	10, 13, 15, 18			
Pb	0.005	+	13	+	10, 13	+	10, 13, 15	0.01		
	0.01	+	13	+	15	-	13			
	0.05	+	10, 13, 15, 18	+	10, 13, 15, 18	+	10, 13, 15			
Р	0.005	_	_	_	_	_	_	0.2		
	0.05	+	_	+	10	+	10			

Table 2. Tendency of copper welded specimens to crack formation and equilibrium coefficient of impuritty distribution in them



The influence of bismuth and lead on porosity of welds on copper, containing 0.04 % P, was also studied. The results of tests of experimental specimens, welded using tungsten electrode in argon, showed that in absence of bismuth and lead the porosity is not observed, at 0.003 % Bi 10 pores were observed, at 0.003 % Bi and 0.03 % Pb 20 pores were revealed. Thus, bismuth and its mutual action with lead increase the porosity of welds even at their low concentrations. In our opinion, this is explained by the fact that due to low distribution coefficient of these elements in copper they sufficiently (as was mentioned above, are by one order and higher) enrich liquid metal at the solidification front and at the final stage of solidification. Being surface-active elements, they decrease surface tension of liquid copper and, thereby, reduce critical radius of gas nucleus:

$$r_{\rm cr} = \frac{2\sigma M}{\rho RT \ln (c/c_{\rm s})} [14],$$

which, in its turn, decreases considerably the work of its formation:

$$\Delta \sigma_{\rm cr} = \frac{4}{3} \pi r_{\rm cr}^2 \sigma.$$

Besides, low-melting impurities with small distribution coefficient due to concentration overcooling facilitates the formation of toothed (cellular) solidification front, that also increases the feasibility of pores origination. To compare the influence of impurities on pores formation below the values of equilibrium coefficient of their distribution are given, calculated by us according to the constitution diagrams of copperimpurity: K = 0.0001 (Bi); 0.02 (Te); 0.004 (S); 0.008 (Se); 0.01 (Pb); 0.01 ([O]); 0.036 (Cd); 0.2 (P); 0.35 (Sb).

The electron fractographic analysis showed (Figure 3) the presence of micropores (nuclei) forming in a liquid interlayer along the boundaries of crystallites under the influence of impurities with small distribution coefficient ($K \le 0.05$). At the presence of antimony (K = 0.35) and phosphorus (K = 0.2) in copper the pores were not revealed. It is obvious that phosphorus facilitates the suppression of pore formation as deoxidizer neutralizing the harmful effect of oxygen [15].

Conclusions

1. Study of influence of combined action of different impurities on tendency of copper to crack formation showed that simultaneous presence of different impurities in copper, including 0.2 % Ni, increases its resistance to crack formation that, in our opinion, is predetermined by formation of chemical compounds and decrease of surface activity of impurities.

2. The increased content of bismuth and lead in copper (within the limits of GOST 859-78) contributes to crack formation in the near-weld zone.

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Figure 3. Pores in liquid interlayer along the boundaries of crystallites in the presence of impurities with K < 0.05(×1250)

3. The level of influence of low-melting impurities on crack formation in weld metal and nearweld zone depends on their distribution coefficient.

4. It was for the first time established that low-melting surface-active impurities with small distribution coefficient (K < 0.05) increase tendency of welded joints to pore formation.

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