Study of the Kinetics of the Elimination of Hydrogen from Copper Alloys

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Abstract: The good quality of the castings out of copper alloys is related particularly to the interest which it is necessary to carry on the elimination of the hydrogen which exerts a negative influence on the properties of liquid alloys. The speed of the absorption of nitrogen and its elimination of liquid alloy decreases appreciably in the presence of low contents of active substances. In our work studies on the influence of certain factors are presented on the kinetics of the elimination of hydrogen starting from copper and its alloys. For the study one chose pure copper, copper with the additions of phosphorus 0.01 and 0. 04%, of tin 10% and nickel 10%, i.e. with components, having various surface activities.

Key words: Copper, absorption, kinetics, phosphorus

INTRODUCTION

Usually the longest process is the moment of the passage of hydrogen through the border separating alloy and gases.

The speed of the elimination of hydrogen is determined by total resistance of the transfer of gas in liquid alloy, its provisional passage through the surface of the phase separating and resistance from the evacuation of gas to surface.

The authors[1-3] consider that the additions of the agents superficially active do not exert an appreciable effect in the process of the elimination of gases, however in the studies[4] noticed, that the presence superficially of oxygen and sulphur in liquid alloys produces a considerable influence on the kinetic characteristics of absorption and desorption of nitrogen in iron.

MATERIALS AND METHODS

The alloys are prepared starting from the copper of purity of 99,99%, tin 99,9%, cathodic nickel 99,8% and the alloys mothers copper phosphorus with a content of 8% phosphorus. The fusion of alloys proceeded in a furnace, in which the heating is carried out using a tungstic reheating, of which the goal to draw aside any interaction of electromagnetic mixing.

For the study of the influence of the temperature on the release of hydrogen, fusion proceeded with a taking away of a sample of each alloy and that according to three values of temperature: 1200, 1300 and 1400°C in the case of pure copper, 1200, 1300 and 1350°C for alloys with

phosphorus and of tin, while for alloys with nickel is about 1300, 1350 and 1400°C.

Succession of the realization of fusions being like continuation: After the load of metal in the furnace one made vacuum 133.10-4 Pa. Then the furnace filled of hydrogen until pressure 1,06.105. after fusion metal was maintained at one duration of 40 min and that for the stabilization of the temperature and saturation equiponderate of hydrogen. Then starting from the furnace hydrogen is pumped until the residual pressure of 266Pa and one added afterwards in the furnace helium. The time of beginning of the pumping of hydrogen until the choice of the first sample is approximately two minutes. The second and the continuation of the samples the time of about thirty minutes with an interval of 1-2min. One quickly extracts the molten metal by quartz probes the assistance from a mechanism of lock then soaked to water. The content of hydrogen in the samples of metal is determined by the method of the vacuum melding.

RESULTS AND DISCUSSION

The results of the tests of fusion enabled us to build the kinetic curves of the variation of the content of hydrogen in copper and alloys during the process of degasification in Fig. 1 to 5.

During the process of degasification the content of hydrogen in liquid alloys approaches in an exponential way of the constant value, which is equal to the balanced solubility of hydrogen in metal at the studied temperatures and the pressure 266Pa.
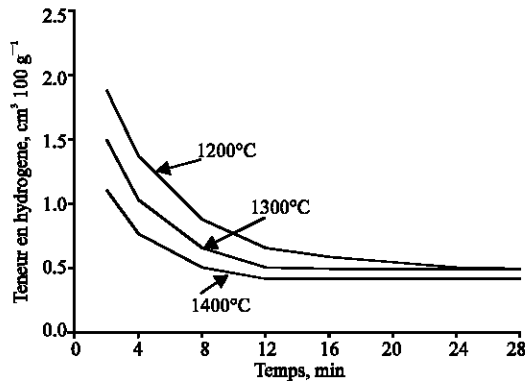
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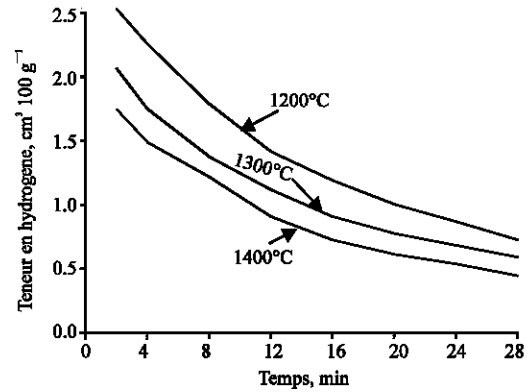Fig. 1: Variation of the content of hydrogen in liquid copper with pressure 266 Pa at the various temperatures
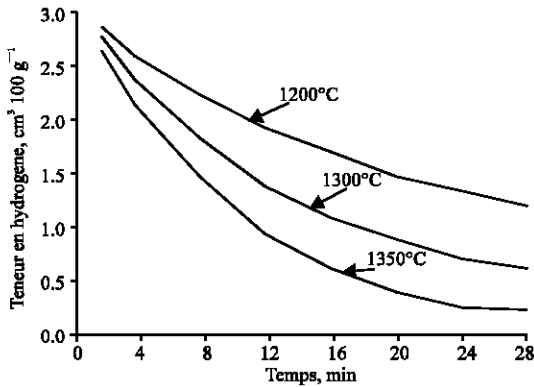
Fig. 2: Variation of the content of hydrogen in liquid alloy with pressure 266 Pa at the various temperatures
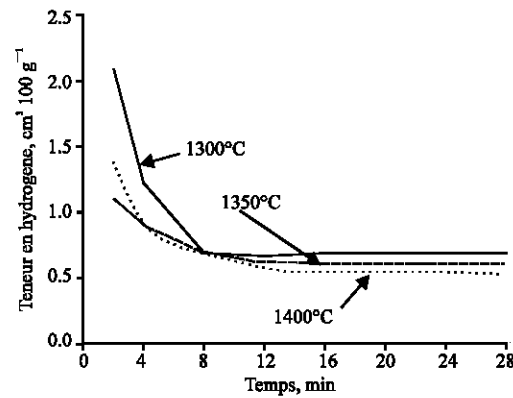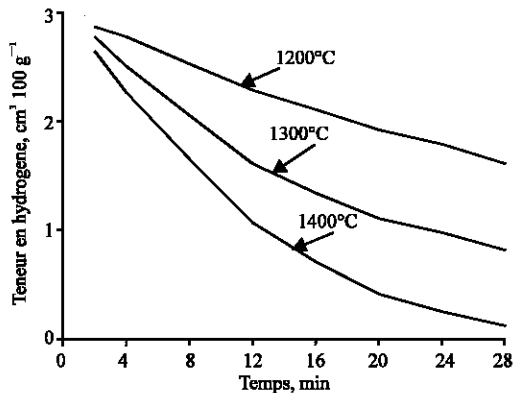
Fig. 3: Variation of the content of hydrogen in liquid alloy Cu-0,01%P with pressure 266 Pa at the various temperatures

The results of the analysis of gas of the sample of metal taken after 30min of degasification in $PH_2 = 266Pa$ and which corresponds to their value of the dissolubility of hydrogen in studied alloys are presented in Table 1.

Fig. 4: Variation of the content of hydrogen in liquid alloy Cu-10% Sn with pressure 266 Pa at the various temperatures

Fig. 5: Variation of the content of hydrogen in liquid alloy Cu-10% Sn with pressure 266 Pa at the various temperatures

Table 1: The process of degasification the content of hydrogen in liquid alloys approaches in an exponential way of the constant value, which is equal to the balanced solubility of hydrogen in metal at the studied temperatures and the pressure 266Pa

N°	Chemical composition of alloy	Température	Balanced solubility of hydrogen	Effective content of hydrogen
01	Cu	1200	0.36	0.56
		1300	0.46	0.50
		1400	0.5	0.50
02	Cu-0.01%P	1200	0.36	1.5
		1300	0.46	1.0
		1350	0.49	0.7
03	Cu-0.04%P	1200	0.36	1.85
		1300	0.46	1.35
		1350	0.49	0.87
04	Cu-10%Ni	1300	0.73	0.52
		1350	0.79	0.65
		1400	0.87	--
05	Cu-10%Sn	1200	0.76	0.60
		1300	0.34	0.5
		1350	0.37	0.4

The greatest difference between the concentration balanced and the real concentration (effective) of hydrogen even after 28 min of degasification took place in

the alloy Cu-0,04%P. In the alloy Cu-10%Ni balance is practically reached after 10-12 min of degasification. In spite of the sufficient duration of the time of the experiment, balance was not reached in the metal-gas system of alloys to phosphorus, which testifies the great influence to the kinetic factors on the processes of elimination of hydrogen.

Calculations the speed of the desorption of hydrogen by copper and alloys studied at the temperature 1300°C and the pressure partial of hydrogen (266Pa) according to the equation of Lingmur shows that, the calculated speed of degasification is three times more than speed obtained in experiments. Consequently, the desorption of the molecules of hydrogen on the surface of metal will not limit the process of the elimination of hydrogen.

It is obvious, that the speed of the elimination of hydrogen is defined either by the chemical reaction, or by the element of diffusion-absorption.

The results of the calculation of the constants speed of the elimination of the hydrogen of alloys are presented in Table 2.

As one notes it on Table 2, the constants speed of degasification at the constant temperature 1300°C are differed primarily by the presence from the allied components. Compared to the values of alloy of tin 10% the constant speed decreases by 2-3 times. The introduction of 0,01% and 0,04% of phosphorus decreases the speed of elimination (4,7-5,3 times). Cavity, this influence of weak additions of phosphorus on the constant speed of the elimination of hydrogen, is dependent that, phosphorus decreases the capacity of adsorption of copper compared to the hydrogen or, certainly, the degree of the filling of its surface.

Since phosphorus is presented in the form of an element of the active tension for copper, therefore on the surface of alloy it will have an absorption of the particles of phosphorus. According to data's of the experiment the variations of the surface tension of copper according to the concentration of phosphorus according to the equation of Gibbs define the adsorption of phosphorus. This adsorption is maximum with a content of 0,02% of phosphorus. In front of the increase in the quality of phosphorus in the volume of the molten metal its concentration in the surface layer remains almost constant, while the values of adsorption decrease because of the increase in the voluminal concentration.

For alloys of copper with 0,01 and 0,04% of phosphorus the surface concentration of phosphorus constitutes 10,3 and 13,2% respectively. Then the

Table 2: The constants speed of degasification at the constant temperature 1300°C are differed primarily by the presence from the allied components

N°	Chemical composition of alloy	Température	Constant speed of degasification C^{-1}x10^{-3}
01	Cu	1200	3.2
		1300	4.9
		1400	6.9
02	Cu-10%Sn	1200	1.2
		1300	1.52
		1350	1.74
03	Cu-10%Ni	1300	8.52
		1350	11.3
		1400	14.0
04	Cu-0.01%P	1200	0.50
		1300	1.03
		1350	1.58
05	Cu-0.04%P	1200	0.33
		1300	0.93
		1350	1.48

circumstance, that near maximum adsorption phosphorus occupies only 13,2%, us A makes it possible to suppose, that in the surface layer phosphorus is dependent in the form of the groupings with copper.

The results obtained make it possible to suppose that the compounds of phosphorus, prevent the passage of the hydrogen of the volume of metal to the surface layer, deteriorating this same redistribution of hydrogen between metal and the gas phase.

The introduction of nickel, cavity, does not change the limiting stage of the process. The increase in the energy of activation of the process of release of the hydrogen of the alloy Cu-10% nickel while appearing with pure copper is bound by the energy of activation of the elimination of hydrogen in the pure nickel which is of twice more, that in copper. The energy of activation of the viscous flow of the alloy Cu-10% of tin constitutes 50,3Kj mol^{-1}, however the value of the energy of activation of the process of the elimination of the hydrogen of this alloy is of 62Kj mol^{-1}, this testifies the limiting role to diffusion.

CONCLUSION

The results obtained make it possible to suppose, that the process of the passage of the hydrogen of the volume of liquid alloy on the border of metal-gas separation is divided into two stages: Diffusion through the surface layer evil stirring up of the molten metal and the passage through the surface of metal-gas separation on which can adsorb by the surface-active elements. In alloys, containing phosphorus, the passage of hydrogen through the surface of

separation of metal-gas separation, obviously a great value acquires, that the transfer of diffusion.

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