Experimental Investigations of Physical Properties of Iron-Copper Alloy

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Abstract. The paper describes the results of experiments aimed at obtaining iron-copper alloys with different iron content using electroslag remelting method. The obtained alloys of iron and copper were carefully examined to study their mechanical and physical properties. The article shows the results of the research work investigating the influence of iron on crystallization characteristics of the copper alloy. It was found, that iron-copper alloys can compete successfully with expensive copper-silver alloys, which are used to manufacture mold walls. The article offers the results of the experiments investigating hardness, wear resistance, thermal conductivity and temperature conductivity of the obtained iron-copper alloys; their casting characteristics were also studied.

1. General description of the problem under study

Modern industrial-scale process of continuous casting of steel puts forward new requirements to the materials used for mold walls of billet continuous casting machines; these materials must be able to withstand high temperatures for long periods of time, cyclic heat shocks and they must show minimum wear during operation.

At present, there are a number of methods to solve this problem: changes in the design of the mold, application of coatings on the mold walls, copper alloying with various metals of the necessary content \cite{1–4}.

Copper alloys with a small amount of alloying elements are used to produce molds; introduction of such alloying elements improves the ultimate strength, yield strength, hardness and recrystallization temperature \cite{3}.

In order to provide high thermal conductivity (more than 90\% of copper thermal conductivity), the concentration level of copper alloys must be very low. The increase in alloying element content does not result in any significant increase of the recrystallization temperature. Thus, the required combination of properties, such as high thermal conductivity and high temperature of softening in comparison with copper, can be achieved by alloying copper with a small amount of alloying elements \cite{5}.

Such alloys as Cu – Ag, Cu – Cr, Cu – Zr, Cu – Sn, Cu – Fe, Cu – Be, Cu – P, Cu – Fe – P, Cu – Sn – Zr, Cu – Cr – Zr and Cu – Co – Be are often used to manufacture mold walls.
To improve the tensile strength, thermal shock resistance and wear-resistance of a tube-type mold, it was suggested to introduce iron and phosphorus in certain proportions into the composition of copper alloy material of the mold. When 0.02-0.15 % of iron and 0.02-0.05 % of phosphorus is introduced into the alloy, a chemical compound of Fe₂P is formed, which strengthens the alloy.

As a result of comparative tests of a number of copper low alloys, it was recommended to use a nickel-copper-silver alloy as a material for mold walls, because this alloy showed higher mechanical properties, as compared with copper, copper-silver alloy and copper-zirconium alloy at high temperature as well as adequate thermal conductivity. Some properties of these alloys are given in Table 1.

| Property                  | Test temperature, °С | Copper-silver alloy | Copper-zirconium alloy | Nickel-copper-silver alloy |
|---------------------------|-----------------------|---------------------|------------------------|---------------------------|
| Tensile strength, MPa     | 20 300                | 20 300              | 20 300                 | 20 300                    |
| Yield strength, MPa       | 60 50                 | 420 300             | 150 –                  | 700 600                   |
| Hardness HB               | 500 380               | 1150 900            | 600 –                  | 2400 2000                 |
| Thermal conductivity λ, W/(m·degree) | 409 393 | 382 377 | 380 – | 196 262 |

As it was mentioned above, alloying with P, Ag, Cr, Zr and Fe as well as cold deformation are used to improve mechanical properties of copper at high temperatures. Copper alloyed with 0.02-0.05 % of phosphorus is commonly used for mold tubes. Its recrystallization temperature is about 350 °C, and the main properties of this alloy are given in Table 2. Copper alloyed with chromium (about 0.65 %) and zirconium has the recrystallization temperature above 500 °C, however, in this case, thermal conductivity of copper decreases by 15-20 %.

| Property                  | Test temperature, °C | 20 200 300 400 500 600 |
|---------------------------|-----------------------|-------------------------|
| Tensile strength, MPa     | 360 310 270 120 90 60 | 60                      |
| Yield strength, MPa       | 350 300 260 50 30 20  | 20                      |
| Relative extension δ, %   | 15 15 15 45 62 65     | 65                      |
| Relative broadening ψ, %  | 70 75 75 92 99 100    | 100                     |
| Thermal expansion coefficient α·10⁻⁶·°C⁻¹ | – 17.3 17.6 17.9 18.3 18.6 |

The main objective of this research work is to obtain an iron-copper alloy with improved performance characteristics, which will be used to manufacture mold walls for molds of billet continuous casting machines.
2. Results of experimental and theoretical investigations of obtaining iron-copper alloys

In the process of the alloy development, which will be used to produce mold walls, it should be taken into account that thermal conductivity of any material has a significant influence on the rate of outer skin growth of the solidifying ingot and on the operating temperature of mold walls.

In [3] it was suggested that the iron-copper alloy (containing 0.05-0.1 wt. % of Sn, 0.02-0.07 wt. % of Fe, 0.01-0.07 wt. % of P, the rest being Cu) may be used to produce molds. The mechanical properties of this alloy are 2-3 times higher than those of Copper 1 and Copper 2. It was found that at room temperature only 0.3 wt. % of iron can be solved in copper. At the same time, the obtained low copper alloy is an α-phase in the form of substitutional solid solution.

The cast specimens were used to study the microstructure of the alloys, the mechanical and thermophysical properties, which determine the qualitative characteristics of mold walls operating capacity.

The specimens containing iron within the solubility limit, that is, $c = 0-0.3$ wt. %, are characterized by a fine-grained structure. The majority of the grains have the form of a polygon with the average size about $d_m \approx 0.09$ mm. Besides, the average grain size decreases when iron content increases, which results in improvement of some mechanical properties of these alloys, for example, hardness. The hardness increases to 0.17 wt. % Fe.

Copper alloys with iron content $c \leq 0.3$ wt.% are single-phase crystalline substitutional solid solutions following Hume-Rothery’s rule. Thus, the conducted metallographic investigations of low alloyed iron copper alloys confirm that the amount of the alloying element, that is iron, has a significant influence on the size and shape of grains in the alloy.

Hardness can change considerably with the changes in the structure, phase composition of the alloy, temperature and different kinds of thermal and mechanical treatment. The hardness of the examined alloys with iron content within the range of $0 < c \leq 0.3$ wt. % is higher than the hardness of the alloys containing over 0.3 wt.% of iron. This difference in hardness of the alloys is explained by the fact, that during crystallization the alloys obtained in the first concentration range form hard substitutional solid solutions in $\alpha$–phase with finer grain, than in the second interval, where during crystallization of the alloys, ($\alpha + \beta$)-phases are formed with coarser grain.

The results of the analysis of wear resistance are shown in Figure 1. Each point plotted on the graph is the average value obtained on the basis of five measurements.

![Figure 1. Relationship between the wear resistance index of low-alloyed Cu – Fe alloys and iron content.](image)

From the diagram Figure 1, one can see that iron content increase to 0.3 wt. % results in sharp increase of wear resistance. If the iron content in copper increases even further, the value of wear resistance changes smoother. This can be explained by the fact that in the range of the concentration level up to 0.3
wt.%, saturation of solid solution of iron in copper reaches the solubility limit forming a substitutional solid solution, thus causing improvement of performance characteristics of the alloys, while further increase of the content does not seem reasonable.

The data of the experiments mentioned above show that alloying of copper with iron is reasonable to 0.3 wt. %. That is why the specimens № 1-6 were further examined in more detail. Differential scanning calorimetry method was used to determine the melting and crystallization temperatures. The results of the research are given in Table 3.

| Specimen number | Fe content, wt. % | Melting, °C | Crystallization, °C |
|-----------------|------------------|------------|---------------------|
|                 |                  | $T_{np}$ (beginning) | $T_{kp}$ (end) | $\Delta T = T_{kp} - T_{np}$ | $T_{np}$ (beginning) | $T_{kk}$ (end) | $\Delta T = T_{kk} - T_{np}$ |
| 1               | 0.065            | 1053       | 1083               | 30 | 1068 | 1052 | 16 |
| 2               | 0.086            | 1045       | 1089               | 44 | 1063 | 1045 | 18 |
| 3               | 0.097            | 1044       | 1091               | 47 | 1060 | 1043 | 17 |
| 4               | 0.17             | 1066       | 1086               | 20 | 1052 | 1041 | 11 |
| 5               | 0.28             | 1072       | 1095               | 23 | 1039 | 1034 | 5  |
| 6               | 0.3              | 1074       | 1098               | 24 | 1037 | 1033 | 4  |

It follows from the analysis of the data from Table 3 showing the temperatures of the start and end of melting and crystallization for low alloyed copper alloys Cu – Fe that:

– the temperature range $\Delta T$ (the difference between liquidus and solidus temperatures during melting) has different values: at $0 < c \leq 0.17$ wt. % of Fe, it reaches its maximum ($\Delta T = 47 \degree C$, at $c = 0.097$ wt. %), and further it decreases to 20 $\degree C$ at $c \geq 0.17$ wt. % and its value remains about the same;

– the temperature range of crystallization for the given iron content changes from the maximum of $-18 \degree C$ at $c = 0.086$ wt. % of Fe to 4 $\degree C$ with the increase of the iron content in the alloy.

Before the experiments, the specimens with the preset iron content were annealed at the temperature of 650 $\degree C$ for 8 hours. After that, they were divided into five sets. Each set of the specimens underwent deformation with different values of percent reduction, the step of reduction was 10%; they also underwent stepped annealing to the temperature of 400 $\degree C$. After annealing, the following parameters were measured:

1) the percentage change of resistance $\Delta R/R_0 = R_0 - R_m$, where $R_0$ is metal resistance at $T = 300$ K; $R_m$ – relative change in resistance after annealing;

2) Brinell hardness.

The results of the investigation of the relationship between $\Delta R/R_0$ and copper HB (copper 1) and the temperature for the preset value of the degree of plastic deformation are given in Figures 2 and 3.

From the analysis of resistance change in the process of annealing of the hardened Copper 1 (Figure 2), one can see that the value of $\Delta R/R_0$ in some temperature range does not change, then it drops monotonically from $T_{np}$ (the temperature of the start of primary recrystallization) to $T_{kp}$ (the temperature of the end of primary recrystallization), and after that when $T$ increases, $T_{kp}$ and $\Delta R/R_0$ reaches the value corresponding to the normalized (annealed) metal.

Figure 3 shows the dependence of Brinell hardness on the temperature of the copper specimens, which
do not contain any iron and which underwent preliminary plastic deformation to a certain value \( \varepsilon \).

The same experiments were carried out for low alloyed copper alloys with the following Fe, % wt. content: 0.097, 0.17, 0.28 and 0.3. The relationships between the hardness HB of these specimens and the reduction value are given in Figure 4. From the graphs in Figure 4, one can see that when the reduction value of the specimens with different iron content increases, their hardness also increases. Supposing that the dislocation concentration in the specimens with different iron content at the given reduction value is the same, then the increase in the hardness can be explained by a greater number of potential obstacles formed due to the impurity introduction. Their number increases with the increase in the concentration of the alloying element.

Thus, as a result of examination of low alloys of Cu and Fe, and on the basis of the obtained results, the research group can offer a number of recommendations for practical implementation:

1. In accordance with the set of physical and mechanical properties obtained in the process of examination of Cu – Fe alloys, the material of choice in the process of mold walls production is the alloy with the iron content within the range of \( 0.17 \leq c \leq 0.25 \) wt. % Fe.

2. In the process of mold walls production, they should undergo rolling of surface with a hard-alloy
roller providing mechanical stress, which is a bit higher than the yield strength of the used alloy. This will make it possible to improve the wear resistance of the wall by 10-15 % as compared with the unprocessed one.

The recrystallization temperature is not the only heat characteristic, which determines the durability of a mold. Its thermal and physical characteristics are just as important. That is why it is necessary to know how the iron content in copper influences its thermal conductivity and temperature conductivity.

To carry out the investigation of the thermophysical properties of low copper alloys, a number of specimens in the form of cylinders 12 mm in diameter and 16 mm in height were manufactured. Before placing them into the process chamber of the installation, all the specimens were annealed at $t = 650^\circ$C for 6 hours [9].

The results of the investigation of the dependence of the thermal conductivity and the temperature conductivity of copper and its low alloys on the temperature showed that thermal conductivity $\lambda$ and temperature conductivity $\alpha$ of pure copper decrease monotonically when the temperature increases, while these characteristics of low alloys increase monotonically with the temperature increase.

In the examined low alloyed copper alloys, the alloying element (iron) changes significantly the energy-band structure, where apart from the 4s-band, 3d-band is formed, where copper is solvent, which can result in general increase in the thermal conductivity when the temperature increases.

Thus, the obtained results of the investigation of the thermal conductivity and the temperature conductivity of low alloy make it possible to come to the following conclusions:

1) At temperatures $T < 400^\circ$C, Cu – Fe alloys have the thermal conductivity and the temperature conductivity, which are 1.5-2 times lower, than the thermal conductivity and the temperature conductivity of pure copper.

2) When the temperature increases ($T > 600^\circ$C), these parameters become very similar to the parameters of pure copper and even exceed them slightly. The mold walls made of copper alloy containing 0.17-0.23 % of iron will have satisfactory thermal conductivity at the temperature of 250-300 $^\circ$C.

3. Conclusions and results

On the basis of the results of the investigation, the following conclusions can be made:

1. The research group determined the liquidus and solidus temperatures of the processes of melting and crystallization of low Cu – Fe alloys, which depend on the iron content in these alloys.

2. All Cu – Fe alloys with the iron content of $\leq 0.3$ wt. % have a finer grained microstructure.

3. It was found that all low Cu – Fe alloys with the iron content $\leq 0.3$ wt. % have a 20% higher hardness, than Copper 1.

4. It was experimentally found that the temperature of primary recrystallization of low Cu – Fe alloys containing less than 0.3 wt. % of iron increased to $T_{pk} = 360^\circ$C.

5. The thermal conductivity and the temperature conductivity of low Cu – Fe alloys at temperatures of up to 400 $^\circ$C is 1.5-2 times lower, than these of pure copper, while at the temperature of $\geq 600^\circ$C, these characteristics are about the same.

6. The performed investigations proved that the low Cu – Fe alloys containing 0.17-0.3 wt. % of iron can be used for production of mold walls.

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