The Structure and Properties of Cast Iron Alloyed with Copper

A A Razumakov, N V Stepanova, I A Bataev, O G Lenivtseva, Iu Iu Riapolova and K I Emurlaev
Materials Science in Mechanical Engineering Department, Novosibirsk State Technical University, 20, Karla Marks ave., Novosibirsk, 630073, Russia
E-mail: stepanova@adm.nstu.ru

Abstract. Cast iron with 3 wt. % Cu was prepared by induction melting and casting in sand molds. The structure of the samples was studied using light microscopy (LM), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The addition of Cu promoted formation of pearlite and slightly decreased the volume fraction of graphite. No Cu inclusions were found by LM and SEM. The nanoprecipitations of ε-Cu in lamellar pearlite were observed by TEM. The properties of the Cu-alloyed cast iron were compared with the properties of cast iron not alloyed with Cu. The hardness of cast iron after alloying with Cu increased and the friction coefficient decreased in comparison with the reference sample.

1. Introduction
Generally, copper is not considered as one of the major alloying elements in steels and cast irons. However, the effect of minor additions of copper on mechanical and functional properties of ferrous alloys was reported in multiple studies (see review in reference [1]). Particularly, minor additions of copper (typically bellow 1 wt. %) significantly improve atmospheric corrosion of low carbon steels [2]. Copper is an important alloying element in high-strength low-alloy steels, which are widely applied in shipbuilding due to their high toughness and perfect weldability [1]. Additions of more than 0.6 wt. % of Cu to steel provides the effect of precipitation hardening during aging. Typical concentrations of Cu in HSLA steel is in the range of 1…2 %. Minor amounts of Cu (typically up to 1 %) are often added to ductile iron to increase the volume fraction of graphite [3]. And the content of Cu slightly above 1 % (e.g. 1.13 wt. %) in ductile cast iron induces formation of the predominantly perlite matrix with a large volume fraction of graphite particles and consequently improves hardness, and ultimate tensile strength [4]. From the above mentionedit follows that an influence of minor concentrations of copper on properties of ferrous alloys is studied relatively well. However, the effect of significant additions of copper on properties of iron is poorly reported in the literature. Due to this reason, this study describes the structure and the properties of cast iron with 3 wt. % addition of copper.

2. Materials and methods
The samples of cast iron were received by induction melting. At the first stage, low carbon steel and graphite were melted and liquid cast iron was produced. After that, commercially pure Cu and Al were added to the molten alloy. The melt was casted in sand molds at 1350 °C.
The elemental composition of samples was measured using an ARL 3460 optical emission spectrometer. Six measurements in different parts of the sample were taken to find the average values of concentrations. The structure of the samples was studied by light microscopy (LM) using a Carl Zeiss Axio Observer Z1m microscope, scanning electron microscopy (SEM) using a Carl Zeiss EVO 50 XVP microscope equipped with an energy dispersive X-ray (EDX) analyzer (Oxford Instruments X-Act), and transmission electron microscopy (TEM) using a Tecnai G2 20 microscope. The samples for LM and SEM were ground using SiC grinding papers and polished using a diamond suspension. Polished samples were etched with 5% nital solution. The samples for TEM were ground using SiC grinding papers before the thickness of 100 µm. After that the dimple was formed in the sample by a Gatan Dimple Gridner apparatus using fine alumina suspension. The final stage of TEM sample preparation was ion milling using a Gatan Precision Ion Polishing System.

The averaged hardness of the samples was estimated using a Brinell hardness tester at a load of 3000 kg. A 10 mm diameter quenched steel ball was used as an indenter. The microhardness of local zones was measured using a Vickers Woulpert Group 402 MVD hardness tester with a diamond four-side indenter at a load of 100 g.

The coefficient of friction was measured according to a disk-on-liner scheme using an II 5018 apparatus. The castiron sample was machined in the form of a ring segment (liner). The steel disk with hardness of 50 HRC and the diameter of 50 mm was used as a counterbody. Mineral oil LUKOIL 10W40 was used for lubrication. The test was carried out at 50 rpm. A load on the friction pair was gradually increased and the friction coefficient was registered at different loads. The convenient cast iron with low copper content (less than 0.1 wt.%) was used as a reference sample.

3. Results and discussion

The elemental composition of the sample, measured using the optical emission spectrometer is shown in Table 1. The cast iron sample alloyed with Cu and the reference samples had similar concentration of carbon and minor alloying elements, such as Al, Mn, Si, P, S, etc.

|                | C  | Mn | Si  | P  | S  | Ni | Cr | Cu  | Al |
|----------------|----|----|-----|----|----|----|----|-----|----|
| Referencesample| 3.13 | 0.53 | 0.26 | 0.017 | 0.016 | 0.04 | 0.04 | 0.09 | 1.05 |
| Cast iron with copper | 3.11 | 0.53 | 0.25 | 0.017 | 0.018 | 0.04 | 0.03 | 3.35 | 1.09 |

Figure 1 shows the images of unetched samples. It can be noticed, that the volume fraction of graphite after addition of approximately 3 wt. % Cu has slightly decreased. The results of the computer analysis of multiple images showed, that the average volume fraction of graphite in a sample, which was alloyed with Cu, was 7.5%, while in the reference sample it was equal to 7.9%. These data contradict to the results of Hsu and Lin [3], who showed that the minor addition of Cu promotes graphite formation in ductile iron. However, in the current research the concentration of Cu in cast iron was considerably higher in comparison with the experiment of Hsu and Lin.

Unalloyed cast iron had a ferrite-pearlite matrix (Figure 2a). The matrix of the alloyed sample was solely pearlitic (Figure 2b), which is consistent with common opinion, that Cu is a good pearlite former element in cast irons [5]. It is known, that Cu is an austenite stabilizer and increases the time of austenite decomposition [6]. During the continuous cooling at the time when pearlite transformation starts, the temperature of the copper-alloyed sample was lower in comparison with the reference sample. The diffusion of carbon at low temperatures is slower, which, according to conventional wisdom in the eutectoid transformation theory, leads to a decrease in the interlamellar distance of pearlite. Some decrease in the interlamellar distance in pearlite can be noticed in SEM images (Figure 3).
It is interesting to note, that according to the ‘Fe-Cu’ phase diagram the solubility of Cu in Fe at room temperature is below 1%. However, no Cu-rich inclusions were found using SEM or LM. TEM investigations revealed that copper concentrated in the pearlite fine structure in the form of nanoscale precipitations of an \( \varepsilon \)-phase (Figure 4). The \( \varepsilon \)-phase is a solid solution of Fe in Cu with FCC structure.

The decrease of interlamellar spacing and precipitation of nanoscale copper inclusions led to a noticeable increase of cast iron hardness. The Brinell hardness increased from 217 HB to 248 HB. The hardness of the pearlite increased from 330 HV to 368 HV.
The dependence of the friction coefficient on pressure is shown in Figure 5. According to the existed theory of lubricated friction, the curves, shown in Figure 5, can be divided into 3 parts corresponding to different stages of friction. At the first stage, when the pressure is not high (in this case below 3 MPa), the coefficient of friction rapidly drops down to ~0.01 and stabilizes at this level. At this stage the hydrodynamic lubrication occurs and the surfaces of the sample and the counterbody are separated with a layer of lubricant. At the second stage, the friction coefficient rapidly increases due to local discontinuity of the lubricant film. At the third stage, which is called the stage of boundary lubrication, the coefficient of friction stabilizes at a relatively high level and the continuous layer of lubricant does not exist anymore. At this stage, the friction coefficient depends not only on the properties of the lubricant but also on tribological properties of friction surfaces. The boundary lubrication is typical for heavily loaded friction elements, for instance, in sliding bearings. It follows from Figure 5 that a friction coefficient of Cu-alloyed cast iron is lower in comparison with the reference sample especially in the boundary lubrication mode.

4. Conclusions
1. Addition of 3 % of Cu in cast iron increases the hardness of the alloy and decreases the friction coefficient in the boundary lubrication mode.
2. The Cu in cast iron predominantly precipitates as a nanoscale ε-phase and as a consequence it is invisible for LM and low resolution SEM.
3. In the Cu-alloyed sample, the volume fraction of graphite is lower in comparison with the reference sample. The Cu alloying changes the cast iron matrix from ferrite-pearlite to purely pearlite.

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