Effects of aluminum and copper on the graphite morphology, microstructure, and compressive properties of ductile iron

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Abstract
The effect of aluminum (0, 2, 4, and 6 wt. %) and copper (0, 2, 4, and 6 wt. %) are investigated on graphite morphology, microstructure and compressive behavior of ductile iron specimens manufactured by sand casting technique. The graphite morphology and microstructure are evaluated using optical microscopy (OM) and scanning electron microscopy (SEM) equipped image processing software. To study the mechanical properties, the compression test is conducted on the ductile iron specimens. The results indicate the surface fraction and nodule count of graphite decrease by increasing the amount of aluminum from 0 to 2 wt. % and then, increasing from 2 to 6 wt. %. In addition, the nodularity of graphite increases by the increment of the aluminum amounts. By adding the amount of copper, the surface fraction and nodule count of graphite increase and nodularity of graphite decreases. The addition of aluminum and copper decreases the surface fraction of ferrite and increases the surface fraction of pearlite in the microstructure. By increasing the amounts of aluminum and copper, compressive stress vs. strain curves are shifted upwards, and modulus of elasticity, yield strength, maximum compressive stress and fracture strain improve. In comparison with copper, aluminum has a greater influence on the mechanical properties of ductile iron.

Keywords: Ductile iron, Copper, Aluminum, Graphite morphology, Microstructure, Compressive properties.

1- Introduction
Cast iron is a group of advantageous engineering alloys that can be applied in many structural and non-structural applications due to its attractive combination of properties such as low cost, high density, low melting point, good castability and machinability, excellent wear and corrosion resistance, high stiffness and compressive strength, exclusive thermal conductivity, and good vibration damping characteristics [1-3]. The industrial applications of cast irons can be increased by improving the mechanical properties [4,5]. The modification of the chemical composition, controlling the cooling and solidification rates during the casting processes, and the proper heat treatment, can improve the graphite morphology and the microstructure of cast irons, resulting in improved mechanical properties [6-9].

It is known that the heat treatment, especially austempering in gray and ductile cast irons, leads to an increase in the final cost [11,12]. Also, it is difficult to control the cooling and solidification rates in the sand mold casting techniques [13]. Thus, the modification of the chemical composition by adding the appropriate alloying elements is the best method to improve the mechanical properties and performance of cast irons [14]. Among the various categories of cast irons, the ductile irons have enhanced mechanical behavior due to the formation of nodular graphite [10]. It is shown the alloying elements have various effects on
graphite morphology, microstructure, and mechanical properties of ductile irons. Silicon is often regarded as a highly graphitizing element and prevents the chilling tendency and the precipitation of carbides in the microstructure [15]. Nickel, manganese, and copper are often recognized as austenite stabilizing elements and, due to high electrochemical potential, enhance the corrosion resistance of cast irons, especially austenitic cast irons [16]. In addition, proper heat treatment in cast irons containing nickel, manganese, and copper can improve the wear and corrosion resistance [17,18].

Adding copper to the cast irons improves the hardness and the strength [19]. Also, copper reduces the friction coefficient and, as a result, increases the wear resistance. The addition of large amounts of copper causes forming of the white cast iron and, consequently, the alloy becomes brittle and the toughness decreases [20]. It was reported that copper increases the rate of homogenous nucleation and the niobium leads to growth and, therefore, the crystalline structure is formed [21]. In cast iron-based bulk amorphous alloy, the minor Al addition enhances not only the glass-forming ability, but also the nanocrystallization behavior [22].

Adding aluminum to the cast irons reduces the amount of graphite and as well as the wear resistance at elevated temperatures [23]. Chromium improves the wear resistance by increasing the volume fraction of chromium carbide [24]. Adding low amounts of molybdenum results in the higher thermal conductivity and high amounts of molybdenum increase the precipitation and solid solution strengthening, thus improving the strength [25]. Although many studies are focused on the influences of the affecting factors on the microstructure, mechanical properties, and performance of the cast irons, the effect of 0, 2, 4, 6 wt. % of aluminum and copper is not investigated in ductile iron. The objective of this work is to study the effects of aluminum and copper additives on the graphite morphology, microstructure, and compressional properties of ductile iron.

2- Materials and experimental method
2-1- Materials and casting technique
In this study, ductile iron specimens containing different amounts of aluminum and copper were manufactured by sand mold casting method. Silica sand with 5 wt. % sodium silicate, as binder, was used in the molding process. The prepared molds contain cylindrical cavities with a diameter of 20 mm and a height of 200 mm. After molding, the mold surfaces were exposed to carbon dioxide gas and after the reaction of sodium silicate with carbon dioxide, the strength of the molds was enhanced. The schematic pattern and mold are shown in Fig.1. The raw materials used in this work are: mild steel scrap (0.25 wt. % C, 0.3 wt. % Si, and 0.5 wt. % Mn), ductile iron returns (3.43 wt. % C and 1.87 wt. % Si), carbon (90 wt. % C), ferro-silicon (0.5 wt. % C and 75 wt. % Si) pure copper (99.9 wt. % Cu), and pure aluminum (99.9 wt. % Cu). The molten iron was prepared using an industrial medium-frequency coreless induction furnace with a capacity of 1 ton (at Kaveh Steel Foundry). The power consumption of the furnace is 550 kW. In the melting process, carbon and silicon were added into the molten iron up to the appropriate amounts. The chemical composition of the molten iron is presented in Table 1.
The sandwich technique was applied to add magnesium to the molten iron and spheroidizing process with Fe-Mg master alloy (containing 8 wt. % Mg) was successfully performed. In this technique, the spheroidizing alloys are covered preferably with the steel sheet. Such a cover delays the reaction. Before pouring process, the molten iron was transferred into a graphite crucible and Fe-Si alloy (65 wt. % Si) was added to the molten iron for inoculation process. The inoculant is to provide the melt with seeds or nucleation on to which the solid phases grow during freezing as nodules. After removing the slag, the proper amounts of additional aluminum and copper were added into the crucible at different stages and the pouring process was performed at 1390 °C after spheroidizing and inoculation. Then, the cooling and solidification of castings were carried out in the sand molds. As a result, ductile iron specimens containing different amounts of aluminum and copper were manufactured after break the mold.

2-2- Graphite morphology and microstructure evaluations

Firstly, casting specimens were cut, hot-mounted, ground, and polished in accordance with standard metallographic procedures (ASTM E2567-11). To study the microstructure of ductile iron specimens, 2% Nital solution was used as proper etchant. The evaluations of optical microscopy were performed on the specimens (before and after etching) and metallographic images were prepared in various magnifications. The MIP™ image processing software was used to analyze the polished and etched microscopic images. In the optical images of polished surfaces, the morphology of graphite including the surface fraction of graphite, graphite nodule count, and nodularity of graphite were determined. In the optical images of etched surfaces, the microstructural parameters including surface fractions of ferrite and pearlite were measured. To determine the microscopic parameter using the image processing software, 10 images were used for each measurement.

2-3- Mechanical behavior

To determine the mechanical properties, compression tests were conducted on the ductile iron specimens containing various amounts of aluminum and copper. The compression tests were performed according to ASTM E9 standard using Zwick Z250 machine with a cross speed of 1 mm/min. To prepare the compressional specimens, the casting specimens were turned on a metalworking lathe using high speed steel cutting tool. The height and diameter of the compressional specimens were selected to be 15 and 10 mm, respectively. For each experimental condition, three ductile iron specimens were pressed, at least.
3- Results and Discussion
3-1- Graphite morphology

The graphite morphology (shape, size, surface fraction, distribution, and nodularity), which depends strongly on the chemical composition, has a significant influence on the mechanical properties of ductile cast irons [26]. It is known that spheroidizing the melted iron with reactive elements such as magnesium, calcium, cerium, and other rare earth elements leads to nucleation and growth of spherical graphite and, as a result, ductility and toughness of cast iron increase. As a spheroidizing agent, magnesium has more significant effect on the nodularity of graphite than other elements [27]. The optical microscopy images of as-polished ductile iron specimens containing different amounts of aluminum are shown in Fig. 2. The spheroidizing with magnesium successfully formed the nodular graphite with a relatively uniform distribution. It is found that the surfaces fraction of graphite, number of graphite nodules, and graphite nodularity depend on the addition of aluminum to ductile iron. The microscopic image processing results of the ductile iron specimens containing different amounts of aluminum are shown in Fig. 3. The results include surface fraction, nodule count, and nodularity of graphite. It is found that the amount of aluminum significantly affects the graphite morphology. By increasing the amount of aluminum up to 2 wt. %, the surface fraction of graphite (Fig. 3-a) and the nodule count of graphite (Fig. 3-b) decrease, and then, increase. Also, graphite nodularity increases by increasing the amount of aluminum. In ductile iron containing low amounts of aluminum, the formation of graphite is restricted and it reduces the surface fraction of graphite [23]. In the ductile iron containing high amounts of aluminum, aluminum is known as a graphitizing element. The effects of aluminum on graphite nucleation and growth is the same as silicon’s [28]. In addition, aluminum can positively affect the formation of complex silicates, which these particles are known as nucleation sites of nodular graphite [27].
Fig. 2. Optical microscopy images of as-polished specimens containing a) 0 wt. % Al, b) 2 wt. % Al, c) 4 wt. % Al, and d) 6 wt. % Al (at 100X magnification).
Fig 3. Effect of aluminum content on a) surface fraction of graphite nodules, b) nodule count of graphite, and c) graphite nodularity.

In the ductile iron, the copper amounts affect the morphology of graphite [29]. The optical microscopic images of as-polished ductile iron specimens containing various copper amounts are shown in Fig. 4. It is seen that adding copper to the ductile iron causes the formation of compacted graphite with nodular graphite. The observed compacted graphite is a short flake-like graphite particle with a vermicular or worm-like shape. The results of image processing, including the surface fraction of graphite nodules, nodule count of graphite, and graphite nodularity obtained for the ductile iron specimens containing various copper amounts are shown in Fig. 5. The surface fraction of graphite nodules and nodule count of graphite increase with increasing copper content. Adding copper to ductile iron decreases the graphite nodularity significantly. It is reported that in a ductile iron containing high amounts of copper (up to 1.5 wt. %), the copper islands are formed, and thin layers of copper are observed around the graphite nodules [30]. Also, the Mg$_2$Cu precipitates are detected in the ductile iron alloyed with copper [31].
Fig. 4. Optical microscope images of as-polished ductile iron specimens containing a) 0 wt. % Cu, b) 2 wt. % Cu, c) 4 wt. % Cu, and d) 6 wt. % Cu.
Fig. 5. Effect of copper content on a) surface fraction of graphite nodules, b) nodule count of graphite, and c) graphite nodularity.

3-2- Microstructural evaluations
The microstructural images of ductile iron specimens with different amounts of aluminum are shown in Fig. 6. It is observed that the microstructure of ductile iron contains the spherical graphite nodules distributed in the ferrite and pearlite. The graphite nodules are encircled by a thin layer of ferrite, known as ferrite halo around graphite nodules. This phenomenon happens because the regions around the growing nodules are decarburized as carbon diffuses and deposits on to the graphite nodules. Adding aluminum (from 0.48 to 2.11 wt. %) to the ductile iron decreases the size of spherical graphite nodules, nodule count increment and pearlite to ferrite ratio. It forms a relatively uniform distribution of graphite nodules in the microstructure. Also, the addition of aluminum can affect the eutectic temperatures and undercooling degree [32].
Fig. 6. Microstructural images of ductile iron specimens containing a) 0 wt. % Al, b) 2 wt. % Al, c) 4 wt. % Al, and d) 6 wt. % Al (magnification 200X, Nital 2%).

The variations of the surface fraction of ferrite and pearlite for the specimens with aluminum additive obtained from microstructural image processing are depicted in Fig. 7. It demonstrated that a higher amount of aluminum in the ductile iron cause a lower surface fraction of ferrite and higher surface fraction of pearlite. Aluminum affects the rate and the time of carbon diffusion. By increasing the amount of aluminum, the rate of carbon diffusion increases, and thus, more pearlite forms. In addition, an increase in the amount of aluminum causes the formation of aluminum oxide in the molten iron and, as a result, improves the rate of heterogeneous nucleation. It leads to an increase in the pearlite to ferrite ratio [33].
The microstructural images of ductile iron specimens containing different amounts of copper are shown in Fig. 8. The images indicated that the microstructure consists of nodular graphite and compacted graphite distributed in the ferrite, and pearlite. A thin layer of ferrite is formed around the graphite particles, and most of the graphite particles are completely surrounded by the ferrite. The addition of copper causes a significant change in the ductile iron microstructure and results in an increase in the pearlite to ferrite ratio [34, 35]. It can be related to eutectoid reactions. Fig. 9 shows the variations of the surface fraction of ferrite and pearlite in the ductile iron specimens with different copper amounts. Adding copper from 0 to 6 wt. % to ductile iron decreases the surface fraction of ferrite and increases the surface fraction of pearlite. By adding copper to ductile iron, carbon diffusion increases in austenite, and as a result, more pearlite can be formed compared to ferrite [31]. It has already been reported that the amount of pearlite increases sharply with increasing the copper content to 1 wt. % [36]. The SEM images and EDS results of ductile iron specimens without aluminum and copper, containing 4 wt. % of aluminum, and containing 4 wt. % of copper are shown in Fig. 10. In all microstructures, ferrite, pearlite and graphite nodules are clearly observed. Also, iron and carbon peaks are formed in the EDS results. Although in the ductile iron containing 1.5 wt. % of copper [30], the formation of copper islands in the microstructure has been previously reported, but in these results no phases containing aluminum and copper are observed.
Fig. 8. Microstructural images of ductile iron specimens containing a) 0 wt. % Cu, b) 2 wt. % Cu, c) 4 wt. % Cu, and d) 6 wt. % Cu (magnification 200X, Nital 2%).

Fig. 9. Effect of copper content on a) surface fraction of ferrite and b) surface fraction of pearlite.
Fig. 10. SEM micrographs and EDS results of ductile iron specimens containing a) 0 wt. % Al and 0 wt. % Cu, b) 4 wt. % Al, c) 4 wt. % Cu.

3-3- Compressional properties
Compressive stress vs. strain curves of ductile iron containing 0 to 6 wt. % Al and 0 to 6 wt. % Cu are shown in Fig. 11. The figure illustrates that adding aluminum and copper to the ductile iron specimens generally shifts the corresponding stress vs. strain curves upward, and the specimens endure greater stresses. The results obtained from stress vs. strain curves, including elasticity modulus, yield strength, maximum compressive stress, and fracture strain, are recorded in Table 2. The elasticity modulus, yield strength, maximum compressive stress, and fracture strain of ductile iron specimen without any addition of aluminum and copper are 20.46 GPa, 134.2 MPa, 348.6 MPa, and 2.49%, respectively. Adding aluminum and copper to the ductile iron leads to an increase in the modulus of elasticity. When 6 wt. % of copper and aluminum is added, elastic modulus increased to 47.63 GPa and 39.67 GPa, respectively. The yield strength, maximum compressive stress, and fracture strain are significantly improved by increasing aluminum and copper contents. It is noteworthy that the addition of aluminum has a more influence on improving the mechanical properties of ductile iron specimens compared with copper. It is known that the addition of aluminum and copper elements leads to solid solution strengthening [37]. In addition, with the increase in the nodule count of graphite, the...
mechanical properties of ductile iron can be improved [38]. It is reported that the copper prevents crack growth in low levels of applied stress [39], and improves ultimate tensile strength, yield strength, and hardness [31]. In austempered ductile irons, copper affects the amount of retained austenite, and consequently, enhances the impact energy [40].

![Graph showing compressive stress vs. strain curves of ductile iron specimens containing different amounts of aluminum and copper.](image)

**Fig. 11.** Compressive stress vs. strain curves of ductile iron specimens containing different amounts of aluminum and copper.

**Table 2.** Compressional properties of ductile iron specimens containing different amounts of aluminum and copper.

| Alloying element | elastic Modulus/GPa | Yield strength/MPa | Maximum compressive stress/MPa | Fracture strain/% |
|------------------|---------------------|--------------------|-------------------------------|------------------|
| Without Al and Cu | 20.46               | 134.2              | 348.6                         | 2.49             |
| 2 wt. % Al       | 41.31               | 179.4              | 752.6                         | 3.71             |
| 4 wt. % Al       | 44.36               | 182.6              | 796.4                         | 3.85             |
| 6 wt. % Al       | 47.63               | 188.8              | 874.5                         | 4.21             |
| 2 wt. % Cu       | 28.04               | 142.6              | 452.2                         | 3.27             |
| 4 wt. % Cu       | 36.78               | 149.8              | 488.4                         | 3.41             |
| 6 wt. % Cu       | 39.67               | 151.4              | 572.8                         | 3.67             |

4- Conclusions

In this study, ductile iron specimens containing 0, 2, 4, and 6wt. % of aluminum and copper were manufactured by sand casting technique. The graphite morphology, microstructure, and mechanical properties were investigated, and the following conclusions were made.

- The graphite morphology of the ductile iron was affected by the amount of aluminum and copper added to it.
- Adding aluminum up to 2 wt. % resulted in a decrease in the surface fraction and nodule count of graphite, while for amounts of greater than 2 wt. % they increase. By increasing aluminum, the nodularity of graphite increased.
- Copper increased the surface fraction and nodule count of graphite and decreased the nodularity of graphite. With increasing copper, the amount of compacted graphite in compared with nodular graphite increased.
Aluminum and copper affected the microstructure of ductile iron. With increasing aluminum and copper, the surface fraction of ferrite decreased and the surface fraction of pearlite increased.

Aluminum and copper had a significant influence on the mechanical behavior of ductile iron in compression. These additives could increase the modulus of elasticity, yield strength, maximum compressive stress, and fracture strain. The enhancing effect of aluminum additives on the compressive behavior of ductile iron was greater than copper additives.

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Captions of tables

Table 1. Chemical composition of the ductile iron, wt. %.
Table 2. Compressional properties of ductile iron specimens containing different amounts of aluminum and copper.

Captions of figures

Fig. 1. Schematic pattern and mold to manufacture different specimens.

Fig. 2. Optical microscopy images of as-polished specimens containing a) 0 wt. % Al, b) 2 wt. % Al, c) 4 wt. % Al, and d) 6 wt. % Al (at 100X magnification).

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Fig. 7. SEM micrograph of ductile iron specimen without aluminum and copper.

Fig. 8. Effect of aluminum content on a) surface fraction of ferrite and b) surface fraction of pearlite.

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Fig. 10. Effect of copper content on a) surface fraction of ferrite and b) surface fraction of pearlite.

Fig. 11. Compressive stress vs. strain curves of ductile iron specimens containing different amounts of aluminum and copper.