Influence of the composition ratio of manganese and copper on the mechanical properties and the machining performance of ductile iron

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In the present investigation, we studied the influence of the composition ratio of manganese and copper on the mechanical properties and the machining performance of a ferritic-pearlitic ductile iron. A series of Y-block specimens and stair specimens were casted using different manganese and copper levels. The experiments indicated that manganese can efficiently improve the strength of ductile iron, but the plasticity and machining performance decrease significantly when the manganese content exceeds 0.9%. To obtain high strength castings at low manganese levels, the Mn-Cu alloying treatment was also investigated here. The results indicated that with 0.6%-0.8% of Mn and 0.5%-0.8% of Cu, the tensile strength of ductile iron can be in the range of 600-725 MPa, the elongation can remain above 5.5%, and the machining performance is satisfactory. Furthermore, the distribution of manganese and copper in the ductile iron matrix was also investigated.

Keywords: Mn-Cu alloying, Ductile iron, Tensile strength, Average hardness, Elongation, Machining performance

Currently, ductile iron is widely used in industrial production because of its favourable mechanical properties and economic advantages over the general irons and steels[1]. The requirements on high strength and high toughness of ductile iron are increasing, and its producing technology has been an important field of research for several years.

The mechanical properties of ductile iron are largely determined by its metallographic structure. An appropriate balance of ferrite and pearlite in the ductile iron matrix can produce satisfactory strength and toughness[2,3]. In ductile iron production, the alloying elements (Si, Mn, Cu, Cr, Sn and Sb) are usually used to control the microstructure and to improve the mechanical properties of the material. Each alloying element doesn’t works independently and exhibits some complex interaction between them. Hence, the appropriate balance of the amount of the alloying elements must be carefully considered in the ductile iron production[4,5].

For further understanding the influence of the addition of manganese and copper on the mechanical properties and machining performance of ductile iron, a series of Y-block specimens and stair specimens were casted using different manganese and copper levels. Using these specimens, the tensile strength, average hardness, percent elongation, pearlitic content, microhardness distribution and surface maximum hardness difference were investigated. In addition, the distribution of manganese and copper in ferritic-pearlitic ductile iron was analysed.

Experimental Procedure

Materials

For decreasing the S and P levels, all of the pig iron was desulphurised and dephosphorised in the cupola and then casted into several pieces of 5 kg ingots. The primary chemical composition of the experimental iron ingots consist of 3.75% C, 1.35% Si and 0.2% Mn, and the contents of S and P are lower than 0.01% and 0.02%, respectively. To obtain good nodularisation, the FeSiMg5RE2 alloy was used in the experiments as the nodulizer because of its strong nodularising ability in ductile iron. The main chemical composition of the FeSiMg5RE2 alloy consists of 48.3% Fe, 4.5% Mg, 1.8% Re, 41.5% Si and 2.6% Ca. Meanwhile, the FeSi75 alloy was used as the inoculant to prevent the carbide formation and promote the separation of graphite during the solidification process. The main chemical compositions of FeSi75 alloy include 23% Fe and 76% Si.
Methods
The iron ingots were molten in the 80 kg medium-frequency induction furnace. The contents of the alloying elements were adjusted in the furnace after melting of iron. Next, the graphite was spheroidised in the casting ladle, and the stream inoculation method was used in the pouring process. In this case, the nodulizer and inoculant addition were 1.5% and 1.0%, respectively. The pouring temperature was limited within 1380°C to 1400°C. Several 25 mm Y-block specimens were casted, and the tensile test specimens were cut from the bottom portion of the Y-block specimens. The chemical compositions of the specimens are given in Table 1, and the schematic of a Y-block specimen and a tensile test specimen are shown in Fig. 1.

Results and Discussion
Effect of manganese
Mechanical properties
Manganese is a strong pearlite-forming element and is always added to ductile iron to enhance the strength, but the plasticity of ductile iron is usually unsatisfactory at high manganese levels. Thus, the manganese level should be limited within a suitable range in ductile iron to guarantee that the strength and plasticity simultaneously satisfy the strength and plasticity requirements. In practice, some empirical values are used to guide the manganese addition in the ductile iron casting process. For understanding the influence of the manganese content on the mechanical properties of ductile iron, a series of Y-block specimens with different manganese level were casted. The tensile strengths, percent elongation, average hardnesses and pearlite contents were obtained. A plot of both the tensile strength and the percent elongation versus the manganese content is shown in Fig. 2(a), and a plot of both the average hardness and the pearlite content versus the manganese content is shown in Fig. 2(b).

In Fig. 2, it is seen that the tensile strength, average hardness and pearlite content increase, but the elongation decreases with increasing manganese content in ductile iron. It is obvious that varying the Mn content from 0.8% to 0.9% increased significantly

| Table 1 – Chemical compositions of the Y-block specimens (wt%) |
|--------------------------|--------------------------|
| C                        | 3.53~3.78                |
| Si                       | 2.39~3.16                |
| Mn                       | 0.2~1.1                  |
| P                        | <0.02                    |
| S                        | <0.01                    |
| Cu                       | 0.03~1.0                 |
| Mg                       | <0.034                   |
| Mo                       | <0.03                    |
| Cr                       | <0.1                     |
| Ce                       | <0.23                    |
| Fe                       | balance                  |

Fig. 1 – Schematic of a Y-block and a tensile test specimen (units: mm)

Fig. 2 – The relationship between the tensile strength, elongation, average hardness and pearlite content versus manganese content (Cu%=0.05%)
the pearlite content and led to a critical mechanical behaviour of ductile iron. On the one hand, high strength and high hardness ductile iron can be produced when the manganese content is more than 0.9%, but the elongation is low in this range. On the other hand, if the manganese content is lower than 0.8%, high elongation can be achieved, but the strength and hardness of the ductile iron are not adequate. The metallographic images of ductile iron containing different amounts of manganese are shown in Fig. 3, and the strengthening mechanisms of manganese are different under low and high manganese levels in the ductile iron.

In Fig. 2(b), Fig. 3(a) and (b), the pearlite content increases only from 20% to 50% when the manganese content increases from 0.2% to 0.8%. In this case, ferrite is the major matrix phase in ductile iron. The solution strengthening effect that the manganese element dissolve into the ferrite and become a strengthening phase in ferrite is the main reason to the ductile iron strength increasing. The dissolvability of Mn in the ferrite increases with the Mn content increasing, thus, the strength of ductile iron is slightly increases with the Mn content increasing. In this case, the maximal tensile strength and average hardness were 522 MPa and 181 HV, respectively, and the elongation can remain above 16.4% when the manganese content increases up to 0.8%.

In Fig. 2(b), Fig. 3(c) and Fig. 3(d), the pearlite content increased sharply when the manganese content exceeds 0.9%. The reason for this increase is that some complex reactions occurred between Mn, Fe and C, which result in a type of alloyed cementite (Fe, Mn)3C forming in the matrix. This type of alloyed cementite finally transforms into tiny pearlite particles that are distributed throughout the entire casting. These pearlite particles enhance significantly the strength and hardness. However, the grain boundary segregation of manganese is a serious problem under the high manganese content level situation, which leads to the formation of a large amount of carbide at the grain boundaries. Additionally, manganese segregation destroys the stability of super-cooled austenite and largely obstructs the graphite nodulising process. Hence, the plasticity of ductile iron decreased sharply in this case. The experimental results indicated, for a manganese content more than 0.9%, that the maximal tensile strength and average hardness achieved 704 MPa and 240 HV, respectively, but the elongation decreased less than 5.3%.

**Machining performance**

As its known, a small amount of hard points in a casting is beneficial to its machining performance, but if the density of hard points exceeds a certain limit, the machining performance can seriously decrease under the same machining conditions. In this case, the microhardness distribution characteristic containing 0.9% Mn and 0.05% Cu alloyed casting was investigated, and the microhardness radial distribution and the metallographic image of the cross-section the tensile test specimen are shown in Fig. 4(a) and 4(b), respectively.

The microhardness values of fifty points from the centre to the surface of the specimen are shown in Fig. 4(a). The maximum and minimum microhardness values are 547 HV and 204 HV, respectively. The microhardness values of the most points are between 200 HV and 300 HV, but there are eight points indicated in the Fig. 4(a) for which the microhardness values are over 300 HV. These high hardness points are identified as the hard points in 0.9% Mn alloyed casting. In Fig. 4(b), some tiny carbide or MnS

![Fig. 3 – The metallography images of ductile iron containing different amounts of manganese](image-url)
particles can be found near the hard points. These compounds are easily created at high Mn levels, tending to form at the grain boundaries, where manganese segregation is likely to occur. The hard points don’t increase only the machining difficulties and shorten the service life of a machine tool but also decrease the surface quality of the castings after machining; thus, the hard points should be avoided in ductile iron microstructure.

Effects of manganese and copper

Mechanical properties at different Mn and Cu levels

In the solidification process, copper can promote pearlite formation and refine the slice distance of pearlite in the eutectoid transformation period. In addition, copper is beneficial to stabilise super-cooled austenite and to increase the closing rate of the austenite shell, which enables graphite to be perfectly spherical shape in ductile iron. To investigate the influence of the manganese and copper content on the mechanical properties of ductile iron, a series of Y-block specimens at different manganese and copper contents were casted, and their resulting mechanical properties are shown in Figs 5(a)-(c).

According to the results given in Figs 5(a) and 5(b), it is clear that the tensile strength and average hardness of the ductile iron specimens increase with increasing copper content for the same manganese level. The strengthening ability of copper in ductile iron is more pronounced for ductile iron with a low manganese level than for ductile iron with a high manganese level.

In Fig. 5(c), the influence of the copper content on percent elongation for different manganese levels is shown. It is clear that the elongation decreased with increasing copper for all manganese levels. For the 0.5% Mn alloyed ductile iron, the elongation decreased from 14.5% to 7.5% with the copper content increasing from 0.3% to 0.45%. However, for the 0.7% Mn alloyed, the elongation decreased from 6.1% to 5.5% with the copper content increasing from 0.3% to 0.9%. When the manganese content reaches 0.8%, the elongation cannot exceed 6%, regardless of the copper content. Furthermore, for the same manganese level, the influence of copper on the elongation is little when the copper content is above 0.6%. This result indicates that the elongation is much more sensitive

Fig. 4 – (a) Microhardness distribution in the radial direction of the tensile specimen and (b) metallograph image of the cross-section (Mn%=0.9%, Cu%=0.05)

Fig. 5 – Relationship between the mechanical properties and the copper content for different manganese levels
to the copper content for a low manganese level than for a high manganese level, and the degree of sensitivity decreases quickly for copper contents more than 0.6%.

**Distribution of manganese and copper**

The distribution of each alloying element in the matrix is inhomogeneous, and the nonuniform chemical composition influences largely the mechanical properties of ductile iron. To understand the strengthening mechanism of the Mn-Cu alloying treatment, the energy dispersion spectrum analysis (EDS) method was used to investigate the distribution of manganese and copper in the matrix of ductile iron. The distribution curves of each chemical composition by linear scanning of a 0.69% Mn alloyed casting are shown in Fig. 6(a). To better understand the distribution characteristics of manganese and copper near the graphite, two sampling regions (“spectrum 1” and “spectrum 2” in Fig. 6(b)) that have different distances to graphite were selected. The contents of all of the elements in the two sampling regions are given in Table 2.

The linear scanning path and the distribution of elements along the path, shown in Fig. 6(a), indicate that the spectral lines of each element are nonuniform in the matrix and in the graphite region. Figure 6(b) shows the spherical graphite morphology and the two examined regions near the graphite. According to the area scanning results of the two sampling regions, it is obtained that the manganese content near the graphite (“spectrum 1”) is 0.11%, which is far below the average manganese content (0.69%) of casting. The manganese content far away from graphite (“spectrum 2”) is 0.78%, which is higher than the average manganese content of casting. This difference indicates that manganese is a positive segregation element in ductile iron, which is usually distributed in the grain boundaries. A high manganese level in ductile iron can lead to serious segregation at the grain boundaries, which causes the grain boundary carburet and the creation of secondary phases along the grain boundary. Such grain boundary precipitates are the primary cause of the degradation of the plasticity of ductile iron.

Meanwhile, the copper content in the region of “spectrum 1” is 0.85%, which is higher than the content in the region of “spectrum 2” (Table 2). This observation indicates that copper is a negative segregation element in ductile iron, and it usually gathers at the interface between the graphite and the metal matrix. Because of the high concentration of copper around the graphite nodules, it is difficult for elemental carbon to diffuse into the graphite region through this layer. As a result, the graphite forms perfectly spheroidal shapes with a uniform size distribution in ductile iron.

**Effects of Mn-Cu on the machining performance**

To compare the machining performance of ductile iron modified by the Mn-Cu alloying treatment method and by the single Mn alloying treatment method, the specimens formed using these treatments should have similar strength and hardness level. Therefore, the ductile iron specimen (0.5% Mn,

<table>
<thead>
<tr>
<th>Sampling region</th>
<th>Fe</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>Cu</th>
<th>O</th>
<th>Mg</th>
<th>Ce</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spectrum 1</td>
<td>79.42</td>
<td>8.94</td>
<td>2.91</td>
<td>0.11</td>
<td>0.85</td>
<td>7.31</td>
<td>0.31</td>
<td>0.15</td>
</tr>
<tr>
<td>Spectrum 2</td>
<td>84.06</td>
<td>3.71</td>
<td>2.64</td>
<td>0.78</td>
<td>0.64</td>
<td>7.77</td>
<td>0.23</td>
<td>0.17</td>
</tr>
</tbody>
</table>

Fig. 6 Energy spectrum analysis results and the relevant sampling regions (0.69% Mn, 0.80% Cu)
0.63% Cu) has been selected to compare with the specimen (0.9% Mn, 0.3% Cu) because of their similar strength (632 MPa) and hardness level (224 HV). Figure 7 shows the microhardness distribution in radial direction in the cross-section of tensile test specimen.

In Fig. 7, there are three points being marked out which microhardness values are over 300 HV. For all of the test points, the maximum microhardness is 368 HV, which is far less than the maximum microhardness value (547 HV) of the 0.9% Mn alloyed specimen. Although the average microhardness here is 247 HV, which is slightly below the 0.9% Mn specimen (259 HV), the mean squared error (MSE) of the microhardness values of all of the test points equals 30.46, which is far less than the MSE value of the 0.9% Mn specimen (MSE = 75.28). This result indicated that Mn-Cu alloying treatment method not only decreases the number of hardness points (HV>300) in the matrix, but also improves the inner distribution of the uniform degree of hardness than the single manganese alloying treatment method.

Because the solidification time at different thicknesses position of casting is different, the hardness distribution of casting is slightly nonuniform. To investigate the thickness sensitivity of the hardness distribution, some stair specimens were casted with various manganese and copper levels. The geometry of the stair specimen is shown in Fig. 8(a). To avoid randomness in the hardness measurements, the Vickers hardness values of three points on each step were tested, and the hardness of a step equals the average value of the three points. The maximum hardness difference (MHD) equals the largest hardness difference between the four steps. The MHD values for different manganese and copper contents were statistically analysed in the commercial software “Originlab”, as shown in Fig. 8(b).

According to the results given in Fig. 8(b), the MHD value of the castings is significantly influenced by the manganese and copper levels. Practice always indicates that a casting with a small MHD exhibits better machining performance than a casting under a large MHD situation. In Fig. 8(b), the largest MHD value equals to 35 HV under the conditions of 0.7% ~ 0.85% Mn and 0.3% ~ 0.45% Cu. The smallest MHD value is 10.25 HV under the conditions of 0.68% ~ 0.75% Mn and 0.66% ~ 0.75% Cu. Furthermore, the results also indicate that the MHD value remains of low levels when the copper content variation range is from 0.55% to 0.8% or below 0.15%, and the MHD value decreases with an increasing manganese content.

Fig. 7 – Microhardness distribution in the radial direction of the tensile specimen (Mn% = 0.5%, Cu% = 0.63%)

Fig. 8 – (a) The geometry of stair specimen and the locations of the sampling points (mm) and (b) the maximum hardness difference for different Mn and Cu levels
Conclusions

Manganese is a strengthening element that can efficiently improve the pearlite content in ductile iron. Enhancing the manganese level can significantly improve the strength and hardness of ductile iron. A critical percentage of Mn for improved strength and elongation of ductile iron using a single manganese alloying treatment was examined in this work. The experiments demonstrated that the tensile strength can reach over 500 MPa and no less than 15% elongation when the manganese content is below 0.8%. Because of the grain boundary segregation of manganese, the grain boundary carburets and secondary phases are easily formed along the grain boundaries. This decreases significantly the elongation for the high manganese levels. When the manganese content increases from 0.9% to 1.2%, the strength can further increase from 650 MPa to 730 MPa, but the elongation decreases to be less than 5%. Meanwhile, the number of hardness points (HV>300) and the hardness difference in the casting increase significantly for the high manganese content (0.9% Mn) situation. Thus, it is difficult to improve the comprehensive mechanical properties and the machining performance of ductile iron by only increasing the manganese level.

The Mn-Cu alloying treatment method can efficiently decrease these negative influences of the single manganese alloying treatment in ductile iron production. Ductile iron casting with high strength and good plasticity can be produced by a reasonable ratio of the manganese and copper contents. In addition, for a similar strength and hardness level, the number of hard points significantly decreases, and the hardness distribution in the matrix becomes more uniform for the Mn-Cu alloying treatment than for the single manganese alloying treatment. For the 0.6%-0.8% Mn and 0.5%-0.8% Cu situation, the tensile strength of ductile iron can reach over 600 MPa to 725 MPa, at the same time, the elongation can remain above 5.5%, and the MHD can be controlled to a level below 30 HV.

Therefore, the Mn-Cu alloying treatment method is an efficient method to produce high strength ferritic-pearlitic ductile iron or full pearlitic ductile iron, which is valuable to take full advantage of ductile iron and increase the applied range of ductile iron.

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