THE EFFECT OF MOLYBDENUM ON THE MICROSTRUCTURE OF NODULAR IRON

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Abstract

This paper is aimed at studying the effect of molybdenum on the microstructure and mechanical properties of nodular iron, especially under casting conditions. In this investigation, five nodular irons were separately manufactured in an induction furnace using different amounts of molybdenum in ladder-type molds. The number of nodules per square millimeter and the percent of nodularity were not significantly affected by this variation in molybdenum content. In the matrix, the nodules and the ferrite phase were analyzed using a scanning electron microscope, which is able to detect only the molybdenum in the matrix. The mechanical properties, such as hardness, micro-hardness, tensile strength, and yield strength limit, showed an increase with the increasing content of molybdenum. Likewise, the ferrite and perlite phases presented a variation in percentage with the increasing content of the alloying element. This in turn had a very marked effect on the inter-lamellar spacing of the pearlite. Based on the results of the study, it was concluded that in these quantities, Mo-ferrite solid solution precipitates during solidification, which improves the mechanical properties of the material.

Keywords: Nodular Iron, Effect of Molybdenum Content, Microstructure, Mechanical Properties.

Introduction

The mechanical behavior of any engineering material depends on their mechanical properties and their microstructure. In turn, these properties depend on the chemical composition, the size of the matrix, the distribution, and the shape of the graphite, especially in the case of iron foundries. These microstructural factors are determined and evaluated by practice, during the production of nodular irons *(Hernández et al., 2005; Sage and Dawson, 1992; Maldonado and Hernández, 1992; Loper, 1969; Shea, 1978; Church, 1971).* In the commercial production of nodular irons, production engineers have achieved good control over the nodularity, the content of nodules, and the number of inclusions. Therefore, with these conditions, the properties can be enhanced due to the effects of modifying the microstructure of the matrix. However, it can also further improve its hardness *(Shea, 1978; Alagarsamy, 1993; Dupin and Shissler, 1984)*. Hence, it is advisable to avoid the presence of carbides in the matrix during solidification, as they reduce the machinability and toughness of nodular iron. To prevent the formation of carbides, it is necessary to maintain an equivalent carbon content (% C + 0.33% Si) of about 4.3%. The presence of a high content of nodules can be used as a criterion for calculating the quality of such nodular irons. However, large degrees of graphitization tend to inhibit the formation of carbides. Hence, it is also recommended that the equivalent carbon content should not exceed 4.7%. This is because greater values of equivalent carbon increase the possibility of the floating of carbon, which increases particularly in thick sections *(Shea, 1978; Dupin and Shissler, 1984).*

In terms of casting, the nodular iron matrix consists of a mixture of perlite and ferrite. However, the relative amounts of each phase are dependent on the cooling rate, the content of nodules, and the alloying elements *(Venugopalan and Alagarsamy, 1990; Askelan and Gupta, 1975).* The effect of alloying elements on the properties of nodular iron is reflected in the relative amounts of ferrite and pearlite in the microstructure of the material as well as in the hardening effect of the constituents (*Goodrich and Jones, 1993*). In ductile iron, the ferrite occurs primarily by solid solution, while the presence of pearlite is due to the refinement of inter-laminar spacing *(Bevan and Sholtz, 1964; Jolley and Gilbert, 1967; Evans et al., 1981)*.

The degree of hardening obtained by the addition of alloying elements depends on the type of matrix. This is expected because the hardening mechanism in perlite and ferrite are the same. However, in nodular irons of mixed matrix, the degree of hardening depends on the amount of phase present. For example, when silicon is added to a pearlitic nodular iron, hardening is reduced because this element increases the amount of ferrite in the microstructure. However, in ferritic iron, the addition of silicon increases the strength due to solid solution hardening *(Alagarsamy, 1993)*. In the same way, the resistance of ferritic iron can be increased by adding copper or manganese, which increases the content of pearlite in the microstructure and therefore favors the hardening of ferrite and pearlite *(Alagarsamy, 1993; Venugopalan and Alagarsamy, 1990; Karsay, 1976)*. Molybdenum, which is present in nodular iron, is an element as well as a strong promoter of carbides. Some research have shown that it is possible to get irons with molybdenum contents of up to 0.5 %, without the massive formation of carbides even in thin sections *(Bevan and Sholtz, 1964)*. This can be achieved mainly by the good practice of inoculation, besides having a good control over pouring temperature. Thus, to obtain good inoculation in these kinds of nodular irons, it is necessary to use inoculants with high contents of calcium, cerium, or magnesium, such as calcium–silicon *(Lalinch and Loper, 1973)*. The functions of this material are to set inoculant nucleation centers for precipitation of the graphite, to reduce white area, to control the graphite structure, to improve the mechanical properties of the piece, and to improve the machinability characteristics in iron casting conditions *(Askelan and Gupta, 1975; Wite et al., 1993)*.

During solidification, molybdenum favors the formation of discrete precipitates of molybdenum carbide, which is virtually invisible under an optical microscope. Research works, which employ the use of scanning electron microscopy have shown that these precipitates are fine particles of about 0.25 microns in diameter. Furthermore, it is believed that these particles are molybdenum carbides *(Goodrich and Jones, 1993)*. It is the presence of these precipitates that is mainly responsible for the significant increase in the strength properties of nodular iron, as a result of its effect on the microstructure.

Experimental Procedure

Nodular iron was experimentally manufactured in an induction furnace of 250 kg capacity, using a cast ingot load, which contained very low levels of phosphorous and sulfur. This was done so as to avoid the need to desulfurize and remove phosphorus during the melting process. However, during this process, a significant de-carbonization of the base metal occurs because of the time it remains at high temperature. Therefore, it was necessary to add 0.1% of C to offset these losses before adding the other alloying elements. Hence, the load was subjected to de-oxidization at a temperature of 1480 °C with 0.5% aluminum and the immediate addition of 99% pure silicon. Molybdenum was added to the ladle or casting pot as a ferroalloy containing 63.85 % of the element. The molybdenum content was increased each time a ladle or casting pot was emptied.

The pelletizing process was conducted in the ladle (preheated), which has a capacity of 30 kg of liquid metal, at a temperature of 1500 °C. To carry out this treatment, structural steel capsules containing 1000 grams of a ferroalloy of Fe-Si-Mg (49-45-06) and 20 grams of pure magnesium, representing the 0.07 % of magnesium within the weight of the nodular iron, were prepared in the ladle. The iron was cast in T-block type sand molds, with a thickness of 25 mm. These were then inoculated using 0.30 % calcium-silicon alloy, containing 1% calcium. Samples of this material were extracted for metallographic analysis in order to determine the hardness. Furthermore, some samples were machined into specimens with 25.4 mm gauge length and 6.25 diameter according to the standard ASTM-E-8-81 to perform the tensile strength test. Also, specimens were machined for impact test under the ASTM-E-238 standard. Furthermore, the latter assay was performed within the temperature range of 15°C and 150°C, in order to determine the effect of temperature on the energy absorbed by the impact, as well as the transition temperature for the various contents of molybdenum.

A quantification of the phases present in the microstructure was performed using the method of points. However, this was done using a standard grid of 144 points on photographs taken at x100. Hardness tests were performed on the Rockwell B scale. This test was carried out considering 800 mm^2 of area, which was performed with 10 trials per test specimen. The micro-hardness of the phases was measured with a Vickers indenter and the tensile test was conducted on a universal machine with a load of 5000 kg.

Results and Discussion

The nodular iron obtained under the above conditions has the chemical composition shown in Table 1. Furthermore, the results of the metallographic analysis and the mechanical properties found in the analyzed material of each of the different compositions obtained are presented in Table 2. All the samples had a structure free of carbides and porosity. Thus, they generally exhibited a matrix consisting of ferrite and pearlite.

Molybdenum's Influence on Microstructure: As shown in Table 2 and Figures 1 and 2, molybdenum has little influence on the number of nodes and the degree of nodularity of graphite. This makes us consider that it may depend on other factors such as the level and effectiveness of inoculation, the pouring temperature, and the section thickness. Iron has a tendency to increase or decrease in the number of nodes and the degree of nodularity as a result of increasing molybdenum content. With an average of 235 in the number of nodules/mm^2, the percentage of nodularity was maintained between 83 and 92 %.

Table 1. Chemical Composition of Nodular Irons Obtained (% in weight)

Sample	C	Si	Mn	P	S	Mg	Al	Mo	C.E.
1	3.05	2.62	0.055	0.025	0.027	0.047	0.032	0.000	3.92
2	3.05	2.54	0.058	0.023	0.018	0.043	0.033	0.086	3.91
3	3.20	2.22	0.061	0.022	0.019	0.027	0.027	0.146	3.94
4	3.44	2.42	0.052	0.025	0.016	0.030	0.029	0.250	4.25
5	3.40	2.40	0.069	0.025	0.020	0.035	0.028	0.380	4.20

Note: C.E. is the equivalent carbon.

Table 2. Results of the Metallographic Analysis and Mechanical Properties of Nodular Iron

Sample	Nodularity (%)	Nodes/mm^2	Ferrite (%)	Micro-hardness (Ferrite, Vickers)	Pearlite (%)
1	92	326	74	200	16
2	90	225	75	205	10
3	88	254	76	217	15
4	91	259	76	231	9
5	83	210	78	206	7

Sample	Micro-hardness (Pearlite, Vickers)	Yield strength (MPa)	Tensile strength (MPa)	Elongation (%)	Hardness (RB)
1	351	481	579	15	81
2	357	510	608	13	86
3	394	520	618	13	90
4	401	530	647	11	87
5	411	539	647	10	86

The effect of molybdenum in proportional amounts of ferrite and pearlite is shown in Figure 3. Here, one can observe as much as 16% decrease in the amount of pearlite for a nodular iron without molybdenum. In addition, one can also observe as much as 7% for about 0.38% molybdenum. There is also a significant increase in the ferrite amount ranging from 74 % to 78 % for the respective contents of molybdenum.

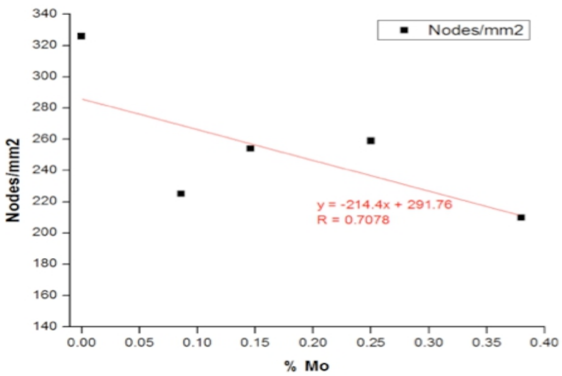


Figure 1. Effect of Molybdenum on the Number of Nodes in Nodular Iron Casting Conditions

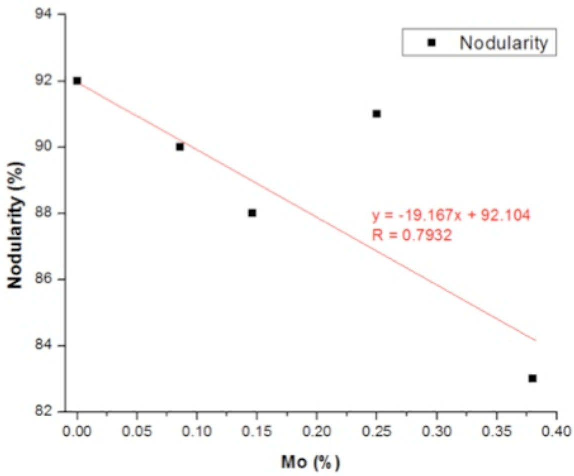


Figure 2. Effect of Molybdenum over the Nodularity under Nodular Iron Casting Conditions

Molybdenum's Effect on Mechanical Properties: Both the properties of yield strength and tensile strength increased with increasing molybdenum content, as can be seen in Figure 4. Here, one can observe a tensile strength of 579 MPa for a nodular iron without molybdenum, and values of 647 MPa for a nodular iron with 0.380 % molybdenum. However, the values of yield strength increased from 481 MPa to 539 MPa for the same contents of molybdenum in iron.

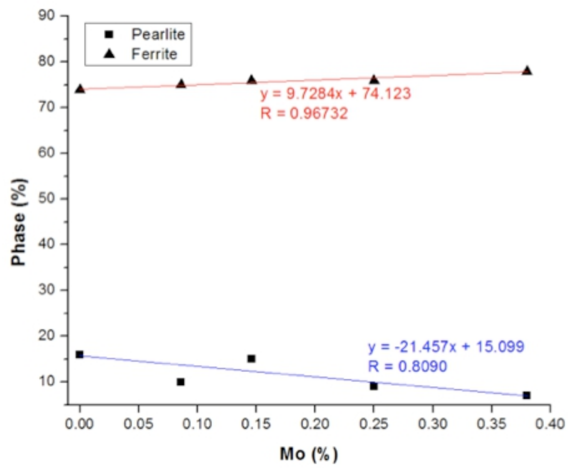


Figure 3. Effect of Molybdenum on the amount of Ferrite and Pearlite in Nodular Iron under Casting Conditions

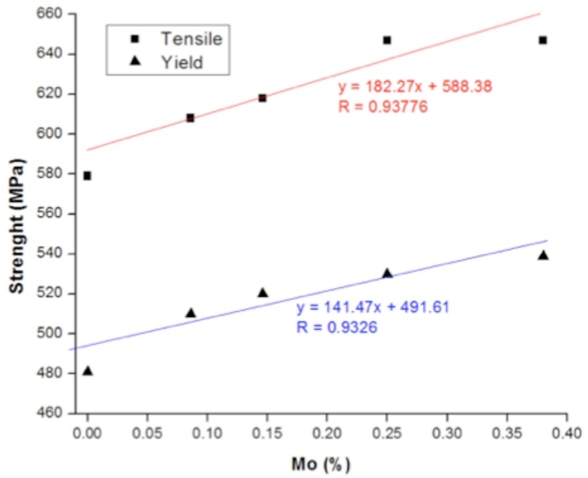


Figure 4. Effect of Molybdenum on the Tensile Strength and Yield Strength in Nodular Iron under Casting Conditions

Figure 5 shows an increase in hardness in ferrite and pearlite phases according to the amount of molybdenum present in the iron. It was found that a lower micro-hardness, ranging between 200 and 351 Vickers, corresponded to ferrite and pearlite respectively for iron without molybdenum. On the other hand, higher values of 206 and 411 Vickers corresponded to ferrite and pearlite respectively for nodular iron containing 0.380 % molybdenum.

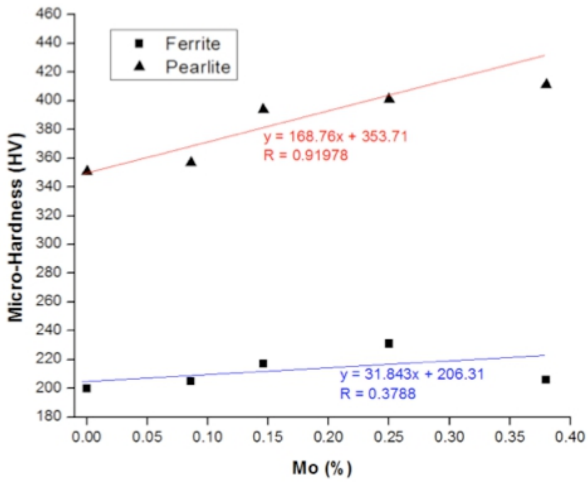
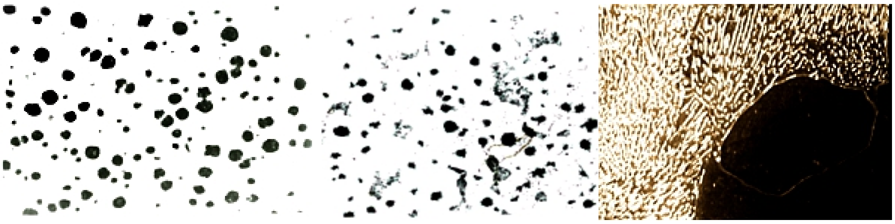


Figure 5. Effect of the Hardness of Ferrite and Pearlite according to the percentage of Molybdenum present in Nodular Iron under Casting Conditions

Figure 6 (a, b, c) illustrates the nodularity, the phases present in nodular iron, the inter-lamellar spacing of pearlite, as well as the cementite in the ferrite phase for a nodular iron without molybdenum.



(a) (b) (c)

Figure 6. Photomicrographs of Nodular Iron without Molybdenum: (a) normal casting conditions x 100; (b) attacked with 2 % Nital x 100; and (c) interlayer spacing of the pearlite x 40,000

The same is illustrated in Figure 7 (a, b, c), but in this case, it is for ductile iron with 0.086 % molybdenum. In the same vein, Figure 8 (a, b, c) corresponds to nodular iron with 0.146 % molybdenum, Figure 9 (a, b, c) for nodular iron with 0.250 % molybdenum, and finally Figure 10 (a, b, c) belong to nodular iron with 0.380 % molybdenum. In all the figures, it is observable that there is a tendency for an increase in phase refining, according to an increasing content of molybdenum in iron.

(a) (b) (c)

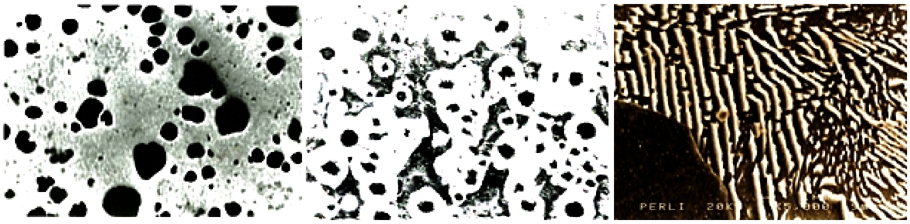
Figure 7. Photomicrographs of Nodular Iron with 0.086 % Molybdenum: (a) under normal casting conditions x 100, (b) attacked with 2 % Nital x 100, (c) interlamellar spacing of pearlite x 40,000

(a) (b) (c)

Figure 8. Photomicrographs of Nodular Iron with 0.146 % Molybdenum: (a) under normal casting conditions x 100, (b) attacked with 2 % Nital x 100, (c) interlamellar spacing of pearlite x 40,000

(a) (b) (c)

Figure 9. Photomicrographs of Nodular Iron with 0.250 % Molybdenum: (a) under normal casting conditions x 100, (b) attacked with 2 % Nital x 100, (c) interlamellar spacing of pearlite x 40,000



(a) (b) (c)

Figure 10. Photomicrographs of Nodular Iron with 0.380 % Molybdenum: (a) under normal casting conditions x 100, (b) attacked with 2 % Nital x 100, (c) interlamellar spacing of pearlite x 40,000

Therefore, the interlayer spacing is much smaller when we have a nodular iron without molybdenum. This can be seen in Figure 6 (c), unlike when we have a 0.380 % molybdenum in nodular iron, as shown in Figure 10 (c). In Figure 10 (c), it can be seen that the spacing ranges varies from 100 nm, for a nodular iron without molybdenum, to 1 micron, for a nodular iron with 0.380 % molybdenum. Thus, this was illustrated in the figures above. As can be seen in Figure (c) of each of the composition of nodular irons, the interlayer spacing increases with increasing molybdenum content. On the other hand, in Figures (a) and (b), it can be seen that the number of nodes and the % of pearlite, decrease with increasing molybdenum contents. That is why we may assume that the number of nodes is affected by other factors, which were mentioned above, and not necessarily by an increase in the percentage of molybdenum in iron. Both the amount of pearlite as the degree of refinement caused by molybdenum and hardening by precipitation of molybdenum carbides in both phases (ferrite and pearlite) could be responsible for the increase in the values of the properties of yield strength and tensile strength in this material. This, however, produces an adverse effect on the ductile properties such as can be seen in Figure 11, where a reduction ranging from 10% to 15% in elongation occurs when the molybdenum content increases for up to 0.380%.

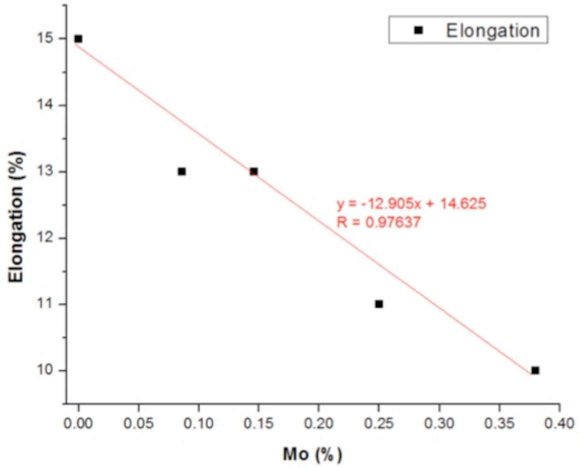


Figure 11. Molybdenum's effect on the Ductility of Nodular Iron under Normal Casting Conditions

These opposing effects on the properties of strength and ductility can be reduced with the good practice of inoculation and controlling tapping temperature. Thus, nodular irons with high yield strength, good tensile strength, and a good degree of ductility can be obtained.

Table 3 shows the results of the Charpy impact test (absorbed energy) for the 5 different irons manufactured.

Table 3. Results of the Charpy test

Sample	C	Si	Mn	P	S	Mg	Al	Mo	C.E.
1	3.05	2.62	0.055	0.025	0.027	0.047	0.032	0.000	3.92
2	3.05	2.54	0.058	0.023	0.018	0.043	0.033	0.086	3.91
3	3.20	2.22	0.061	0.022	0.019	0.027	0.027	0.146	3.94
4	3.44	2.42	0.052	0.025	0.016	0.030	0.029	0.250	4.25
5	3.40	2.40	0.069	0.025	0.020	0.035	0.028	0.380	4.20

Commonly, the impact properties are improved by increasing the nodularity of graphite, thus decreasing the transition temperature. The absorbed energy is increased due to an increase in the volume of graphite as well as the number of nodes. This is because graphite exists in a very soft phase and with great ability to absorb energy during impact produced by the test. Consequently, when there is a constant nodularity and a constant volume, the material's behavior on impact is determined by the structure and composition of the matrix of iron. In our case, both the nodularity as well as the number of nodes are equal for the five chemical compositions of irons produced. Moreover, the volume of graphite is maintained at an average value of 12.8 %. This was because it was expected that this variable can be affected by matrix structure and alloying elements such as molybdenum. In addition, changes in the transition temperature are very noticeable, because as the molybdenum content increases, the impact resistance properties are affected by increasing transition temperature. Thus, this is shown in Figure 12.

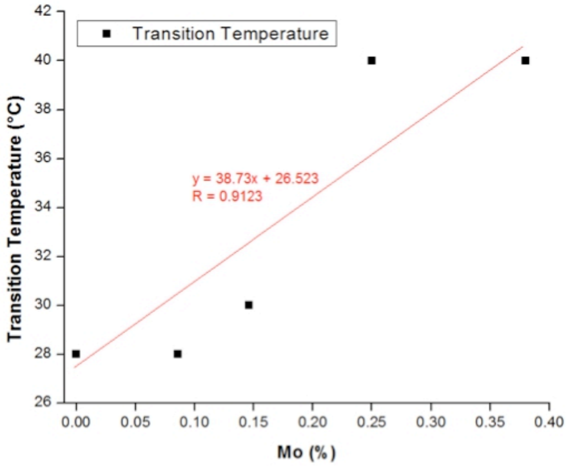


Figure 12. Effect of Transition Temperature on Nodular Iron

Conclusion

Molybdenum, resulting from its strong tendency to promote stabilization of the ferrite phase in ductile iron content, tends to increase the relative amount of this eutectoid constituent. Therefore, increasing molybdenum content increases the hardness of ferrite. This is because molybdenum is dissolved by the mechanism of solid solution in the ferrite phase. Molybdenum is one of the most effective elements for increasing strength properties. Moreover, it is possible to obtain nodular irons under casting conditions with a tensile strength of around 620 MPa, a yield strength of 516 MPa, a ductility of 13 %, and a molybdenum content of 0.380%. This avoids the formation of carbides, which can weaken the material.

In this research, it was observed that molybdenum, when in suitable amounts, has a marked effect on the interlayer spacing of pearlite. Hence, it is believed that this effect is responsible for much of the increase in property values of tensile strength and yield strength of the material.

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