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Effect of alloying elements on thermal shock resistance of gray cast iron

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ABSTRACT

The effect of some alloying elements on the thermal shock resistance of low alloyed gray cast iron was investigated. Alloying of molybdenum, chromium, nickel and tin to the gray cast iron ingot with specified composition was performed to identify optimum composition of alloyed gray cast irons for the best thermal shock resistance. Tensile and thermal shock tests were conducted to investigate the relationship between those two parameters. Scanning electron microscope was used to observe the morphology of cracks which were occurred during thermal shock tests on the surface of specimens. Eventually the results showed that the thermal shock resistance of the gray cast iron, containing (wt.%) 0.8 Mo, 0.2 Cr and 0.08 Sn of alloying elements was enormously increased in comparison with unalloyed and other low alloyed gray cast irons.

1. Introduction

Gray cast iron has become a popular cast metal material which is widely applied in modern industrial production, because of its low cost (20–40% less than steel) and wide range of desirable/achievable mechanical properties such as good castability, convenient machining property and better wear resistance [1–5]. The microstructure of gray cast iron is characterized by graphite lamellas dispersed into the ferrous matrix. Foundry practice can influence nucleation and growth of graphite flakes, so that size and type enhance the desired properties. The amount of graphite and size, morphology and distribution of graphite lamellas are critical in determining the mechanical behavior of gray cast iron [1]. According to the different graphite shapes the cast iron can be divided into flake graphite iron, vermicular graphite iron and nodular graphite iron. Though these kinds of cast irons were applied to diverse engineering parts according to their different properties, for instance, the flake graphite iron is used for brake drums and cylinder caps [6,7]; the vermicular graphite iron is used for steel molds and brake discs of train [8]; the nodular graphite iron is used for hot rolls [9]. The fracture of materials under rapid heating and cooling cycles is called “thermal shock”. Thermal shock can be viewed as an extreme case of thermal fatigue which is generally occurring at a less severe temperature differential and/or slower thermal cyclic rate. Thermal stress and transformation stress are the primary reasons for such failure [10]. Formation of surface cracks during thermal cycling is a common occurrence in gray cast iron components. The cracking – usually referred to as thermal fatigue, heat checking or crazing – results from cyclic stresses in the component caused by none uniform heating, differential thermal expansion of micro constituents and phase transformations [11]. Since the mechanical and thermal properties of a material are responsible for its thermal shock behavior [10], it was the purpose of this study to investigate the best composition of alloying elements such as, molybdenum, chromium, nickel and tin, influencing thermal shock resistance of the low alloyed gray cast iron.

2. Experimental procedures

2.1. Alloy composition and preparation of specimens

The raw material for casting experiments was gray cast iron consisted of no alloying elements. In order to generate work pieces with desired content of alloying elements (Mo, Cr, Ni, Sn) appropriate additives such as ferroalloys and tin sheet were added to the melted base gray iron. The chemical composition of the primary none alloyed gray cast iron was as follows (wt.%): 3.7 C; 1.03 Si; 0.25 Mn; 0.08 Ni; 0.03 Cu; 0.02 (Cr, Al); 0.01 (P, Mo, Mg); 0.006 (Sn, Co); <0.003 (As, B, Pb, S, Ti, W, V); the remainder was Fe. Five batches of castings were prepared by the variation of alloying elements. The content of each alloying element in these batches was as follows (wt.%): batch 1, raw/base gray iron; batch 2, (0.2–0.5–0.8) Mo; batch 3, (0.2–0.35–0.5) Cr; batch 4, (0.5–1–1.5) Ni; batch 5, 0.8 Mo–0.2 Cr–0.08 Sn.

When the molten metal’s temperature attained the range of 1335–1365 °C, the dross and slag were removed and then several casting sets were poured into different sand molds.

The first set of castings was Y-blocks designed according to the guidelines given in the ASTM standard A436-84 [12]. Tensile test specimens were machined from them.

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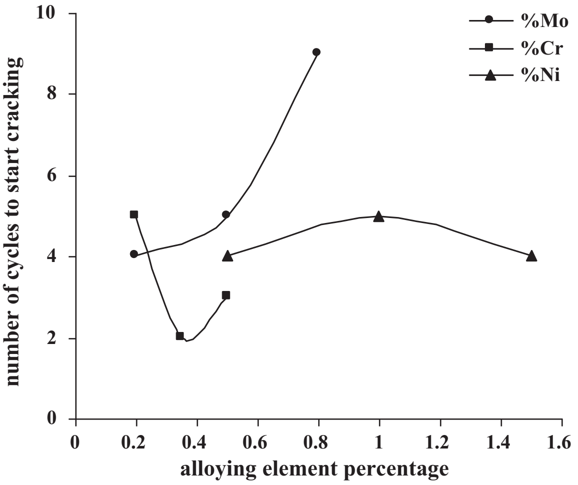

Fig. 1. Variation in the thermal shock resistance (the number of thermal shock cycles to first major crack of the alloyed gray cast iron) as a function of alloying elements percentage.

The second set of castings consisted of disk form specimens for doing thermal shock tests and crack morphology observations. The details regarding to these specimens are explained by Roehring [13].

2.2. Thermal shock test

The resistance of a material to thermal cycling is best determined under service conditions. Laboratory tests can be used to screen candidate materials to predict the results of real situation however, the tests have to be done with great care since the tests conditions usually do not reproduce service circumstances. To obtain results in a practical time period, exposure times at high temperature are shorter and the stresses created during thermal cycling are often much higher than in actual service [13]. Since there have been no standard methods for thermal shock/fatigue testing [10], a shape of specimen was selected which was suitable for experimental set up conditions. Thermal shock tests were conducted on all the gray cast irons under study employing the specimen geometry as demonstrated by Roehring [13].

At first the specimen was immersed in the molten aluminum bath at 985–1015 °C then cooling procedure was performed in the water at 15–35 °C. The heating–cooling procedure was repeated until the first major crack became visible. In order to evaluate thermal shock resistance the number of cycles to first major crack was recorded.

2.3. Tensile test

Tensile testing was performed at room temperature by using Dartec dynamic testing machine. The samples for tensile test were cut from the Y-block castings, and then they were machined to standardize dimensions. The configuration of 12.5 mm round tension test specimens was in accordance with ASTM standard E8M-95a [14].

Specimens were pulled uniaxially until fracture and the average rate of straining was 0.25/s during deformation.

3. Results and discussion

3.1. Thermal shock resistance

At first thermal shock test was done on unalloyed gray cast iron. The first major crack was created after 2 cycles. The effect of alloying elements percentage on the thermal shock resistance of the alloyed gray cast iron is shown in Fig. 1.

It is evident that thermal shock resistance increased as the molybdenum content increased from 0.2 to 0.8 wt.%. Whereas it can be seen that the addition of chromium from 0.2 to 0.5 wt.% did not improve thermal shock life of gray cast iron and nickel (0.5–1.5 wt.%) did not have any effect on it. There are some equations describe different parameters affecting the thermal stress and thermal shock resistance of materials.

Table 1
Thermal conductivity of the various micro constituents in cast irons [16].

Microconstituents	Thermal conductivity (W/(m K))		
	0–100 °C	500 °C	1000 °C
Graphite along *C*-axis	84	–	–
Graphite along basal plane	290–420	84–126	42–63
Ferrite	71–80	42	–
Pearlite	50	42	–
Cementite	7.1	–	–

Lee and Weng [10] quoted the thermal stress equation proposed by Dieter and Minkoff:

$$\sigma_{th} = \frac{E \cdot \alpha \cdot \Delta T}{1 - \upsilon} .F \qquad (1)$$

where σ_{th} is the thermal stress, α is the thermal expansion coefficient, ΔT is the temperature difference, F is the geometry factor and υ is the Poisson's ratio.

They [10] also quoted the following thermal fatigue or thermal shock related equation proposed by Eichelberg and Radon et al. for thermal fatigue life of iron and steel as:

$$Q = \frac{(1 - \upsilon) \cdot K}{\alpha \cdot E} \qquad (2)$$

where Q is the thermal fatigue resistance index, K is the thermal conductivity coefficient and υ, α, E is as defined in Eq. (1).

To resist thermal stress, an iron should have a low modulus of elasticity and high resistance to plastic deformation at elevated temperatures [13].

Eq. (2) shows that thermal shock resistance generally increases with thermal conductivity (K). According to the Fourier's heat transfer equation, it is clear that temperature difference (ΔT) is inversely proportional to the thermal conductivity. So, it can be seen from Eq. (1) that the thermal stress in the materials is minimized by a high thermal conductivity. That is, higher K value would essentially reduce the detrimental effect of the temperature difference and consequently thermal stress within the material itself.

The relationship between σ_{th} and Q can be shown by substituting $E \cdot \alpha/(1 - \nu)$ from Eq. (1) into Eq. (2) and rearranging to form Eq. (3):

$$\sigma_{th} = \frac{K \cdot \Delta T}{Q} \cdot F \qquad (3)$$

Eq. (3) shows that the lower the thermal stress, the longer the thermal fatigue/shock life a component will have.

Several investigations have been performed to better understand the relative effects of alloy additions to the properties of gray iron. Boegehold [15] demonstrated the beneficial effects of alloy additions on the thermal properties of irons. Boegehold [15] reported that a 1.4 wt.% Ni cast iron exhibits the lowest thermal expansion coefficient in comparison to plain cast iron and Mo cast iron. His data on other irons demonstrate that increase in molybdenum content from 0.37 to 0.73 wt.% will decrease the thermal expansion coefficient of cast iron [15].

According to Eq. (2) and Boegehold's reports [15], thermal fatigue life of gray cast iron would increase if the content of alloying elements such as Mo, Cr and Ni increased. But Fig. 1 shows this relation only in presence of molybdenum. Other than thermal expansion coefficient, there are some other effective parameters that might be considered in discussing the results of thermal shock resistance including thermal conductivity, graphite volume fraction, toughness and crack propagation conditions.

The thermal conductivity of cast iron is influenced by microstructure, temperature and composition [16]. The effects of various metallographic micro constituents can be seen by their individual thermal conductivities presented in Table 1. The presence of the graphite raises the thermal conductivity in gray irons,

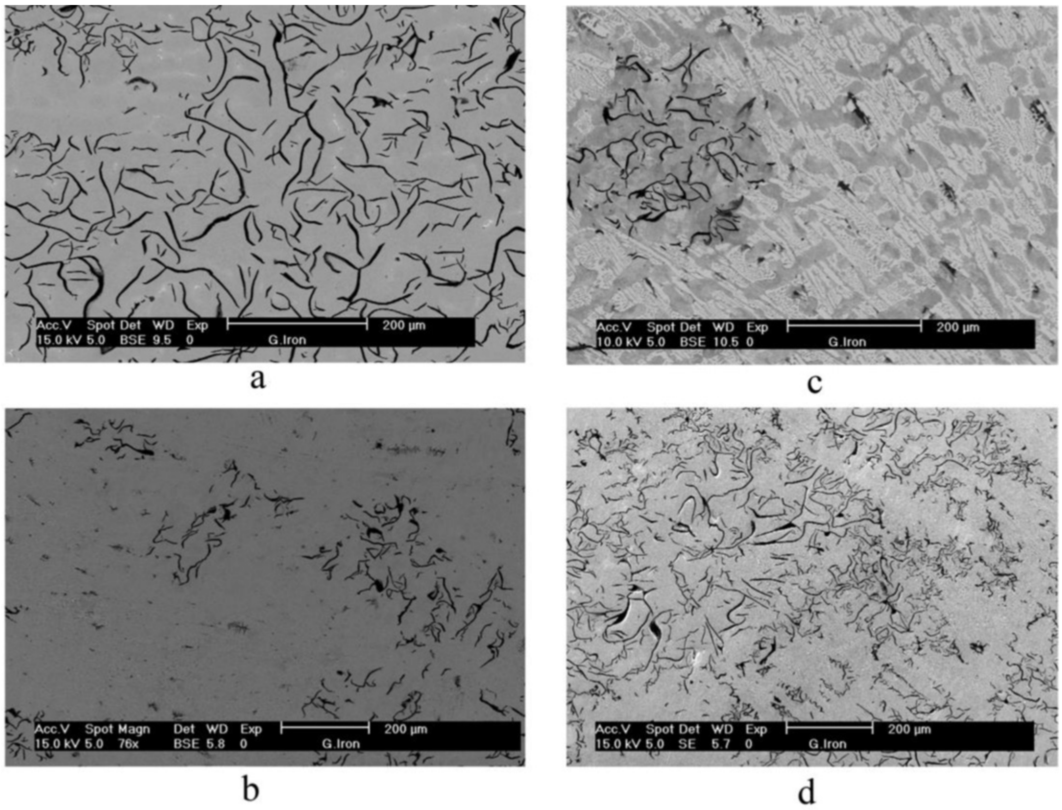

Fig. 2. SEM micrographs of some gray cast iron samples. (a) Unalloyed, (b) 0.5 wt.% Mo, (c) 0.5 wt.% Cr, and (d) 1.5 wt.% Ni.

and ferritic irons usually have higher thermal conductivities than pearlitic irons [17], however thermal conductivity is affected by chemical composition.

A limited work has been performed to determine the effect of varying chemical composition on thermal conductivity of cast iron. Clearly any increase in carbon content that produces an increase in graphite volume will increase thermal conductivity and flake graphite is much more effective than spheroid graphite [18].

It must be kept in mind that the graphite phase in gray cast irons has two beneficial effects: one is to decrease the modulus of elasticity and the other is to reduce temperature gradient and the surface temperature due to an increase in thermal conductivity when the energy input to the heated sides is constant [13]. Cracking in materials containing either flake graphite or nodular graphite is associated with the graphite phase. Crack propagation in structures containing flake graphite is facilitated by the interconnecting nature of graphite and the small spacing between the flakes. Cracking can occur almost entirely in the graphite phase in the gray irons [11]. A high tensile strength and high fatigue strength, especially with respect to strain cycling, are necessary to withstand thermal stresses and external stresses imposed by the design. Furthermore, if the operating temperature exceeds 500–600 °C, the iron must also have resistance to oxidation and structural change. For gray irons, internal oxidation along the graphite flakes is very deleterious because it weakens the iron and decreases thermal conductivity. It is also responsible for some of the growth (dimensional instability and increase in volume at high temperatures [18]) occurring in gray iron and is accelerated by thermal cycling [13].

The influence of molybdenum and chromium on thermal conductivity has also been shown in Bertodo's work [19]. He did show that chromium and molybdenum lowered thermal conductivity slightly [19]. According to Eq. (2) and Bertodo's reports [19], thermal fatigue life of gray cast iron would decrease if Mo and Cr content increased. However, Mo curve (in Fig. 1) is not corresponding to the Bertodo's results [19].

The effect of molybdenum, chromium and nickel on graphite volume fraction of the gray cast iron can be seen by comparing the microstructures presented in Fig. 2. Addition of either molybdenum or chromium also reduced the graphite content, however, addition of nickel raised graphite volume fraction. Since there is a direct correlation between thermal conductivity and graphite content of the gray cast iron, it can be concluded from Fig. 2 and Eq. (2) that thermal shock resistance increases as the nickel content increases

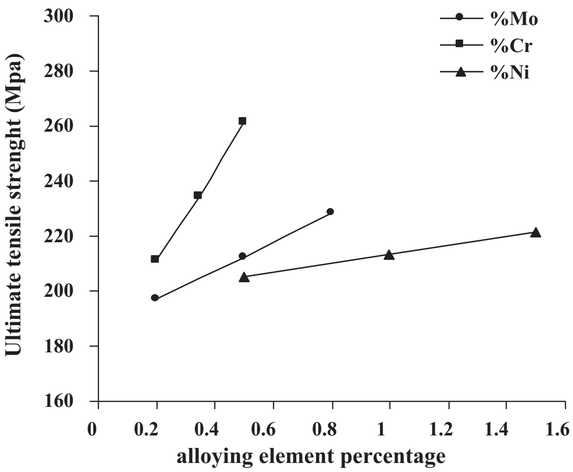

Fig. 3. Variation in the ultimate tensile strength of the alloyed gray cast iron as a function of alloying elements percentage.

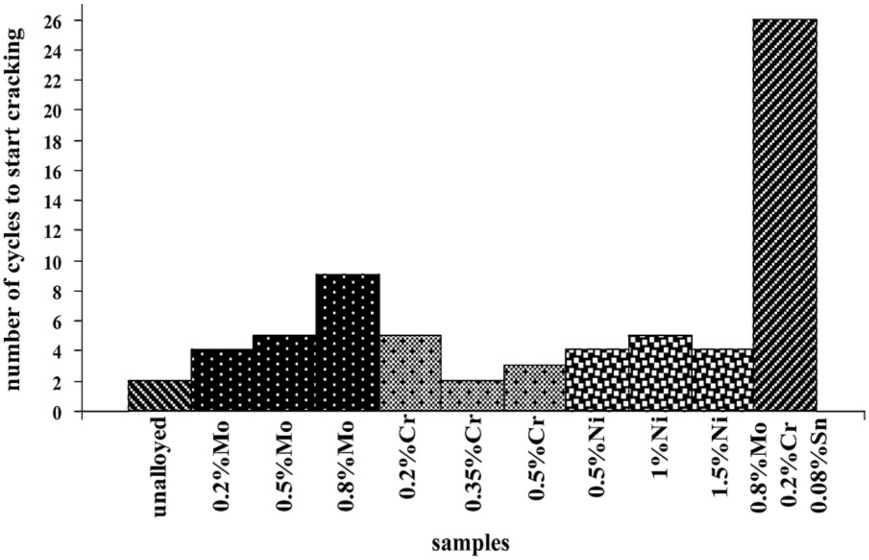

Fig. 4. The number of thermal shock cycles to first major crack of the alloyed gray cast iron samples.

and decreases as the chromium and molybdenum content increase. But Fig. 1 did not show this behavior.

It is speculated that the amount of molybdenum has an optimum content (approximately 0.8 wt.%) and the strong influence of Mo on thermal shock resistance of gray cast iron is due to decreasing in thermal expansion coefficient, lowering of the graphite flakes as the crack nucleation sites and subsequently reducing the oxidation along them.

Turnbull and Wallace [20] demonstrated the beneficial effects of chromium and molybdenum additions on the stress–rupture properties of gray irons at 425, 540 and 650 °C. Their results show that molybdenum addition up to 2 wt.% to an unalloyed iron continuously raise the stress to rupture in 100 h at all three temperatures. In a 0.6 wt.% Cr alloyed base iron, the stress to rupture in 100 h increased with increasing molybdenum content up to 0.8 wt.% at these temperatures.

Therefore with regard to an improvement of thermal fatigue life an optimum content of Mo (in combination with Cr) can be 0.8 wt.%.

The number of cycles to first major crack versus alloying elements percentage, as shown in Fig. 1, indicates that chromium addition did not improve thermal shock resistance of the gray cast iron. Thermal shock resistance of the gray cast iron with 0.35 wt.% Cr was the lowest whereas 0.2, 0.5 wt.% Cr gray cast irons exhibited maximum thermal shock resistance. It was observed that for chromium content more than 0.2 wt.% the crack width was increasing as the chromium content was raising and eventually when it reaches the 0.5 wt.% the specimen was broken into two pieces.

An increase in chromium content as a strong stabilizer of carbide causes effects such as:

- Decreasing of the graphite volume fraction [21] (see Fig. 2).
- Decreasing of thermal conductivity [19].

Although the thermal expansion coefficient of Cr carbide specially was not readily available, it might fall in the range of 2–5 × 10^{-6}/°C [10], while that of pearlitic/ferritic matrix may be

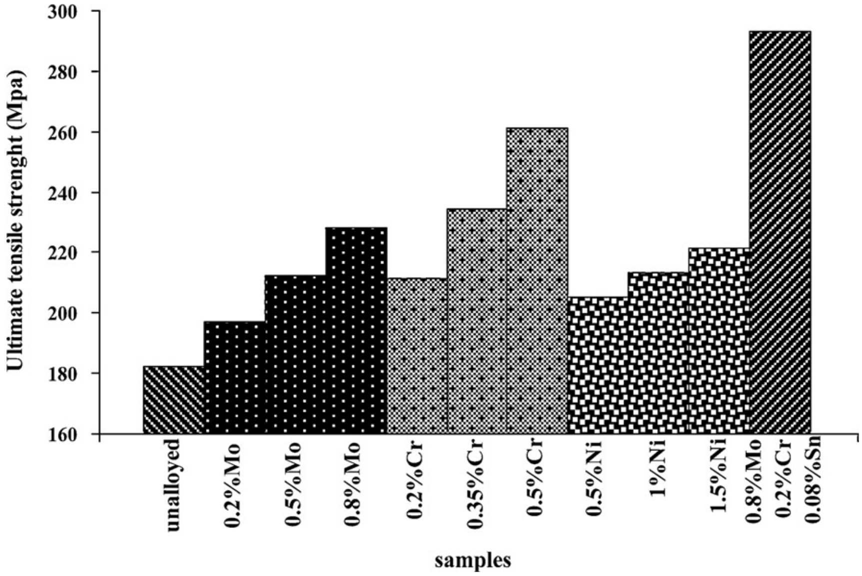

Fig. 5. The ultimate tensile strength of the alloyed gray cast iron samples.

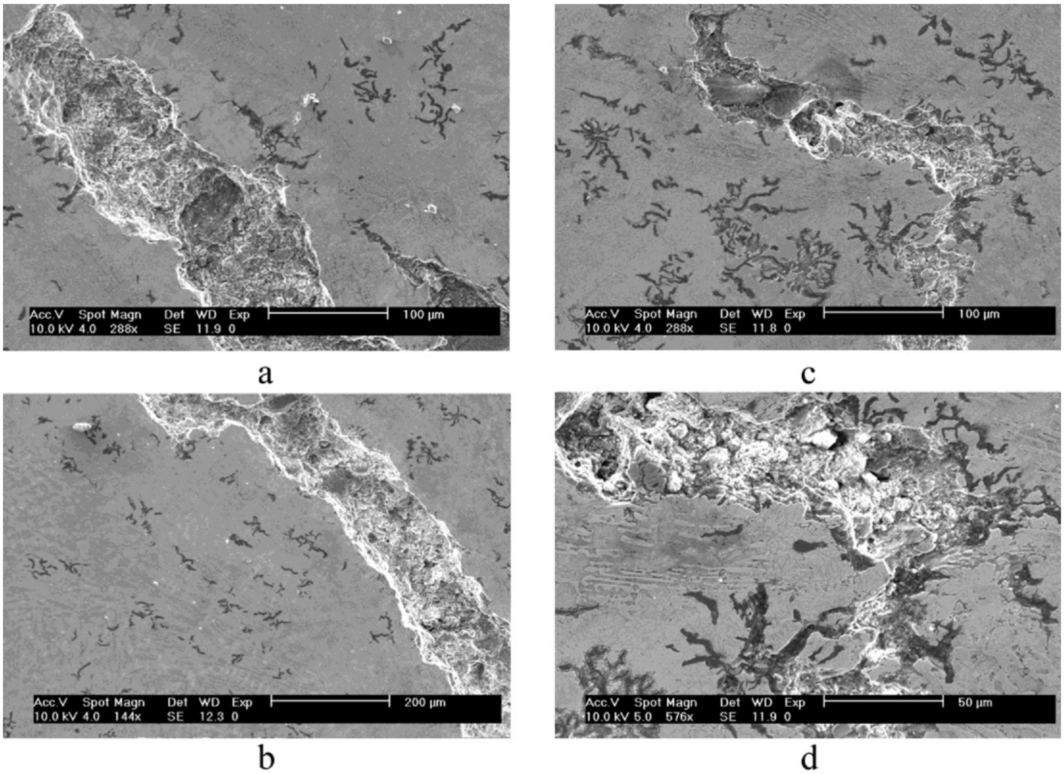

Fig. 6. The SEM micrographs showing cracks in two samples. (a and b) 0.5 wt.% Mo and (c and d) 0.8 wt.% Mo–0.2 wt.% Cr–0.08 wt.% Sn.

between 10 and $14 \times 10^{-6}/^{\circ}C$ at the temperatures between 20 and 700 °C [18].

Fig. 2b and c shows the evidence of stronger influence of Cr than Mo in formation of carbides.

Therefore it can be concluded that the graphite volume fraction in presence of 0.2 wt.% Mo is much more than this fraction in presence of 0.2 wt.% Cr. So, the oxidation along the graphite flakes and lowering thermal conductivity due to this oxidation might be the major reason why the 0.2 wt.% Mo gray cast iron exhibited inferior thermal shock resistance than the 0.2 wt.% Cr gray cast iron.

From Fig. 2 it can be seen that in the same content of Mo and Cr (0.5 wt.%) the volume fraction of Cr carbides is much more than the Mo carbides, so it seems that the total thermal expansion coefficient is larger in presence of Cr.

It seems that the reduction of thermal shock resistance as a result of chromium addition from 0.2 to 0.35 wt.% is due to the increase in thermal expansion coefficient and reduction of thermal conductivity. Furthermore, the reason for sudden fracture in 0.5 wt.% Cr gray cast iron is the serious stress concentration, reduction of toughness and increase in brittleness due to the increase in chromium carbide.

It can be observed from Fig. 1 that thermal shock resistance was not influenced by the nickel content (0.5–1.5 wt.%) in the gray cast iron. Addition of nickel increased the graphite volume fraction in the gray cast iron as shown in Fig. 2d. Consequently thermal conductivity of gray cast iron alloyed with nickel is higher than the others.

It is reported that a 1.4 wt.% Ni cast iron has a lower thermal expansion coefficient [15].

Therefore it can be concluded (from Eq. (1)) that thermal shock resistance increases with increasing in Ni percentage but Fig. 1 did not show this relation. It seems that the reason for these changes in thermal shock resistance in presence of Ni is: (1) the increase in oxidation along the graphite flakes which weakens the gray cast iron and lowers the thermal conductivity. (2) Facilitation of cracking and crack propagation with the graphite phase.

As it can be seen in Fig. 1, the Ni curve is between the Mo and Cr curves. It is speculated that the poor performance of gray cast iron in Ni curve is due to the oxidation along graphite phase and in Cr curve is due to the reduction of toughness in presence of Cr carbides.

3.2. *Tensile strength*

The tensile test was done on unalloyed gray cast iron and the ultimate tensile strength (σ_{uts}) measured as 182 MPa and the other specimens were also tested. The relative results are presented in Fig. 3 (ultimate tensile strength as a function of alloying elements percentage). It can be observed that, similar behavior in all curves is evident in such a way that as the alloying elements content increases, the ultimate tensile strength also increases. It can be seen that the increasing rate of σ_{uts} in Cr curve is higher than in Mo curve.

Deterioration of mechanical properties occurs concurrently with growth as a result of structural decomposition. Investigators have shown that alloy additions stabilize the pearlite whereas it reduces the growth. It is reported that addition of Cr together with Mo is effective in limiting the growth, as well as the addition of Cr, Mo together with Ni [18]. According to Bertodo's reports [19] the effect of Cr on structure stabilizing and reducing the decomposition of pearlite, seems to be the reason for the strong influence of Cr on enhancing of σ_{uts}.

Fig. 2 shows this effect of Cr by reducing the amount of graphite. So it can be concluded that chromium is the most effective element in limiting the growth and pearlite decomposition. In Fig. 3, this effect is shown as the greatest σ_{uts}.

The increase in graphite volume fraction that is resulted from a rise in Ni percentage can be attributed to an increase in type A graphite. The rise in Ni content up to 0.54 wt.% causes the enlargement of graphite flakes. However, further increase in Ni percentage decreases the graphite flake's size and also causes to an increase in volume percent of pearlite and consequently decreases the pearlite grains size [22].

It seems that the rise in σ_{uts} in presence of Ni is related to the increase in small grain size pearlite.

The last gray cast iron which was alloyed with (wt.%) 0.8 Mo–0.2 Cr–0.08 Sn was also studied for thermal shock resistance. The main reason for addition of tin is the strong influence of this element on increasing the tensile strength and the volume fraction of pearlite. Tin is one of the pearlite promoting alloying elements. The increase in Sn content up to 0.1 wt.% will lead to produce pearlitic structure [23]. It is reported that the tensile strength at elevated temperatures rises with the increase in pearlite percentage [24].

Therefore it seems that Sn can easily improve the thermal shock resistance of the gray cast iron. Finally, the thermal shock and tensile strength tests were performed on these samples with the combination of (wt.%) 0.8 Mo–0.2 Cr–0.08 Sn alloying elements. The number of cycles to create the first major crack and the ultimate tensile strength for these samples were 26 cycles and 293 MPa, respectively.

Two important factors that are necessary to withstand thermal and external stresses are a high tensile strength and high fatigue strength [13]. These two properties for all the specimens are collected and the variations of them with respect to alloying elements are drawing.

Figs. 4 and 5 show the thermal shock cycles to the main major crack of the alloyed gray cast iron samples and their ultimate tensile strength, respectively. As it is shown, the last sample exhibited the greatest thermal shock resistance and the highest σ_{uts}. The addition of Cr and Ni to gray cast iron samples had the least beneficial effect while the addition of Cr plus Mo in combination with Sn brought about the most significant improvement. It is speculated that the simultaneous presence of Mo, Cr and Sn has produced this improvement due to the enhancement of pearlite volume fraction, reduction in the pearlite grain size and the volume fraction of graphite phase. In this test series, there was good correlation between tensile strength and the number of cycles to the first major crack.

3.3. Crack morphology

The SEM micrographs in Fig. 6 are regarding to cracks in two different samples.

It can be seen that cracking was associated with the graphite and occurred mostly in the graphite phase. However, the cracks did not progress in all instances from the flake tips but followed the shortest path between flakes normal to the applied stress. Crack propagation from the sides of graphite flakes was therefore frequently observed. Fracture through the matrix of the samples was random and not influenced by grain boundaries or interfaces. The matrix characteristics neither changed the nature of the cracking nor improved the resistance to crack propagation. Observations of the cracking behavior suggest that the controlling step in the thermal fatigue process is the nucleation rate of cracks in the graphite flakes. Crack propagation then proceeds at an initial rapid rate through the graphite phase with little influence of the matrix.

These results have also been observed in previous laboratory investigations [25,26].

4. Conclusions

In gray cast iron:

1. An increase in the molybdenum, chromium and nickel content (wt.%) in the range of 0.2–0.8, 0.2–0.5 and 0.5–1.5 respectively in the gray cast iron (Fe–3.7 wt.% C) resulted in an increase in σ_{uts}.
2. Mo was the most effective alloying element for the increase in thermal shock resistance of the gray cast iron.
3. Thermal shock resistance of the gray cast iron was not affected by the addition of Ni as alloying element.
4. Approximate composition of the gray cast iron which exhibited maximum thermal shock resistance was (wt.%) Fe–3.7 C–0.8 Mo–0.2 Cr–0.08 Sn.
5. Crack initiation occurred in the interior of the graphite flakes and propagated mainly along the flake length.
6. Crack propagation throughout the structure did not always progress between flake tips but at times appeared to follow the shortest path between flakes normal to the stress, regardless of pearlite orientation.

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