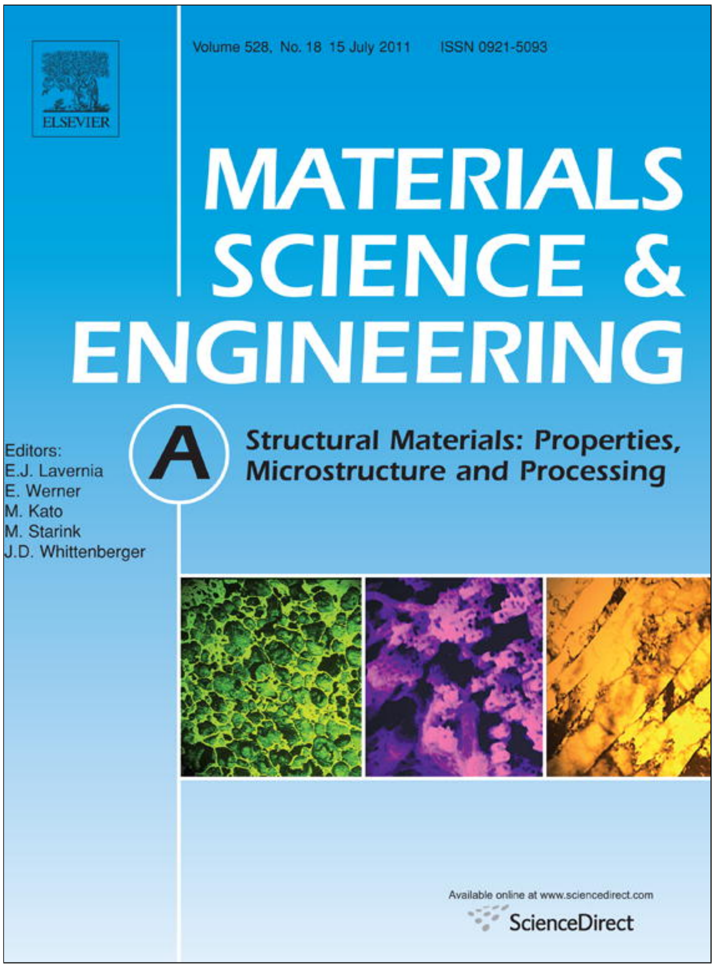
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Development of carbon—Low alloy steel grades for low temperature applications

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ABSTRACT

Low alloy steels are processed to fulfill the requirements of low temperature applications. Besides the chemical composition, the steel should receive a suitable heat treatment to ensure the targeted mechanical properties at low temperature. In other words, the steels are designed to delay the ductile to brittle transition temperature to resist dynamic loading at subzero temperatures. Steel alloys processed for liquefied gas pipeline fittings are examples for applications that need deep subzero impact transition temperature (ITT).

The main purpose of the present work was to find a suitable heat treatment sequence for alloys LC2 and LC2-1. Further, it aimed to correlate the impact toughness with the microstructure and the fracture surface at different sub-zero temperatures.

The steels under investigation are carbon-low alloy grades alloyed with Ni, Cr and Mo. LC2 steel alloy has been successfully processed and then modified to LC2-1 alloy by addition of Cr and Mo. Oil quenching from 900 °C followed by tempering at 595 °C was used for toughness improvements. Hardness, tensile and impact tests at room temperature have been carried out. Further impact tests at subzero temperatures were conducted to characterize alloys behavior. Metallographic as well as SEM fractographic coupled with XRD qualitative analysis are also carried out.

Non-homogenous martensite–ferrite cast structure in LC2 was altered to homogeneous tempered martensite structure using quenching–tempering treatment, which is leading to shift the ITT down to −73 °C. Addition of Cr and Mo creates a very fine martensitic structure in LC2-1 alloy. Quenching–tempering of LC2-1 accelerates ITT to −30 °C. It is expected that the steel was subjected to temper embrittlement as a result of phosphorus segregation on the grain boundary due to Cr and Mo alloying, as it was concluded in reference no. [6].

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1. Introduction

Nickel does not form any carbide compounds in carbon-low alloy steel grades, where it remains in solution in the ferrite leading to strengthening and toughening the ferrite phase. Nickel steels are easily heat treated because nickel lowers the critical cooling rate. In combination with chromium, nickel produces alloy steels with greater hardenability, higher impact strength, and greater fatigue resistance than can be achieved in carbon steels [1]. Nickel, like manganese, is useful for improving the notch toughness of steel at low temperatures [2].

The increase in hardenability due to Cr addition is often sufficient to develop a martensitic microstructure, which provides high upper-shelf energy [2]. Furthermore, chromium helps in the formation of carbides, which contributes to enhancing matrix strength [3].

Molybdenum is frequently used to increase hardenability, and it influences notch toughness primarily through its effect on microstructure. 0.5–1.0% Mo can be added to alloy steels to reduce their susceptibility to temper embrittlement [2]. Molybdenum helps in the formation of carbides, which contributes to enhancing matrix strength and assists in refining the grain size and thereby contributing to an improvement in toughness [3].

Quenching and tempering has been applied to carbon-low alloy steels to produce finer aggregates of tempered martensite to raise both the strength and notch toughness. Tempering temperature was proposed to be not less than 595 °C [4]. Li in his work published on year 2000 [5], concluded that steel castings that have been quenched and tempered have higher notch toughness than similar castings in the as cast, annealed, or normalized condition.

In a review article dealing with temper embrittlement of structural alloy steels published by ZabiĺSkii [6], it was discussed the effect of alloying with Cr, Mn, Ni, and Mo. The temperature range of

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Table 1
Chemical composition of the processed alloys.

Code	Chemical composition (mass %)							
	C	Si	Mn	P	S	Ni	Cr	Mo
LC2	0.199	0.388	0.574	0.0203	0.015	2.73	–	–
LC2-1	0.219	0.448	0.581	0.0265	0.0269	2.82	1.87	0.536

temper embrittlement is 400–600 °C taking into consideration the cooling rate [7]. A distinguishing future of temper embitterment of steel containing phosphorus >0.05% is the intergranular (transcrystalline) nature of fracture and the consequent higher temperature of the ductile-brittle transition [8]. The real cause of temper embrittlement is segregation on grain boundaries of interfaces-active additives, like phosphorous and antimony, in the presence of carbide forming elements like Cr, Mn, and Mo [6]. The lack of temper embrittlement in ordinary carbon steel with high C/P ratio is due to the competition between C and P atoms, i.e., by the displacement of the "deleterious" P by the useful C from the grain boundaries [6].

The main aim of the study was to obtain further evidence or understanding to correlate heat treatment (necessary for optimizing sub-zero toughness requirements) with microstructure and accordingly sub-zero toughness for these steels.

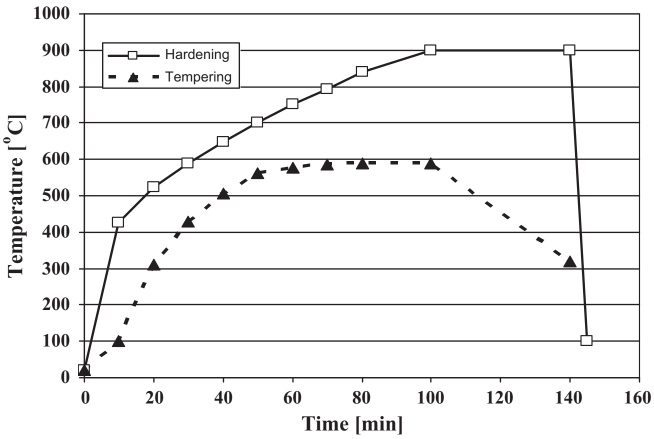


Fig. 1. Hardening and tempering treatment cycles for both alloys.

2. Experimental work

Induction furnace was used for melting scrap and the alloying elements to compensate the deficiency of these elements in the melt. Alloy LC2 was sand cast from the melt in the form of two Y-blocks weigh 20 kg each. A modification was made on the rest of the melt (60 kg) to obtain alloy LC2-1 by adding Fe–Cr and Fe–Mo to the melt. Two Y-blocks were cast representing alloy LC2-1. The chemical composition of both alloys is shown in Table 1.

Hardening (quenching)–tempering cycles are used to develop the targeted properties. Fig. 1 represents the actual records of both treatment cycles.

Hardness, tensile and impact tests at room temperature have been carried out. Further impact tests at subzero temperatures were conducted to characterize the alloy behavior. Metallographic as well as SEM fractographic coupled with XRD qualitative analysis have been done.

3. Results and discussion

The chemical composition of both processed grades LC2 and LC2-1 are matched with that stated in ASTM A352. Both grades are suitable for valves, flanges, fittings, and other pressure containing parts intended primarily for low temperature services.

Fig. 2 represents the as-cast as well as heat treated microstructure of LC2 alloy. The microstructure shown in Fig. 2(a) contains martensite matrix with some ferrite aggregates. This microstructure is a heterogeneous microstructure which would lead to low mechanical properties, consequently a suitable heat treatment cycle like quenching–tempering is required in order to make a homogeneous microstructure with martensite better mechanical properties.

Quenching process transforms the ferrite aggregates to form totally hard-brittle martensite phase. The tempering process is done in order to produce less brittle martensite (tempered martensite) as illustrated in Fig. 2(b) and to relief the internal stresses that occurred during quenching. The microstructure becomes homogeneous and fine after quenching–tempering treatment which would lead to high mechanical properties [9].

The mechanical properties of alloy LC2 are presented in Fig. 3. Fig. 3(a) represents the mean value of hardness of the as-cast and heat treated LC2 specimens. It is clear that hardness of heat treated specimens increased by 9.4 [HRA], which reflects the positive effects of the applied heat treatment cycle. Furthermore, the tensile properties presented in Fig. 3(b) ensure that UTS of quenched-tempered specimens is higher than of the as-cast ones. UTS results confirm what have been obtained from the hardness

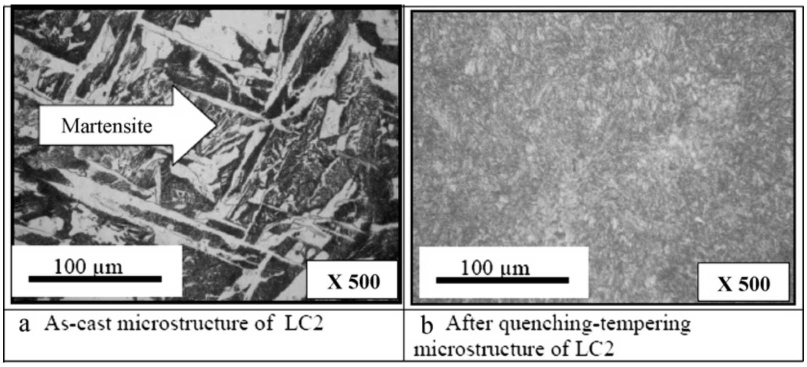
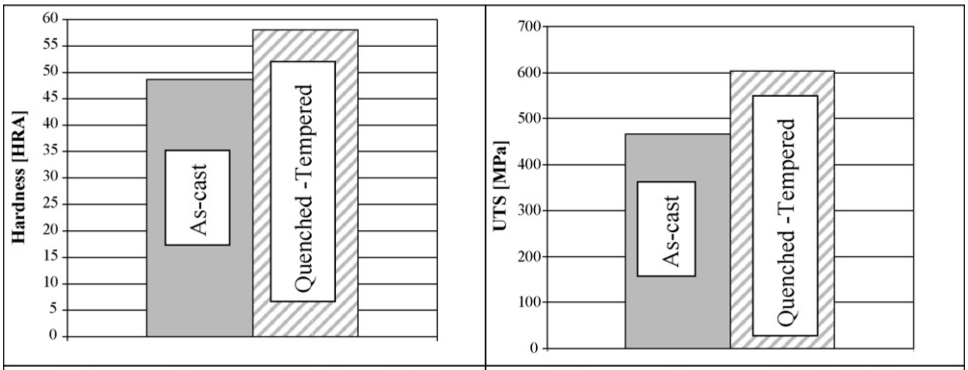


Fig. 2. As cast and heat treated microstructures of LC2.



(a)As-cast and heat treated Hardness of LC2 | (b)As-cast and heat treated UTS of LC2

Fig. 3. Hardness and UTS of alloy LC2 for as cast and heat treated conditions.

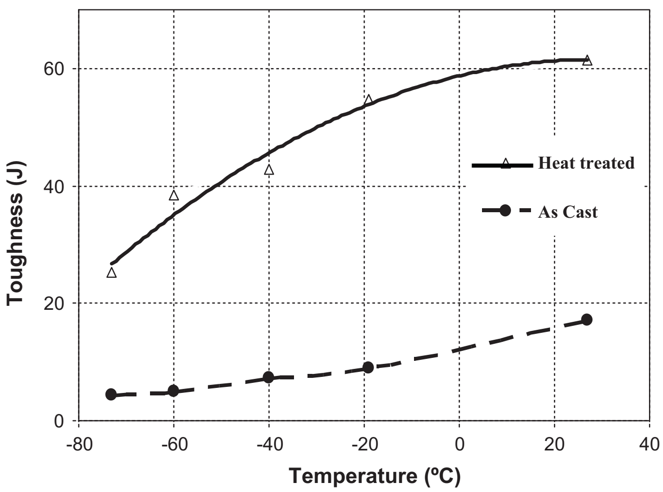


Fig. 4. Toughness of as-cast and heat treated state of Alloy LC2.

measurements ensuring that the heat treatment cycle was properly selected. The present results fulfill the requirements stated in the ASTM A352 standard [4]. The improvement of the mechanical properties which is accompanied by the heat treatment cycle is attributed to the homogenous and fine microstructure as presented in Fig. 2(b).

Impact is one of the most important tests necessary to characterize the behavior of the steel alloy at both room and subzero temperatures. Fig. 4 represents impact results for as-cast and heat treated conditions at different temperatures for alloy LC2. At room temperature, it is clear that the impact value for the as cast condition has a lower value (17.2 J) than that of heat treated condition (61.5 J). This is clearly reflecting the successful effect of heat treatment cycle and confirming what have been concluded previously [9].

Table 2
XRD analysis of grain boundary precipitates of alloy LC2 in the as-cast state.

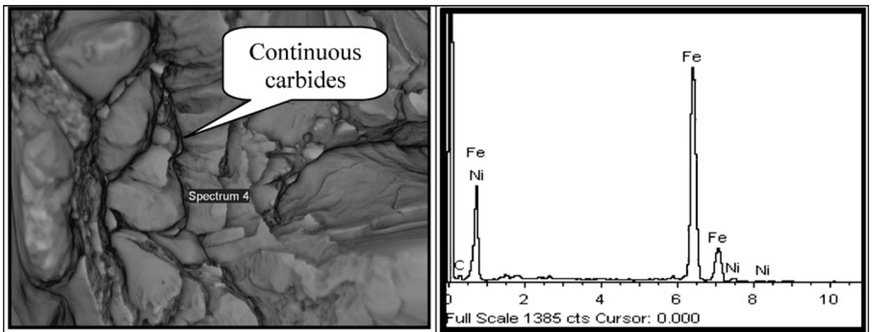
Element	C	Fe	Ni
Atomic %	23.86	74.26	1.88

On the other hand, it is observed that toughness decreases continuously with the decrease of testing temperature for both conditions. Furthermore, toughness of the heat treated condition is always higher than that of the as cast condition which is another positive effect of the heat treatment cycle [10].

Fracture surfaces of the impact specimens were examined by a scanning electron microscope (SEM) to determine fracture mode. Fig. 5(a) illustrates the fracture surface of impact specimen for the as cast stat tested at room temperature, while Fig. 5(b) represents the XRD qualitative analysis on the grain boundary precipitates of LC2 alloy.

A vast majority of the fracture surface is cleavage facets with thin layers of precipitates imbedded between the facets. This fracture pattern reflects the low value of toughness at the room temperature. The fracture pattern in Fig. 5(a) confirms the results of impact and other mechanical tests. The continuous carbide film forms net-like shape, facilitating the crack propagation [11].

Table 2 represents the XRD qualitative chemical contents of the grain boundary precipitates. It can be summarized that the precipitates are mainly iron carbide and precipitated on the grain boundary of the alloy LC2.



(a) Fractograph of LC2 alloy tested at room temperature | (b) XRD qualitative analysis on the grain boundary precipitate of LC2 alloy

Fig. 5. Fracture surface and XRD qualitative analysis on the grain boundary precipitate of LC2 alloy.

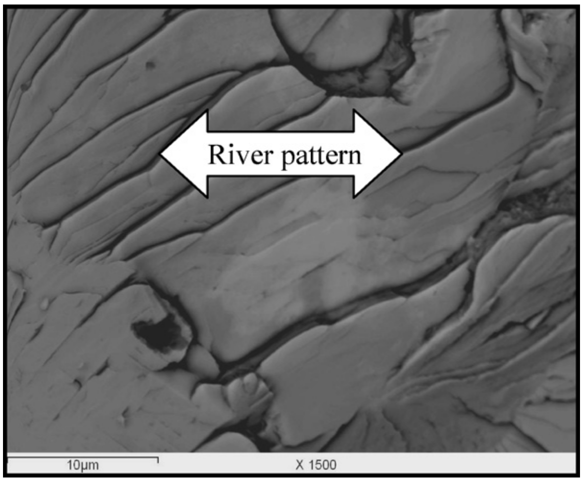


Fig. 6. SEM fractographic for LC2 at −60 °C for the as cast state.

Fig. 6 represents the fracture surface which contains river pattern for LC2 at −60 °C for the as-cast state.

The river pattern indicates that the alloy becomes more brittle at −60 °C than at room temperature and the impact toughness will be decreased as a result of lowering the testing temperature, which is confirmed by the work published by Li [10].

Fig. 7 represents the SEM fractographs for LC2 after quenching–tempering heat treatment tested at room temperature and at −40 °C.

Both figures clearly show the successful effect of the heat treatment cycle applied on alloy LC2. The fracture surface presented in Fig. 7(a) contains fully fine dimple rupture reflecting high values of impact toughness, where these fine dimples indicate considerable ductility [10].

Fig. 7(b) represents the fracture mode of heat treated alloy LC2 at −40 °C. The fracture mode indicates that the alloy goes towards brittle behavior, as the fractograph changed from complete fine dimples at room temperature to mixture of dimples with considerable amount of facets. The dimple portion determines alloy ductility level [9].

4. Alloy LC2-1

Fig. 8 represents the microstructure of the as-cast, (a) and quenched-tempered condition, (b) of alloy LC2-1.

The as-cast microstructure is totally martensitic structure as a result of the alloy modification with Cr and Mo. Early forming of molybdenum carbide (Mo_3C) and chromium carbide (Cr_3C) during solidification are leading to fine martensitic structure where both carbides were working as nuclei or seeds for martensite creation. This result is confirmed by the work early done by El-Bitar, and El-Banna [11].

The microstructure presented in Fig. 8(b) contains mixture of damaged (non homogeneous) martensite structure as a result of unsuitable quenching–tempering treatment cycle. In one of the reviews dealing with temper embitterment [6] it was confirmed that alloying with Cr and Mo in combination with Ni promotes the temper embitterment process, which would result in damaging the impact properties [11].

Fig. 9 represents the hardness as well as tensile strength properties of alloy LC2-1.

After quenching–tempering treatment, LC2-1 alloy shows a non significant increase in hardness indicating that the heat treatment was not effective. At the same time, ultimate ten-

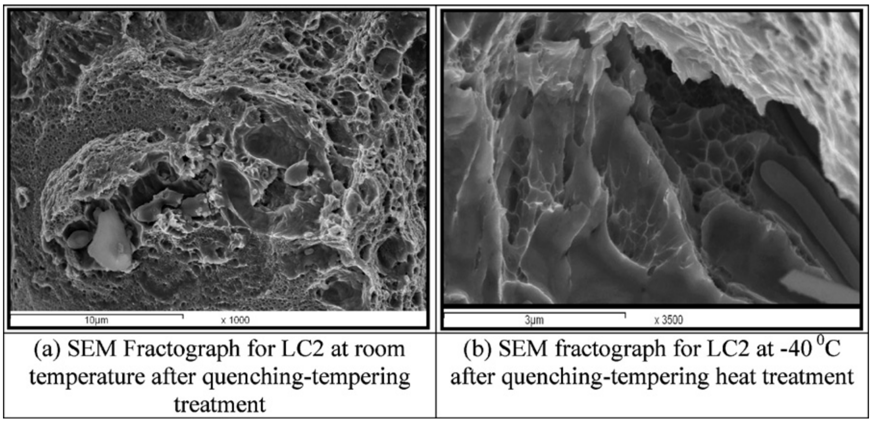


Fig. 7. SEM fractographs for LC2 at room temperature and at −40 °C after quenching–tempering treatment.

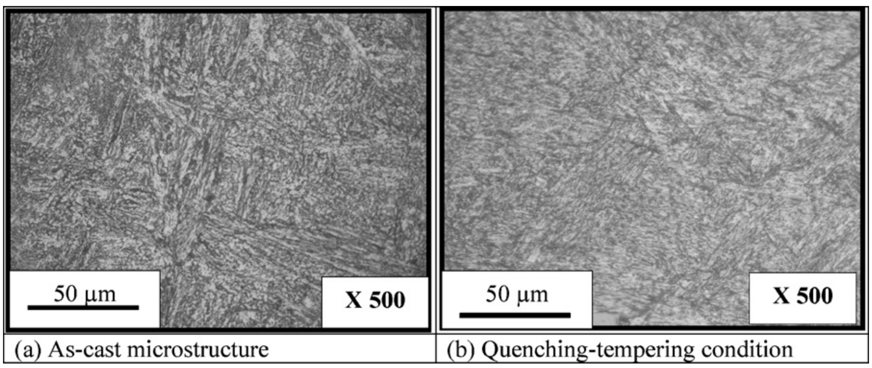
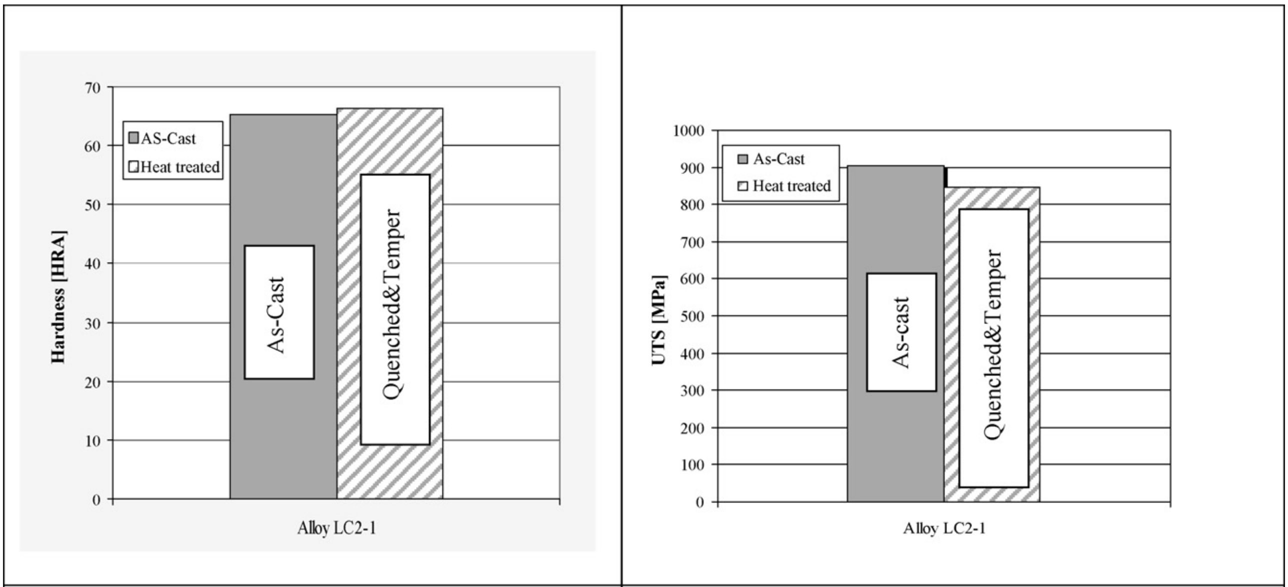


Fig. 8. As cast and heat treated microstructure of alloy LC2-1.



(a) As-cast and quenched-tempered Hardness of LC2-1

(b) As-cast and quenched-tempered UTS of LC2-1

Fig. 9. Hardness and UTS of alloy LC2-1 for as-cast and quenched-tempered conditions.

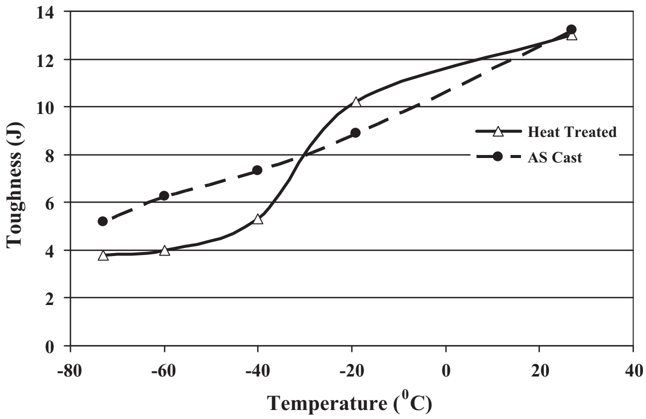


Fig. 10. Impact toughness results for alloy LC2-1 before and after quenching–tempering.

sile strength has been decreased after treatment confirming that quenching–tempering is not the proper treatment to enhance the mechanical properties [6].

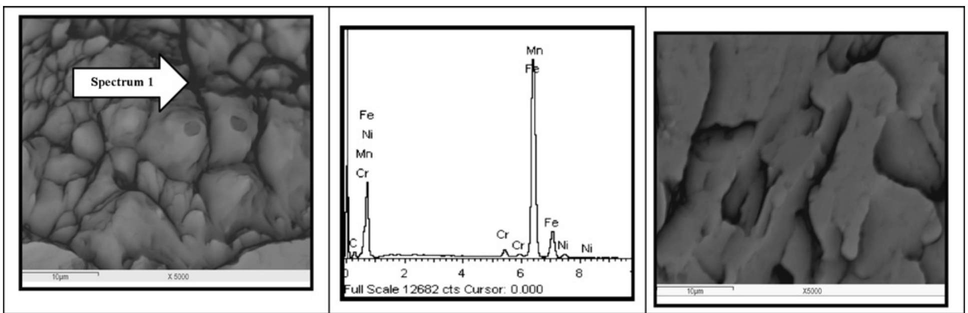
Fig. 10 represents the impact toughness results for alloy LC2-1 before and after quenching–tempering at different temperatures.

The impact results reflect the negative effect of applying a non proper heat treatment cycle, especially at low temperature (−30 °C to −73 °C) where the impact value of the heat treated was lower than the as cast condition. The present results were previously confirmed by the review article on temper embitterment [6].

Fig. 11 represents

(a) fractograph of LC2-1 alloy tested at room temperature for the as-cast state;
(b) XRD qualitative analysis on the grain boundary precipitates of LC2-1 alloy;
(c) fractograph of LC2-1 alloy tested at −50 °C for the as cast state.

The fracture surface presented in Fig. 11(a) shows coarse dimple rupture and continuous carbide film impeded between this dimple.

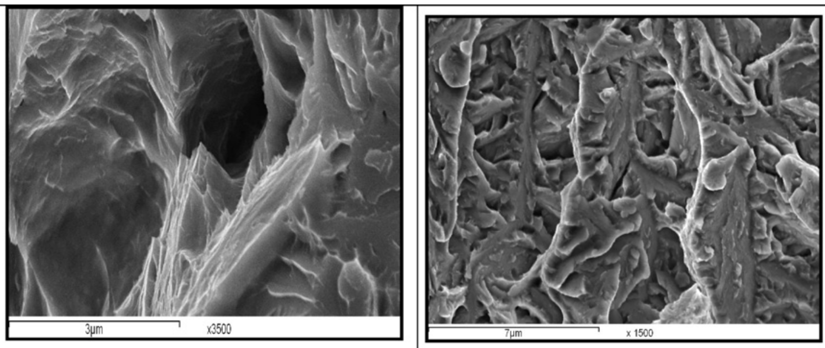


(a) Fractograph of LC2-1 alloy tested at room temperature at the as-cast state

(b) XRD qualitative analysis on the grain boundary precipitate of LC2-1 alloy

(c) Fractograph of LC2-1 alloy tested at -50 ^{0}C at the as cast state

Fig. 11. Fractograph of LC2-1 alloy tested at room temperature and at −50 °C for the as-cast state combined with XRD qualitative analysis on the grain boundary.



(a) SEM Fractographic for Alloy LC2-1 after quenching-tempering treatment tested at room temperature	(b) SEM Fractographic for Alloy LC2-1 after quenching-tempering treatment tested at -50 °C

Fig. 12. Fractographs of LC2-1 alloy after quenching–tempering treatment impact tested at room temperature and at −50 °C.

Table 3
XRD analysis for alloy LC2-1 at the as-cast state.

Element	C	Cr	Mn	Fe	Ni
Atomic %	25.44	1.45	0.54	70.71	1.85

The continuous impeded carbide film reflects the low impact value of alloy LC2-1 at room temperature as obtained in Fig. 10.

A qualitative analysis (XRD) on a triple point on the fracture surface of LC2-1 is presented in Fig. 11(b). Table 3 includes the peak values of the containing elements. The comparing XRD pattern and Table 3 can be concluded that the grain boundary precipitates are chromium carbides.

Fig. 12(a) illustrates the fracture surface of alloy LC2-1 after quenching–tempering treatment cycle and then impact tested at room temperature. It is clear that the fracture surface shows coarse dimple rupture with some impeded carbides. However, Fig. 12(b) represents fractograph of the alloy but it was tested at −50 °C. It is obvious that the fracture surface contains complete facets with many impeded flaky carbides (dark), which are considered as a strong micro cracks initiators. This would badly affect on the impact toughness at sub-zero temperature as a result of improper quenching–tempering cycle.

5. Conclusion

1. Molten LC2 steel alloy can be modified into LC2-1 by addition of Cr and Mo.
2. Oil quenching from 900 °C followed by tempering at 600 °C is essentially for LC2 alloy to alter the non-homogenous martensite–ferrite cast structure into homogeneous tempered martensite structure.
3. The impact transition temperature (ITT) for quenched-tempered LC2 alloy was not detected down to −73 °C.
4. Alloying molten LC2 steel alloy with molybdenum and chromium creates fine martensitic structure in the modified alloy LC2-1.
5. Improper quenching–tempering of alloy LC2-1 leads to form facets impeded with flaky carbides as a result of temper embrittlement.

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