Temper Embrittlement Sensitivities of 3Cr–1Mo and 2.25Cr–1Mo Low Alloy Steels

Hossein ARABI, Shamseddin MIRDAMADI and A. R. ABDOLMALEKI

Department of Metallurgy and Materials Engineering, Iran University of Science and Technology, P.O. Box 16844-13114, Tehran, Iran. E-mail: arabi@iust.ac.ir, shmirdamadi@iust.ac.ir, abdolmaleki@iust.ac.ir

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Contradicted results have been reported on sensitivities of Cr–Mo low alloy steels to fracture toughness, so it seems further investigations is required in order to establish the reasons for this contradictions. This study tried to rationalize the causes of contradiction and establishes the reasons for variations in the observed changes in fracture toughness of two types of low alloy steels namely 3Cr–1Mo and 2.25Cr–1Mo steels.

For investigating the embrittlement sensitivity in this research, a factor called J used since there are some clams that Cr–Mo low alloy steels with higher *J*-Factor are more sensitive to temper embrittlement.

For inducing temper embrittlement on these alloys, a step-cooling operation from high temperature to room temperature for a period of 234 h was employed. Then some of the mechanical properties of the embrittled sample and unembrittled alloys were determined and compared. The results showed that step cooling operation had no noticeable effect on tensile and hardness properties of the steels but strongly affected their resistance to impact. In the alloy having a low *J*-Factor of equivalent to 107, changes in both FATT and TT54J were about 11°C, this was relatively low, while in the alloy having a high *J*-Factor equivalent to 224, these changes were 70°C and 78°C respectively which indicated this alloy was highly sensitive to temper embrittlement. Changes in temper embrittlement of the two alloys used in this research were found and we tried to justify these changes in this article.

KEY WORDS: *J*-Factor; temper embrittlement; Cr–Mo steels; toughness; sensitivity; step-cooling; FATT; TT54J.

1. Introduction

Cr–Mo low alloy steels are extensively used in petroleum industries, hydrocracker and Isomax reactors, heat exchanger shells and petroleum fireheater tubes due to their good mechanical properties. However these ferritic alloys usually suffer from temper embrittlement when expose to temperature range of 370–550°C for a long period.[1–4] Two embrittlement mechanisms are suggested for these types of alloys.

1. The gradual migration of impurity elements such as P, Sn, As, and Sb to grain boundaries and formation of brittle phase in there, causes brittleness.[3–5] These phases are usually very small but can be detected by TEM.[6]
2. Changes in size and morphology of carbides in a long time, causes brittleness of the alloys.[7,8]

Factors affecting temper embrittlement of low alloy Cr–Mo steels are suggested to be as follow.[4,9]

- Chemical composition
- Temperature
- Holding time
- Applied stress

Among these factors, the effect of chemical composition and temperature on temper embrittlement has mostly been investigated by most of researches. For example, Low *et al.*[4] observed the formation of higher amounts of brittle phases in the boundaries when the amounts of impurities in these types of alloys were increased. However, one should be also aware of the effect of time, as the diffusion rate strongly depends on both time and temperature. So the higher the temperature and the longer the time of diffusion, the more can be the amounts of brittle phase precipitates within the boundaries, hence the more is expected to be the amount of embrittlement of the alloy.

Some other researchers[9] have studied the effect of tensile stress on the rate of embrittlement of low alloy steels. They said that application of tensile stress causes an increase in the embrittlement of the steel, but its effect is much less than other parameters mentioned earlier.

Two methods for investigating temper embrittlement phenomena are as follow.[6]

- Isothermal aging technique (holding the alloy for a long time at a constant temperature).
- Using a step-cooling process.

Since isothermal aging requires a long period of time, it is not very adequate method, and the second method is usually employed for embbrittleness investigation. **Figure 1** shows a typical step-cooling operation which used by

American Petroleum Institute (API).[6] This heat treatment operation is said to be equivalent to approximately 100 000 h isothermal aging. For investigating the sensitivity of Cr–Mo steels to temper embrittlement, Miyano and Watanabe[3] defined the following *J*-Factor:

$$J\text{-Factor}=(\text{Mn}+\text{Si})(\text{P}+\text{Sn})\times 10^4$$

J-Factor is a dimensionless factor related to the amount of elements indicated above, and its value indicates the sensitivity of steel to temper embrittlement. Its value for low alloy Cr–Mo steels is usually between 100–400. For measuring the amount of temper embrittlement in Cr–Mo steels, FATT (fracture appearance transition temperature) and TT54J (54 J transition temperature) parameters before and after heat treatment are usually measured; differences between these parameters indicate the higher amount of induced temper embrittlement in the alloy.[10)]

2. Materials and Experimental Procidure

The compositions of the two types of ferritic steels with ferrite–bainite sub-structure were used in this research, are presented in **Table 1**.

The composition of 3Cr–1Mo steel (coded A) was according to ASTM A387 Gr. 21 and the composition of 2.25Cr–1Mo (coded B) steel was based on ASTM A387 Gr. 22 class 2. Samples of 3Cr–1Mo steel were cut from the shell of a condemned Isomax reactor, which had been in service for 22 years. The reactor was worked at 465°C and 19 MPa and served as a hydrocracker (Isomax) reactor. The cut out samples from both steels were first dehydrogenated at 630°C under a vacuum of 10^{-5} T (1.33×10^{-3} Pa) for 2 h to eliminate hydrogen which had penetrated during service. Then samples of 3Cr–1Mo were de-embrittled by annealing at 635°C for 2 h, and subsequently quenched in water to inhibit the formation of harmful phases. The 2.25Cr–1Mo samples were heat treated at 920°C for 3 h and then cooled in air. They were finally tempered of 690°C for 3 h. All the above mentioned samples were termed as treated samples in contrast to the samples taken from the end cup of the reactor, **Fig. 2**, and mechanically tested without being subjected to any heat treatment cycles, prior to mechanical testing; these samples were termed as untreated samples. Tensile tests were performed in an Instron 6027 Universal machine according to ASTME12 standard.

Thirty charpy impact test specimens for each of treated and untreated steels were prepared according to ASTM E 23. The impact tests were performed at various temperatures so that brittle to ductile transformation diagram for each case can be drawn. It should be mentioned that for homogenizing the temperature before impact test, the specimens were hold for 10 min at a certain temperature, and then the impact tests were performed immediately. In any test temperature, 5 impact specimens were performed. To establish the percentage of crystalline and shear fracture surface, comparative method according to ASTM E23 was used.

For producing temper embrittlement in the specimens, they were subjected to heat treatment operation shown in Fig. 1 in a fully controlled element furnace for a period of 234 h. After heat treatment of the specimens, their surfaces were carefully polished before performing various mechanical tests.

ICP (induction coupled plasma) method was used for analysis of Sn and Mn, and spectro Gravimetery method for analysis of P and Si.

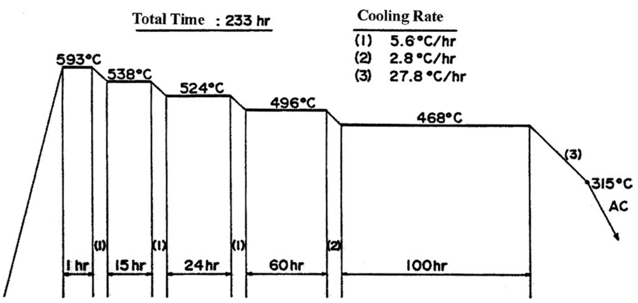

Fig. 1. Step-cooling heat treatment used in this research.[6)]

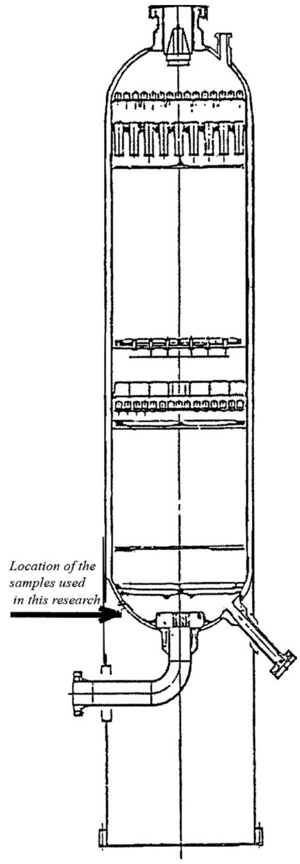

Fig. 2. Position of the specimens that cut from Isomax reactor.

Table 1. Compositions of the two alloys used (wt%).

Alloy Type	Code	C	Mn	Si	P	Cr	Mo	S	Sn	Cu	Ni	V	Fe
3Cr-1Mo	A	0.112	0.491	0.282	0.016	2.7	0.86	0.0013	0.013	0.22	0.3	0.1	Rem.
2.25Cr-1Mo	B	0.078	0.471	0.2434	0.013	2.1	0.96	0.0014	0.002	0.011	0.03	0.009	Rem.

Table 2. Position of the specimens that were cut from Isomax reactor.

Steel Code	State	Proof stress 0.2%(MPa)	UTS (MPa)	Elongation in 50 mm (%)	Reduction of Area (%)
A	Untreated	312±5.5	522±4.8	32±1	67±2
	treated	341±4	550±3.4	32±1.5	63±1.5
B	Untreated	365±3.8	500±3.5	32±1	82±1
	Treated	368±2.5	508±2	32±1.6	81±1.8

Table 3. Results of Rockwell B hardness test.

Steel Code	State	Average Hardness No.	Hardness Range	No of Test Points
A	Untreated	81.5±0.8	79.9-85.9	8
	treated	86.5±0.9	83.9-89.3	8
B	Untreated	82.7±0.5	81.4-84.8	11
	Treated	85.7±0.6	81.1-87.2	12

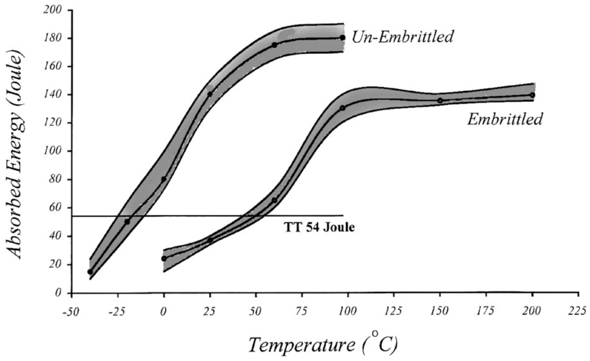

Fig. 3. Variation of impact energy *versus* temperature for 3Cr–1Mo low alloy steel in embrittled and unembrittled condition, shaded areas indicate the amounts of deviation in absorbed energy at any temperature.

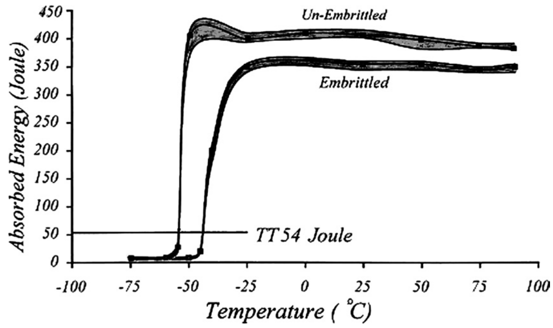

Fig. 4. Variation of impact energy *versus* temperature for 2.25Cr–1Mo low alloy steel in embrittled and un-embrittled condition, shaded areas indicate the amounts of deviation in absorbed energy at any temperature.

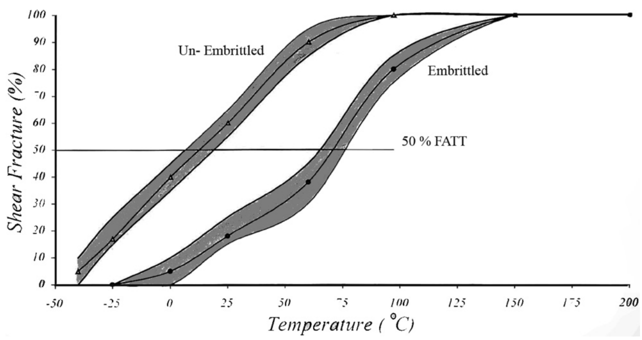

Fig. 5. Percentage of shear fracture *versus* temperature of 3Cr–1Mo low alloy steel in treated and untreated states.

3. Results

J-Factors for the two alloys used were calculated by putting the weight percents of Sn, Mn, P and Si in the *J*-Factor formula proposed by Miyano and Watanabe. So, for the steels A and B this factor was as follow:

Steel A: $J_A=(0.491+0.282)(0.016+0.013)\times10^4=224$

Steel B: $J_B=(0.471+0.243)(0.013+0.002)\times10^4=107$

The result of tensile tests at room temperature for both type of steels are shown in **Table 2**.

Table 2 indicates that heat treatment had a little effect on tensile properties of both steels, although it's effect on steel A was slightly more than that of steel B. By inducing temper embrittlement in steel A, Yield strength was increased by 9.3% and UTS by 5.5%, while induction of temper embrittlement in steel B resulted to an increase of about 1% and 1.6% in yield strength and UTS respectively. The results of Rockwell B hardness test on the steels A and B are presented in **Table 3**. The results show a slight increase in hardness of both steels after heat treatment.

The results of impact tests are shown in **Figs. 3**–**6** and **Table 4**. Figure 3 indicates that temperature related to 54 J energy (TT54J) in 3Cr–Mo steel before heat treatment was −20°C while after heat treatment and application of step-cooling process this temperature changed to +50°C. This is an average change of 70°C in TT54J due to induction of brittleness in 3Cr–Mo steel. This figure also shows that impact energy of 3Cr–1Mo steel at room temperature (25°C) reduced from 140 to 37 J after being subjected to temper embrittlement operation. This means a reduction of about 80% in impact energy of 3Cr–1Mo steel.

Impact energy of 2.25Cr–1Mo steel is shown in Fig. 4. This figure shows that TT54J before and after application of heat treatment was −54°C and −43°C respectively. So an increase of 11°C in TT54J occurred as the result of application of step-cooling operation on 2.25Cr–1Mo steel. This means temper embrittlement of 2.25Cr–1Mo steel did not affected critically the impact resistance of this steel, as it affected 3Cr–1Mo steel. Another point observed in Fig. 4 is that a change in transition temperature was about 10°C which is an indication of sudden change in toughness behavior of this steel.

Figure 5 shows variation of shear fracture percentage as a function of temperature for 3Cr–1Mo steel. This figure shows the average 50% FATT for unembrittled 3Cr–1Mo steel was about +10°C, while this temperature for embrit-

Table 4. Average transition temperature related to various impact tests of the samples before and after heat treatment for steels A and B extracted from Figs. 3–6.

Steel Code	State	J-Factor	TT54J(°C)	FATT (°C)	ΔTT54J(°C)	ΔFATT (°C)
A	Untreated	224	-20	+10	70	60
	Treated	224	+50	+70		
B	Untreated	107	-54	-53	11	11
	Treated	107	-43	-42		

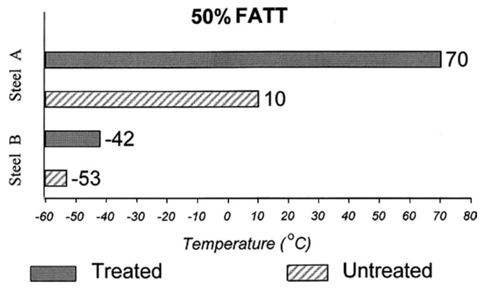

Fig. 6. Comparison of 50% FATT for treated and untreated conditions of steel A and steel B.

tled 3Cr–1Mo steel was about +70°C. This is an average change of 60°C in FATT due to heat treatment applied on 3Cr–1Mo steel.

Finally, comparison of 50% FATT for both steels, *i.e.* A and B is presented in Fig. 6. This figure shows that while the average change of 30% FATT for steel A is 60°C, this change for steel B is only 10°C.

4. Discission

The results obtained in this research show that sensitivity to brittleness is a function of *J*-Factor. *J*-Factor itself is said[3)] to be a function of the percentage compositions of Mn, Si, P and Sn as indicated earlier. Therefore one expects that sensitivity of steel coded A in Table 1 be higher than that of steel B as it's *J*-Factor was much more than that of steel B, see Table 4. Worth mentioning that some other researches such as Yu *et al.*[5)] attributed higher sensitivity of this type of steel only to the content of Sn and P, so when these elements increase within the compositions of steels, their sensitivity to embrittleness, expected to increase. The results obtained in this research justifies to some extent the above argument as the sensitivity of steel A having higher amounts of these elements relative to steel B was higher. On the other hand the rate of diffusion of P and Sn can be improved in the presence of the other elements such as Mn and Si in low alloy ferritic steel according to Yu *et al.*[11)] Therefore one may say that reduction of these elements would result to decrease in embrittleness sensitivity in low alloy ferritic steel due to lowering diffusion rate of P and Sn within the substrate, thus once more, it would be reasonable to conclude that the lower contents of Mn and Si in steel B relative to steel A caused a decrease in diffusion rate of P and Sn which in turn decreased it's sensitivity more than steel A. In addition lowering the diffusion rates of P and Sn causes the amounts of these elements within matrix in the form of solute atoms to decrease. Therefore the remainder of these elements would probably remained within the grain boundaries and formed various compounds of Sn and P with Fe which in turn could caused an increase in brittleness of the steel B. Considering the above discussion, one may say that in order to reduce the sensitivity of low alloy ferritic steel to embrittleness, the total amount of Mn and Si within the composition of the steel should be minimized.

The results of tensile tests (Table 2) showed tensile strengths of both steels improved after induction of embrittlement and this improvement in steel A was slightly more than that of steel B. This might be related to the amounts of Si and Mn which were higher in steel A than steel B and consequently caused higher brittleness in steel A as indicated above. However, since the amounts of improvement in tensile strength and hardness properties were not substantial (*i.e.* less than 10% and 5% respectively) changes, these properties would not be a good measure for establishment of sensitivity to embrittleness of this type of steels. Thus, for quantification of temper embrittleness and its effect on mechanical properties, it would be better to use impact data, as it has also been recommended in Ref. 5).

Changes in FATT after step-cooling heat treatment for steels A and B, are 60°C and 11°C respectively. Differences in temper embrittlement of these steels possibly related to the amounts of their impurities. Impurities in steel B was less than that of A, therefore, according to the above assumption its temper embrittlement was expected to be less than that of steel A.

Comparing various curves presented in Figs. 3 to 6 indicates that a large amount of embrittleness has induced due to step-cooling operation in steel A. The amount of changes in 50% FATT before and after induction of embrittleness is consistence with the work of other researchers[2,3)] who showed the maximum change in FATT for all the family of steel A, is about 70°C due to temper embrittlement.

Figure 6 shows 50% FATT for treated and untreated steel B is about 11°C. This means, applications of step-cooling on steel B has a small effect on the 50% FATT of this steel (*i.e.* the toughness did not change). This is consistence with finding of Vignarajah[7)] who stated that step-cooling process does not produce temper embrittlement in Cr–Mo steels. However, the finding of Vignarajah contradicts the result obtained by Watanabe *et al.* This contradiction seems to be due to compositional effect of steels on their embrittleness. The compositions of the type of steels used by Vignarajah are close to steel B used in this research. This steel had a little amount of Mn and Si in comparison to steel A which had a compositions close to the type of steels investigated by Watanabe *et al.* Therefore, one may conclude that the amount of Mn and Si in low alloy steels play a crucial role in their sensitivity to temper embrittlement. It may also be said that Cr–Mo low alloy steels having higher *J*-Factor are more sensitive to temper embrittlement.

5. Conclusions

(1) For evaluation of low alloy steel's sensitivity to temper embrittlement, using *J*-Factor parameters is credited in this research.

(2) Low alloy Cr–Mo steels with smaller *J*-Factors are less sensitivity to temper embrittlement.

(3) Changes in tensile and hardness properties of tempered Cr–Mo low alloy steels were less than 10% in comparison to their non-tempered states, these amounts were lowered by decreasing *J*-Factor.

(4) The amounts of Mn and Si in the compositions of Cr–Mo low alloy steels were very important in determining their temper embrittleness sensitivity.

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