THE EFFECT OF HEAT TREATMENT ON HARDNESS PROPERTIES AND MICROSTRUCTURE OF 9Cr-Mo-V T91 ALLOY STEEL

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Abstract. The effect of heat treatment on hardness properties and microstructure of 9Cr-Mo-V T91 alloy steel have been investigated. In this study, T91 alloy steel were austenitized at 1050 °C for 40 minutes and then quenched in different media such as forced air, air at room temperature, sand and furnace. The austenitization was followed by tempering at 730 °C for 40 minutes with two different quenching media (water and air). The hardness of all T91 steels with different conditions was measured using Micro-Vickers hardness test. The microstructure analyses were examined using optical microscope and field emission scanning electron microscopy (FESEM), while electron dispersive x-ray (EDX) with low kV mode, was used to analyse the chemical compositions of the precipitate in T91 tempered alloy steel. It can be seen from hardness results, the austenitized T91 steel cooled in furnace had shown large grain size and boundaries of ferrite in a martensitic structure which caused decreased in hardness properties. Tempered alloy steel showed the decreased in the hardness value as compared to the austenitized condition due to the coarsening of carbides and breakdown of lath martensitic. Based on EDX analysis, it was confirmed that iron (Fe) and chromium (Cr) were indeed the highest alloying element in T91 alloy steel, and carbide precipitations of $M_{23}C_6$ are dispersed along the prior austenite grain boundaries (PAGB) and sub-grains. Slowest quenching rate after austenitization, which is furnace cooling, was proven to produce ferrite in the matrix of martensite which caused premature failure of T91 alloy steels used in power plant industries. FESEM/EDX utilizing low kV mode (15 kV) was able to analyse precipitate successfully.

Keywords: T91 alloy steel, heat treatment, tempering, hardness, microstructure analyses

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Introduction

Heat treatment is a series of time-temperature treatments in which heat is used to alter or create certain properties in a metal or alloy [1]. It can be used to control the mechanical properties of steel, especially hardness, ductility, strength, toughness and internal stresses. Also, heat treatment of ferrous alloys is considered as an essential industrial process because almost 80 % of all metals widely used are iron and steel. Steels are very advantageous due to their capability to achieve high strengths through heat treatment, while still keeping some degree of ductility. They can be strengthened by increasing the carbon content in the alloy [1].

Grade 91 is an example of low alloy steels with tempered martensite and dispersion of alloy carbides. It is widely used for high-temperature applications due to its enhanced creep strength [2]. The 9-12 wt.% Cr alloy steels have been used widely in steam power plant since the eighties. Thus, Grade 91 steel is one of the reliable options in critical conditions of temperature and pressure because of its enhanced mechanical properties. Furthermore, the modified 9 wt.% Cr-1 wt.% Mo steel is considered as one material with potential for the next generation nuclear power plant in the application of reactor pressure vessels at a maximum temperature of 650 °C [3].

According to the American Society for Testing Material (ASTM), A213 Grade 91 is referred to as T91 for tube and P91 steel for pipe based on various specifications [4]. Although Grade 91 steel has been successfully utilized in fossil power plants for the past two decades, incidents of premature failures during services have been reported [5]. The mechanical properties of the Grade 91 steel rely on the formation of a precise microstructure and the maintenance of that microstructure throughout its service life. According to Cohn et. al. [5], the precise addition of alloying elements such as vanadium (V), niobium (Nb) and nitrogen (N) and the controlled normalizing process that transforms austenite to martensite phase influences the superior properties of Grade 91 steel. Controlled tempering is necessary after the normalizing process so that the alloying elements can precipitate into carbides and carbon nitrides at the defect sites in the microstructure [6].

The presence of ferrite which is soft and ductile that formed by slow cooling rate after heat treatment process may induce the low hardness and strength which further contributes to fracture and premature failure of Grade 91 steel. If the proper microstructure is not achieved during the steel production or maintained during component fabrication, it will either disrupt the precipitates or fully tempered martensite structure will not be formed. These effects will further compromise the mechanical properties of the alloy [6]. Therefore, the objectives of this study are to investigate the effects of heat treatment processes (austenizing and tempering) and medium quenching on the hardness and microstructure of T91 alloy steel. These effects are important in order to reduce the risk of premature failure due to the formation ferritic-martensite microstructure during the services of the T91 alloy steel in power plant industries. The objective also includes the possibility of measuring the composition of the precipitates by FESEM/EDX using low KV method as it is simpler compared to TEM/EDX. However, it is anticipated the TEM/SEM technique is more accurate than FESEM/EDX.

Materials and Methods

In this study, the as-received T91 alloy steel tube that complied with the ASTM A213-15 standards was used. The T91 alloy sample was cut into small cubic dimensions of 10 x 10 x 10 mm. The chemical composition of T91 alloy steel is given in Table 1. There are 13 samples prepared with various conditions of heat treatment and cooling media. Table 2 shows the type of heat treatment conditions for each sample of T91 alloy steel.

Table 1: Chemical compositions of the T91 alloy steel (wt.%) [4]

Steel	**C**	**Mn**	**Cr**	**Mo**	**Ni**	**Si**	**P**	**S**
T91	0.07-0.14	0.3-0.6	8.0-9.5	0.85-1.05	0.4	0.2-0.5	0.02	0.01

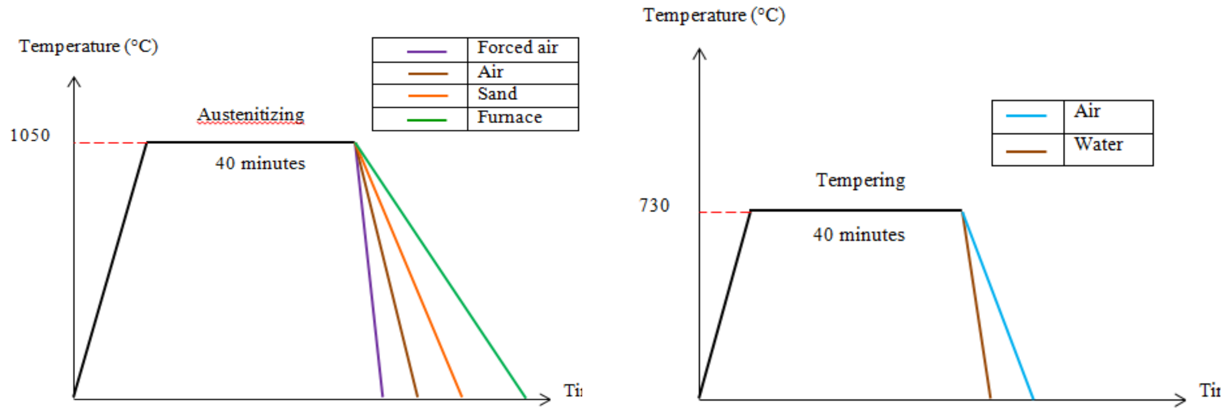
Table 2: Heat treatment conditions for each T91 alloy steel sample

Code	**Heat treatment conditions**
AR	As-received T91 steel with no heat treatment.
FA	T91 steel austenitized at 1050 °C and quenched in forced air
QA	T91 steel austenitized at 1050 °C and quenched in air
QS	T91 steel austenitized at 1050 °C and quenched in sand
CF	T91 steel austenitized at 1050 °C and cooled in furnace
OAFA	T91 steel austenitized at 1050 °C and quenched in forced air. The sample is then tempered at 730 °C and quenched in air.
OAQA	T91 steel austenitized at 1050 °C and quenched in air. The sample is then tempered at 730 °C and quenched in air.
OAQS	T91 steel austenitized at 1050 °C and quenched in sand. The sample is then tempered at 730 °C and quenched in air.
OACF	T91 steel austenitized at 1050 °C and cooled in furnace. The sample is then tempered at 730 °C and quenched in air.
WFA	T91 steel austenitized at 1050 °C and quenched in forced air. The sample is then tempered at 730 °C and quenched in water.
WQA	T91 steel austenitized at 1050 °C and quenched in air. The sample is then tempered at 730 °C and quenched in water.
WQS	T91 steel austenitized at 1050 °C and quenched in sand. The sample is then tempered at 730 °C and quenched in water.
WCF	T91 steel austenitized at 1050 °C and cooled in furnace. The sample is then tempered at 730 °C and quenched in water.

The hardness and microstructure of the as-received T91 alloy sample were determined before undergoing heat treatment processes. The samples were austenitized to a temperature of 1050 °C for 40 minutes and quenched in four different media which are forced air, air at room temperature, sand and furnace. The samples were then tempered at 730 °C for 40 minutes and quenched in air and water respectively. Figure 1 shows the heat treatment cycle for austenitizing and tempering processes of the samples.

The heat-treated samples were then cold-mounted and ground with series of silicon carbide papers with 240 to 600 grits, while polishing of the samples was done using 6 µm polycrystalline and 1 µm monocrystalline diamond suspension to achieve a mirror-like surface. An etching process was performed using Vilella's reagent containing 1 g of picric acid, 5 ml of hydrochloric acid (HCL) and 100 ml of ethyl alcohol prior to microstructure evaluation and hardness test.

The hardness properties were determined using micro-Vickers hardness digital tester with a penetration load of 500 gf and holding time of 10 sec (model: 401MVD), where five indentations were performed and the average hardness for each sample was taken while the microstructure analyses of the samples were done by using optical microscope (Model: Olympus BX51M) and FESEM (model: Hitachi SU-8020) operating at 15 kV. Meanwhile FESEM attached with an Energy Dispersive X-ray (EDX detector) was used to determine the chemical composition of the particles/phases observed in the microstructure of the selected samples in as tempered condition.



(a)

(b)

Figure 1: The heat treatment cycle diagram for (a) austenitizing and (b) tempering processes

Results and Discussion

Hardness Properties

Figure 2 shows the hardness results of the as-received T91 alloy steel and austenitized T91 alloy steel samples after quenching in four different media namely; forced air, air at room temperature, sand and furnace. The as-received T91 alloy steel sample had the least hardness (240.36 Hv) among all the samples while the CF and FA samples had the least and maximum hardness (320.14 Hv and 407.56 Hv) respectively among the austenitized samples. It was believed that the lower hardness of CF sample (6 °C/min cooling rate) was caused by the indentations at the individual ferrite, martensite and mixture of ferrite-martensite boundaries in the microstructure. The hardness results agreed with the results reported by Khiyon and Mohd Salleh [7] which explained that the decreased in cooling rate decreased the hardness of alloy steel.

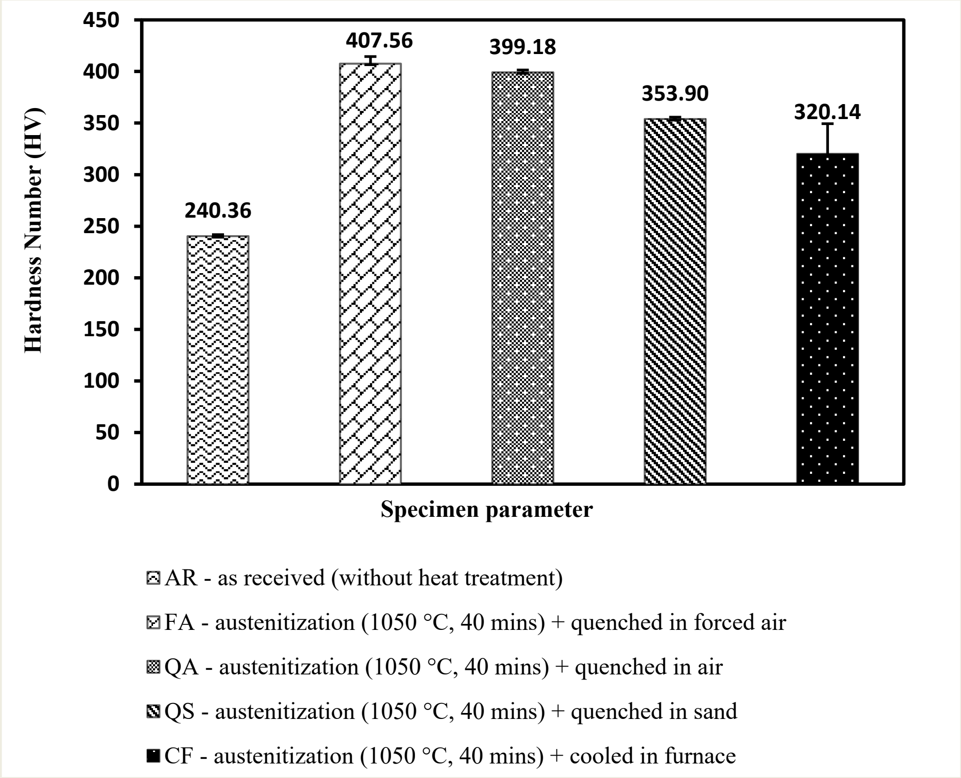


Figure 2: Average hardness test results for as-received T91 alloy steel and austenitized T91 samples quenched in different media

Figures 3 and 4 show the hardness results of tempered samples, quenched in air and water, respectively, after austenitizing and quenching in different media. It was found that the hardness results of tempered samples (Figures 3 and 4) were lower than that of the austenitized and quenched conditions (Figure 2). This may attribute to the formation of tempered martensite as a result of the breakdown of the lath martensite in the microstructure of the austenitized and quenched samples. The decreased hardness values of tempered samples led to increase in the toughness and ductility properties.

The hardness test results showed that the tempered T91 steel samples quenched in water (Figure 4) recorded no significant difference in hardness compared to the tempered T91 steels quenched in air (Figure 3). This is true as tempering at 730 °C for 40 minutes did not change the prior martensite to austenite, as the temperature was below Ac1 line for T91 alloy steel. Subsequent quenching from this temperature (730 °C) to either air or water did the change in the microstructure as austenite was not present at 730 °C. Heating at 730 °C had only altered the martensitic structure to tempered martensitic structure and was retained regardless of subsequent cooling rate applied afterward (air or water). Slight increase in hardness observed in water quenched samples was probably due to stress formed during rapid cooling in water. The hardness values of tempered OAFA, OAQA, OAQS and OACF samples quenched in air are 306.25, 299.34, 282.78 and 248.82 Hv, respectively, while the tempered hardness of WFA, WQA, WQS and WCF samples quenched in water are 313.48, 303.48, 285.8 and 255.54 Hv respectively. The decreased in hardness of tempered T91 steel compared to the austenitized condition was linked to the coarsening and dissolution of $M_{23}C_6$ precipitates and the breakdown of the martensitic lath structure [3].

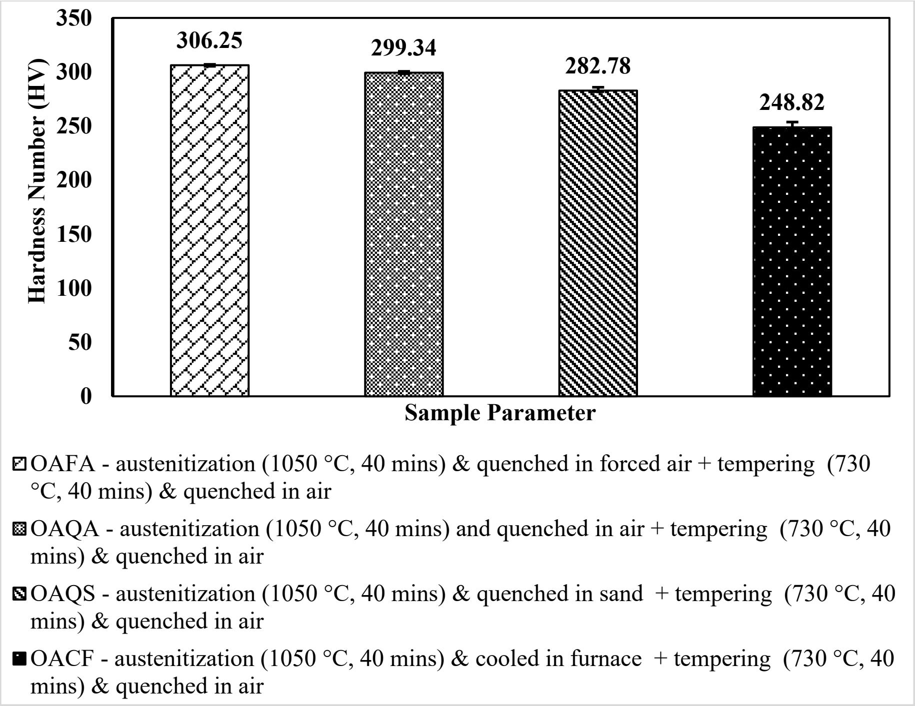


Figure 3: Average hardness test results for austenitized and quenched T91 samples after tempering and quenched in air

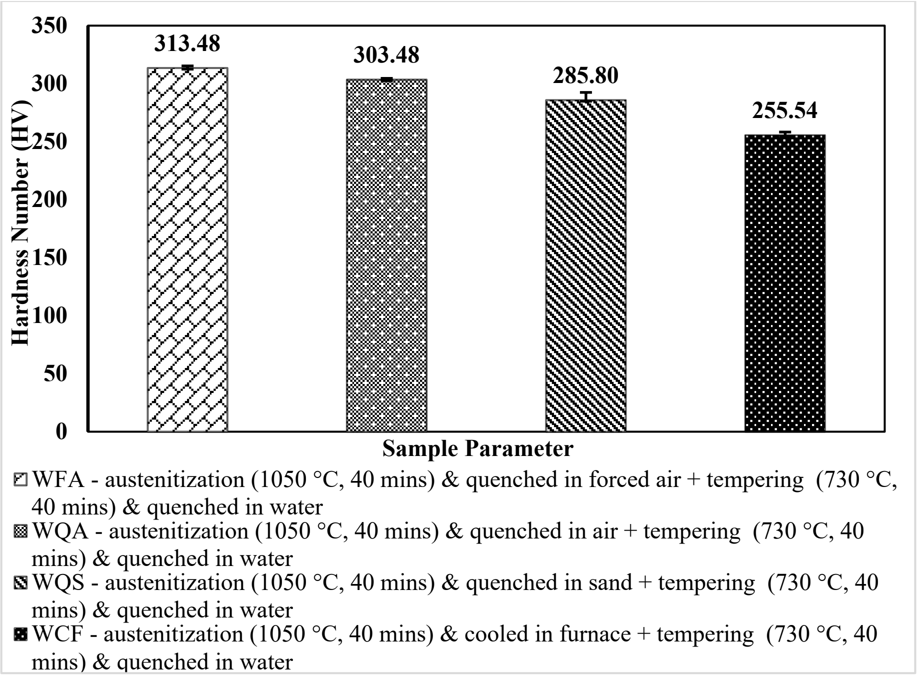


Figure 4: Average hardness test results for austenitized and quenched T91 samples after tempering and quenched in water

It can be concluded that different heat treatment processes gave different results in terms of decrease in hardness values, as the quenching rate went from fastest to slowest. The hardness results indicated that the after-austenitized T91 alloy steel, quenched in forced air is the hardest steel compared to the tempering conditions because the tempering treatment serves the purpose to increase the ductility of the material. Tempering is one of the heat treatment processes chosen to achieve a desirable combination of hardness and ductility. The decreasing hardness values indicated that tempering improves the ductility of the steel at great expense [8]. It is worth noting that, the tempering temperature should be always above the application temperature to avoid failure during operation as the result of inadequate tempering temperature. In power plant the T91 boiler super heater tubers were normally operated at 550 °C to 620 °C and the tempering temperature should be above this temperature range.

Optical Micrographs

The as-received, austenitized and tempered samples of T91 alloy steel were examined using optical microscope. The microstructure of as-received T91 steel in Figure 5 shows laths martensitic with the presence of significant amounts of carbides. The carbides are indicated by the black-coloured matter along the grain boundaries showing that the as-received microstructure of T91 alloy steel has fine precipitates along the grain boundaries [9].

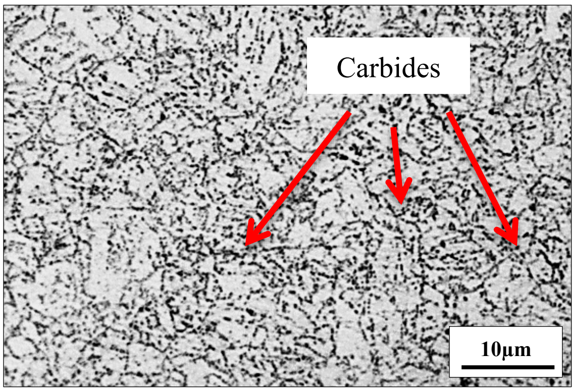


Figure 5: The optical micrograph of as-received T91 alloy steel

Figure 6 shows the microstructure of austenitized T91 samples quenched in (a) forced air, (b) air at room temperature, (c) sand and (d) furnace. The gradual increased in grain boundary sizes and distance can be observed in the microstructure as the cooling rates decreased. The martensitic lath blocks of the austenitized T91 steel cooled in furnace (CF) is separated by the dominant ferritic structure that appears in large boundaries. Shrestha et al. [3] reported that decreased in hardness of steel was due to the coarsening of the precipitated carbides. The slowest cooling rate (CF condition) results in more coarsening of the precipitated carbides which leads to decrease in hardness properties (Figures 2 and 6(d)) .

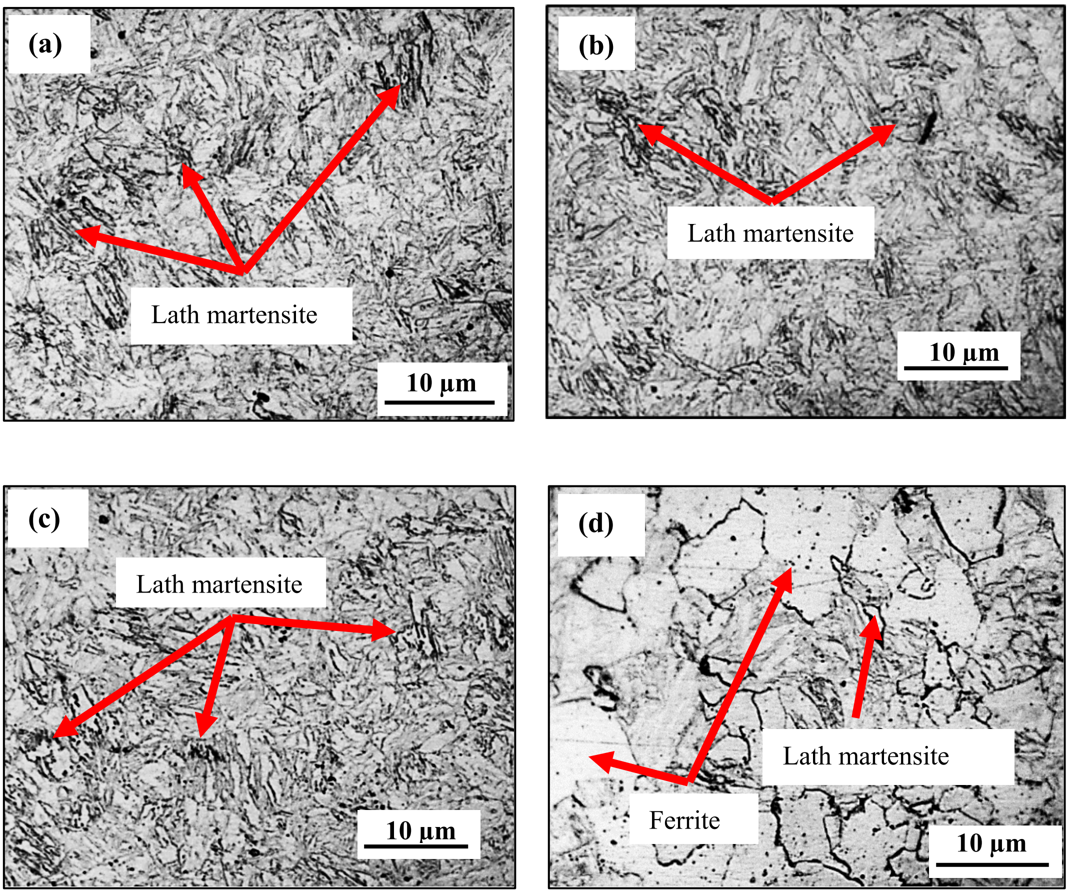


Figure 6: The optical micrographs of T91 samples austenitized at 1050 °C for 40 minutes and then quenched in (a) forced air (FA), (b) air (QA), (c) sand (QS) and (d) furnace (CF)

On the other hand, the tempered microstructures of T91 samples quenched in air are shown in Figure 7(a) to (d). The tempered microstructures of T91 steel quenched in air after being austenitized and quenched in four respective media; forced air, air, sand and furnace showed that the lath martensitic structure of each sample start to develop into a more relaxed tempered martensite structure in agreement with the reports by Shrestha et al. [3]. The tempering treatment causes the relief of the internal stresses in T91 steel prior to the austenitization at high temperature. The grain size of each sample is significantly increased due to the tempering heat treatment process. However, the grain size of the austenitized T91 steels quenched in sand and furnace (OAQS and OACF) followed by tempering process shows the largest grain due to the presence of retained austenite and ferrite developed after the austenitizing process. The tempering process results in coarsening and dissolution of $M_{23}C_6$ precipitates and the breakdown of the lath martensitic structure [3].

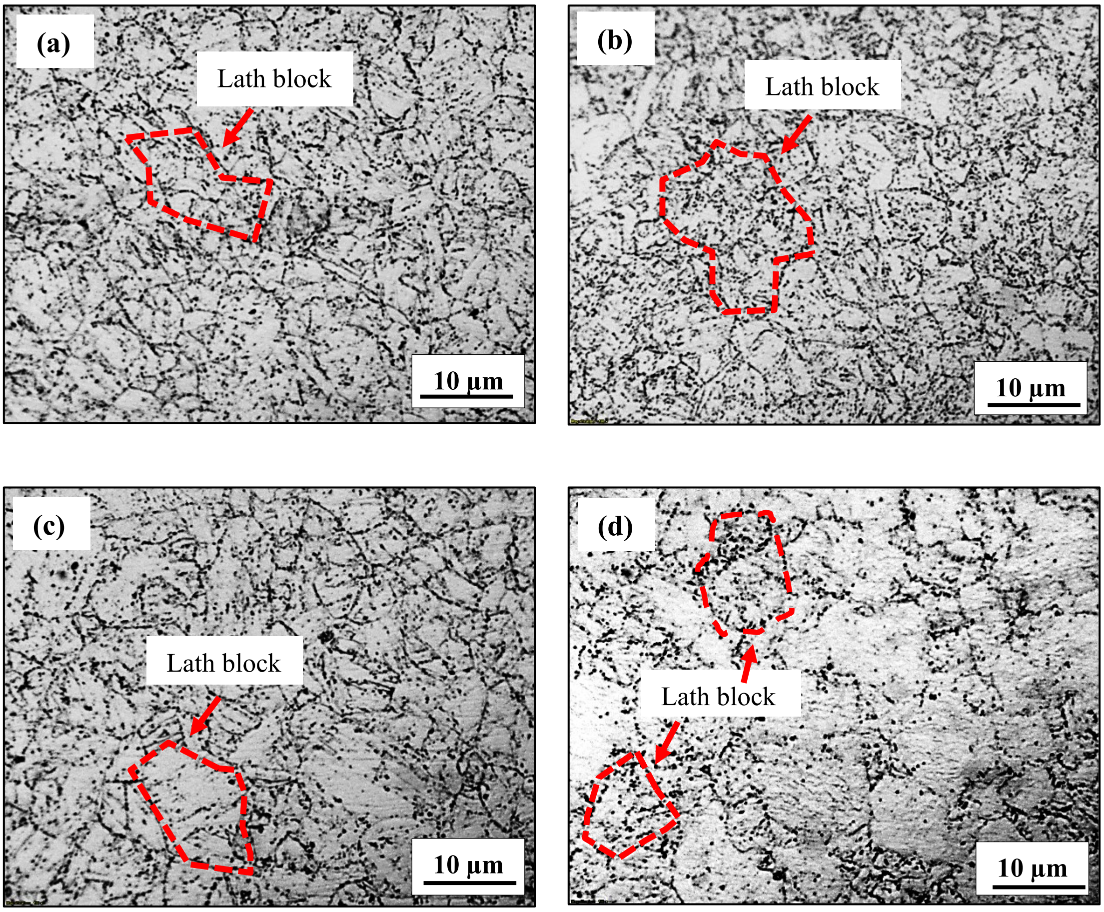


Figure 7: Microstructure of T91 steel tempered at 730 °C then cooled in open air after austenitizing at 1050 °C followed by (a) quenched in forced air (OAFA), (b) quenched in air (OAQA), (c) quenched in sand (OAQS) and (d) cooled in furnace (OACF)

FESEM Analysis

For FESEM analysis, three samples were selected to examine the effect of heat treatment processes on their microstructures. The selected samples are QA, CF and OAQA. The QA sample (Figure 8(a)) is the sample austenitized at 1050 °C and cooled in air or simply known as the normalising process while, the CF sample (Figure 8(b)) is austenitized at 1050 °C and cooled in the furnace or simply referred to as annealing process. The tempered T91 steel, OAQA is shown in Figure 8(c).

It can be noticed from Figure 8 that there are sub-grains in the prior austenite grain boundaries (PAGB) which are divided into packets, where blocks or parallel laths are located. The lath martensitic structures can be seen by the existence of the columnar lath in both normalised and annealed T91 steel. The normalised sample (QA) contains a much smaller grain size and finer martensitic needles in lath block that is closely packed to each other compared to the annealed T91 steel (CF), that has bigger grain size and lath martensitic structure with large amount of ferrite. All these characteristics may contribute to the premature failure during service and in decreasing the hardness value of the T91 alloy steel [6]. For the tempered martensite structure of T91 steel (OAQA), the grain boundaries are distributed in a much equal size which indicates that it is a stress-free tempered martensitic structure with reduced dislocation density showing that hardness is decreased while the ductility is increased [9].

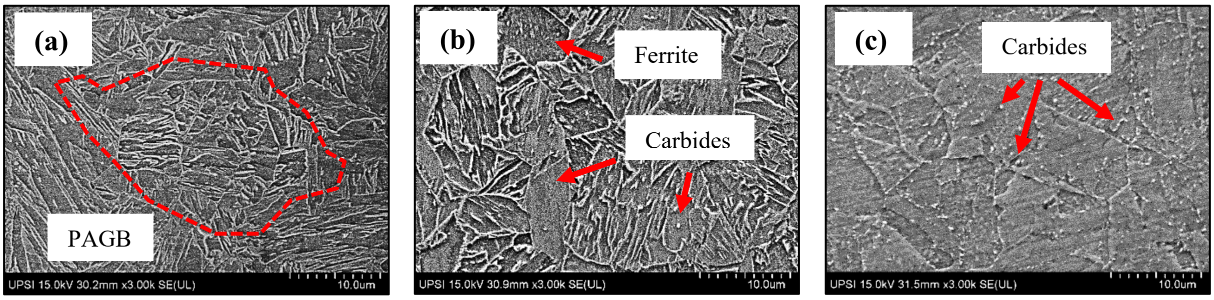
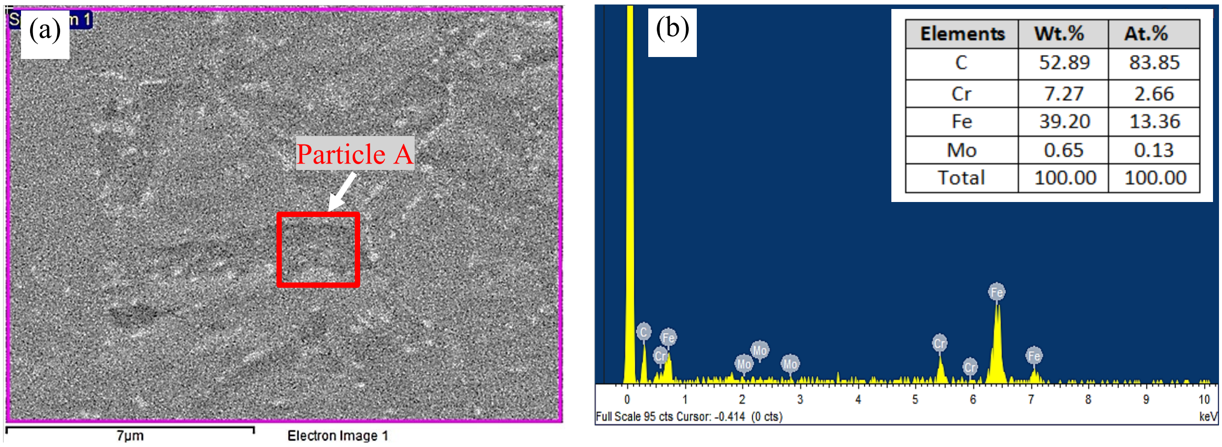


Figure 8: FESEM micrographs of T91 alloy steel with (a) OA, (b) CF and (c) OAQA conditions

In order to evaluate the capability of *FESEM-EDX* in analysing precipitate using low KV mode, the FESEM-EDX analysis was performed on the precipitate A of T91 alloy steel sample in OAQA condition (T91 alloy steel austenitized at 1050 °C and then quenched in air, followed by tempered at 730 °C and quenched in air) as shown in Figure 9. From FESEM-EDX analysis, the chemical composition of the precipitate A was determined. It can be seen that the existence of peaks C, Cr, Fe and Mo in EDX spectrum. From the EDX analysis, precipitate formula can be identified based on the weight percent (wt. %) or atomic percent (at. %) of elements present in the precipitate of T91 alloy steel. The EDX analysis confirms that the particle A is $M_{23}C_6$ type where M might be from Cr, Mo and Fe elements. Analysing precipitate using SEM/EDX is very demanding as the x-ray penetration on the precipitate could be deep and will pick-up the elements from the base metal (T91 alloy steel) instead of the precipitate itself. Utilizing low kV mode using FESEM/EDX will allow the shallow x-ray penetration that analysing the actual precipitate rather than the underneath base metal. According to Fetni et al., [9] the improved properties of T91 steel is due to its solid microstructure comprised of matrix of tempered martensite rich in dislocation and precipitates. From the EDX spectrum, the strong presence of $M_{23}C_6$ carbides precipitates is achieved due to the high Fe and Cr contents in T91 steel. This type of precipitate is dispersed along the prior austenitic grain boundary (PAGB), blocks or lath martensitic structures during tempering heat treatment [8,10].



Elements	Wt.%	At.%
C	52.89	83.85
Cr	7.27	2.66
Fe	39.20	13.36
Mo	0.65	0.13
Total	100.00	100.00

Figure 9: (a) FESEM micrograph of T91 alloy steel in OAQA condition showing the particle labelled A and (b) EDX spectrum of precipitate A with its elemental analysis

Conclusions

The effect of heat treatment processes and different media quenching on the hardness properties and microstructure of T91 alloy steel have been investigated by means of hardness test and microstructure analyses. It can be concluded that the microstructure of ferrite in lath martensitic structures that causes premature failure of the superheater tubes was achieved by quenching the austenitized T91 alloy steel in furnace (slow cooling rate or annealing). The annealed T91 alloy steel is proven to have the lowest hardness due to the slow cooling rate allowing sufficient time for carbon diffusion to take place and residual austenites to transform into ferrite. Maximum hardness was achieved by quenching the austenitized T91 alloy steel in forced air (normalising). However, it is unsuitable to be used in industrial applications without tempering, since the martensitic needles formed in the microstructure are too brittle due to the high internal stresses caused by rapid quenching. The normalised T91 should be tempered before it can be put in operation.

The fully tempered martensite is the best condition of T91 alloy steel to be used in power plant industries due to the increased ductility compared to the brittle martensite formed by austenitization and quenching. The increase in carbide precipitates developed in the tempered martensite increases the toughness of the T91 alloy steel. Lastly, the reduced hardness of T91 alloy steel after tempering is attributed to the dissolution of $M_{23}C_6$ carbides, coarsening of precipitates and the breakdown of lath martensitic structures observed in their microstructure. FESEM/EDX utilizing low kV method can be used to identify precipitates in T91 alloy steel which probably provides the simpler method compared to TEM/EDX. Futher more FESEM provides smaller beam size at low kV compared to other SEM (Tungsten and LaB6 source). This enables FESEM/EDX to analyse the actual precipitate rather than analysing the surrounding T91 alloy steel.

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Author Contributions

All authors contributed toward data analysis, drafting and critically revising the paper and agree to be accountable for all aspects of the work.

Disclosure of Conflict of Interest

The authors declare no potential conflict of interest in the publication of this work.

Compliance with Ethical Standards

The work is compliant with ethical standards.

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