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The Effect of Tempering Treatment on the Microstructure and Mechanical Properties of DIN 1.4021 Martensitic Stainless Steel

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Abstract

To investigate the effect of tempering treatment on mechanical properties and the microstructure of DIN 1.4021 Martensitic Stainless Steel, austenite treatment was conducted for the samples at 1000 ºC temperature for 60 min and then the samples were oil quenched. Later, tempering treatments were performed for the samples at 500 ºC and 700 ºC temperatures for 2 and 5 h, respectively; then quenching in oil was conducted. After the heat treatment, hardness, tensile strength and impact tests were performed to investigate mechanical properties. Moreover, optical microscopy and field emission scanning electron microscopy (FESEM) were performed to investigate microstructure observations and fracture surfaces. X-Ray diffraction (XRD) was carried out to measure the austenite retained in the samples. The results showed that due to the formation and precipitation of alloy carbides Cr_7C_3, the tempering treatment at a temperature of 500 ºC increases hardness, tensile strength and yield strength and reduces the amount of impact energy of the samples as well.

Keywords: DIN 1.4021, Martensitic stainless steel, Temper; Mechanical properties, FESEM.

1.Introduction

Martensitic stainless steels are widely used in marine, aerospace and petrochemical industries due to their optimum mechanical properties and high corrosion resistance [1-3]. Meanwhile, DIN 1.4021 martensitic stainless steel with 13% chromium and 2 % carbon is used in the production of turbine blades, rocket nozzles, jet engines, compressors parts, pumps, etc.[3-5]. Microstructure of these alloys at ambient temperatures consists of a martensitic area with a small percentage of fine carbide precipitation and retained austenite. The amount of retained austenite depending on carbon percentage, the austenite-generating elements and heat treatment conditions will be different [6]. Martensite phase is a major factor to enhance the properties of the alloy. Nevertheless, increasing the strength along with toughness and flexibility of steel is subject to existence of other phases in the structure such as retained austenite and scattered deposits in the area. For example, a uniform distribution of retained austenite on grain boundary in the lath martensite structure plays a significant role in simultaneous improvement of the flexibility and impact resistance of the steel. The reason for this behavior is generating homogeneous martensite by applying a suitable tempering operation [7,8]. In recent years, martensitic stainless steels have been known to contain Ni and Mo with corrosion resistance and good flexibility features.

Mo in the martensitic stainless steels improves corrosion resistance and carbide precipitation phase. Due to improvement of the ductility of intermetallic compounds, the strong austenite-generating element (Ni) increases the fracture toughness, strength and corrosion resistance of the samples [9,10].

In the present study, after austenitizing the samples at 1000 ºC for 60 min and then oil quenching, effects of temperature and time parameters of tempering on mechanical properties and microstructure of DIN 1.4021 martensitic stainless steel has been evaluated.

2. Experimental Procedure

In this study, DIN 1.4021 martensitic stainless steel product by AK Steel Company has been investigated. The chemical composition of the steel is presented in Table 1.

Table 1. Chemical composition of DIN 1.4021 martensitic stainless steel (by weight percent).

%C	%Cr	Mn%	%Si	%Mo	%Ni	%P	%Cu	%Al	%V	%W	%S
0.18	12.6	0.54	0.19	0.02	0.4	0.015	0.11	0.012	0.02	0.04	0.005

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At first, by melting stages, as bars with diameter of 400 mm and length of 3000 mm, this steel was casted in electric arc furnace. Forging operations of bars were performed in the temperature range of 1150-1180 ºC, then bars were air cooled. Later on, they were annealed at a temperature of 700 ºC for 2 h. Standard samples selected longitudinal tensile and impact tests strength in a shape of the disk blocks and were cut by a band saw. Finally, tensile and impact samples were prepared semi-finished and separated. For heat treatment, the samples were preheated at a heating rate of 8 ºC/min to 620 ºC for 30 min, then samples were austenitized at the same heating rate up to a temperature of 1000 ºC (austenite stability range) for 60 min and were quenched in 30 ºC oil. To investigate the effect of tempering time and temperature on mechanical properties, quenched samples were tempered at the temperature of 700 ºC and 500 ºC for 2 and 5 h and then they were quenched in 30 ºC oil. Fig. 1 shows a schematic of heat treatment cycle applied in the present study. List of acronyms for the heat treatment samples have been reported in Table 2.

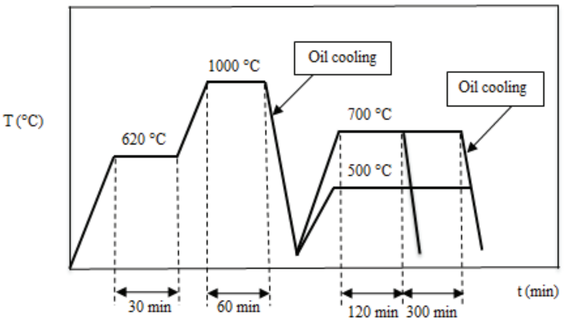

Fig. 1. Schematic of applied heat treatment cycle.

Table 2. List of acronyms for the heat treatment samples (Q= Quench, T= Temper).

Sample code	QT-1	QT-2	QT-3	QT-4
Heat treatment conditions	Q = 1000 °C/ 60 min/ oil T= 500 °C/ 2 h/ oil	Q = 1000 °C/ 60 min/ oil T = 500 °C/ 5 h/ oil	Q = 1000 °C/ 60 min/ oil T = 700 °C/ 2 h/ oil	Q = 1000 °C/ 60 min/ oil T = 700 °C/ 5 h/ oil

The mechanical properties were evaluated by a tensile test (tensile test machine, model ZWICK2410) in accordance with DIN-EN10001-2 standard. Hardness test was performed by Rockwell C according to DIN-EN6508 standard with hardness test machine, model EMCO M4U750; and Charpy impact test (impact test machine, model ZWICK5111) was carried out on the heat treatment samples according to DIN-EN10045 standard. To study the structure of the samples the Villela etching solution was used and to investigate the microstructure of samples the Olymous optical microscope, PMG3 model and scanning electron microscopy, LEO435VP model, were utilized. Moreover, the fracture surface of the samples after the test was examined by field emission scanning electron microscopy, MIRA3 TESCAN model. To identify the type of precipitated carbide, EDS analysis was used and also to study the distribution of phosphorus element in the fracture surface of all the samples the X-Ray Map analysis was carried out. To study the phase structure of the samples after tempering operation, X-ray diffraction (XRD), PW3710 model, and Cu kα radiation were used.

3. Results and Discussion

3.1. Microstructure

Fig. 2 shows the microstructure of QT-1, QT-2, QT-3 and QT-4 samples. Microstructure of DIN 1.4021 martensitic stainless steel consists of ferrite and spherical Cr23C6-type carbides in the annealed condition 11). After the heat treatment (austenitized at the temperature of 1000 ºC for 60 min and tempered at the temperatures of 700 ºC and 500 ºC for 2 and 5 h), the low-carbon tempered martensite with a lath morphology is the main phase in the microstructure.

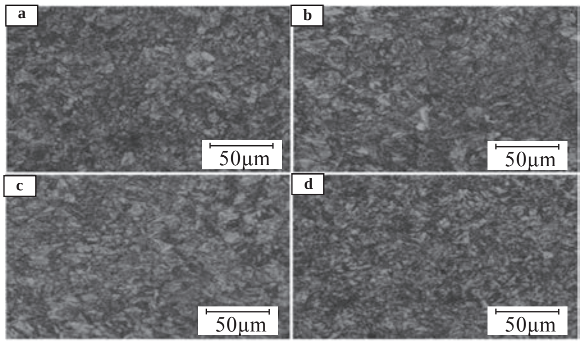

Fig. 2. Microstructure of DIN 1.4021 martensitic stainless steel samples after the heat treatment a) QT-1, b) QT-2, c) QT-3 and d) QT-4.

3.2. The effect of tempering time and temperature on mechanical properties

To investigate the effect of tempering time and temperature on mechanical properties, samples austenitized at the temperature of 1000 ºC for 60 min were under tempering treatments at the temperatures of 700 ºC and 500 ºC for each sample for 2 and 5 h. The results of hardness test under different tempering operations are given in Fig. 3.

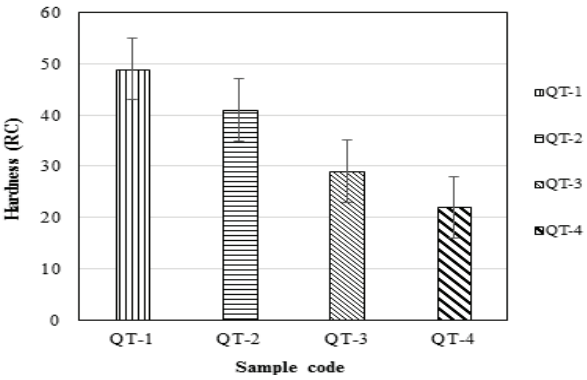

Fig. 3. Changes in hardness under different tempering treatments.

As can be seen, the degree of hardness in QT-1 and QT-2 samples are 49 (HRC) and 41 (HRC), respectively. While this amounts for QT-3 and QT-4 samples are about 29 (HRC) and 22 (HRC), respectively. Based on these results, tempered samples at the temperature of 500 ºC have higher hardness than tempered samples at the temperature of 700 ºC. This is because of the precipitation and formation of alloy carbides Cr_7C_3 at 500 ºC. Later, by increasing the tempering temperature up to 700 ºC, hardness of the structure decreases due to the dissolution of carbides and transformation of alloy carbides from Cr_7C_3 to $Cr_{23}C_6$ and coarsening of the structure. However, the results of EDS analysis confirm this issue. Fig. 4 shows the results of EDS analysis for QT-1 and QT-3 samples. As can be seen, EDS analysis of point A in QT-1 sample indicates the formation of $Cr_{23}C_6$ carbide alloy and, EDS analysis of point B in QT-3 sample represents the formation of $Cr_{23}C_6$ carbide alloy.

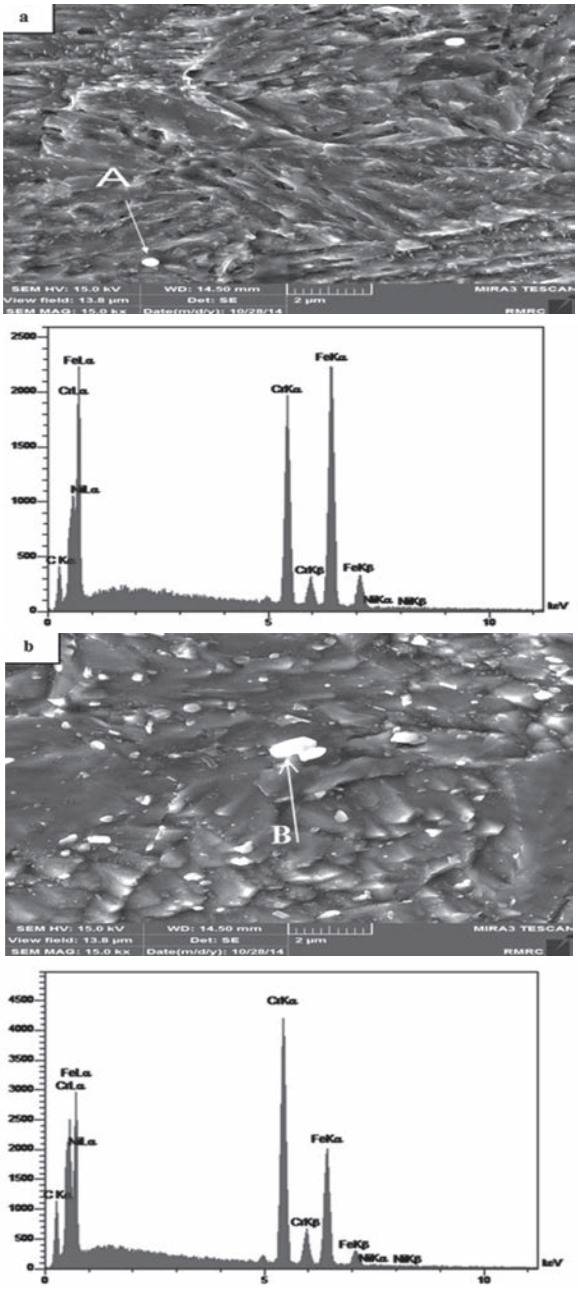

Fig. 4. EDS analysis of DIN 1.4021 martensitic stainless steel samples after heat treatment a) QT-1 and b) QT-3.

Amini et al.[12)] conducted a study on stainless steel DIN 1.4057. In their study, martensitic precipitation of Cr_7C_3 carbides was observed in the temperature range of 350-420 ºC. The reason for the hardness decrease in the temperature range of 450-650 ºC was transformation of carbides from Cr_7C_3 to $Cr_{23}C_6$ and coarsening of the structure. The results of the study is consistent with the results of Naseri et al.[13)] on the same steel which showed precipitation and formation of alloy carbides Cr_7C_3 in the temperature range of 400-500 ºC.

In Table 3, the relationship between tensile strength, yield strength and elongation under different tempering operating conditions has been shown. As can be seen, tempered samples at the temperature of 500 ºC (QT-1, QT-2) have much higher tensile strength and yield strength compared to samples tempered at the temperature of 700 ºC (QT-3, QT-4). The increase at the temperature of 500 ºC can be the result of hardness of martensite phase and precipitation of Cr_7C_3 carbides. The precipitation of Cr_7C_3 carbides delayed connection of micro-cracks caused by tension in order to make a shift in their way [13)]. The results of the study for DIN 1.4057 martensitic stainless steel are in perfect match with the results obtained by Amini et al.[12)].As can be seen in Fig. 3 and Table 3, in QT-1 and QT-2 samples, as the tempering time increases (from 2 to 5 h), hardness, tensile strength and yield strength decrease as well. To investigate this type of behavior, microstructure of both samples were examined by scanning electron microscopy. These images for QT-1 and QT-2 samples are shown in Fig. 5. It can be seen, by increasing tempering time from 2 to 5 times, that the size of carbide increases by 0.59 µm to 0.73 µm.

While in the study by Ning et al. [14)] which was on the super martensitic stainless steel 13Cr-4Ni-1Mo, holding time has little effect on hardness. But only in the 3-to-6-h period, reducing from 20.5 (HRC) to 19.2 (HRC) was observed in the hardness; and hardness after holding time of more than 6 hours remained almost constant.

Table 3. Results of the yield strength, ultimate tensile strength and elongation percent under different tempering operations.

Yield strength (MPa)	Tensile strength (MPa)	Elongation (%)	Sample code
QT-1	10	1545	1148
QT-2	14	1530	1118
QT-3	19	892	748
QT-4	24	858	713

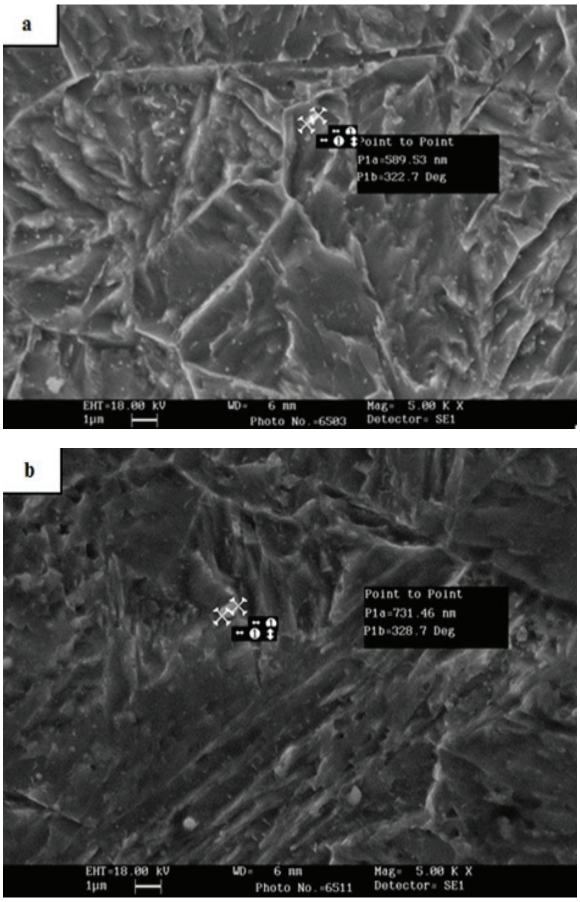

Fig. 5. Changes in the microstructure of DIN 1.4021 martensitic stainless steel samples after the heat treatment a) QT-1 and b) QT-2.

As shown in Table 3, it can be seen that in the QT-3 and QT-4 samples, by increasing tempering time (from 2 to 5 h), elongation percent increases. To investigate this type of behavior, X-ray diffraction analysis was performed on each sample. The results for QT-3 and QT-4 samples are shown in Fig. 6.

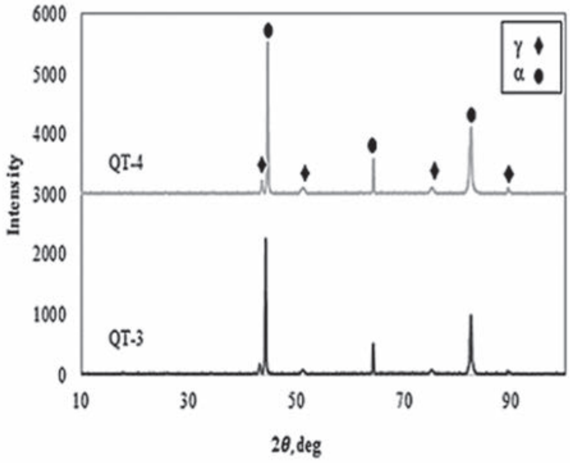

Fig. 6. X-ray diffraction pattern for the QT-3 and QT-4 samples.

According to the results, by increasing the holding time at the tempering temperature of 700 ºC which is because of transformation of martensite to austenite, austenite increased. The presence of austenite between laths of martensite microstructure due to fracture energy absorption improves the toughness of AISI 420 martensitic stainless steel [13)]. Increasing holding time at 700 ºC according to Table 3 and Fig. 3 reduces the mechanical properties (tensile strength, yield and hardness strength) and increase the percentage of elongation. The reason for this phenomenon is increasing the amount of austenite by increasing tempering time. In a study conducted by Ning et al.[14)] on the super martensitic stainless steel 13Cr-4Ni-1Mo tempering temperature of 600 ºC for 6 and 12 h, by increasing tempering time, retained austenite grains are stretched and the percentage of retained austenite increases. Researchers believe that the percentage of retained austenite tends to increase with increasing of impact energy.

The obtained results from the impact test under different tempering treatments are given in the Fig. 7.

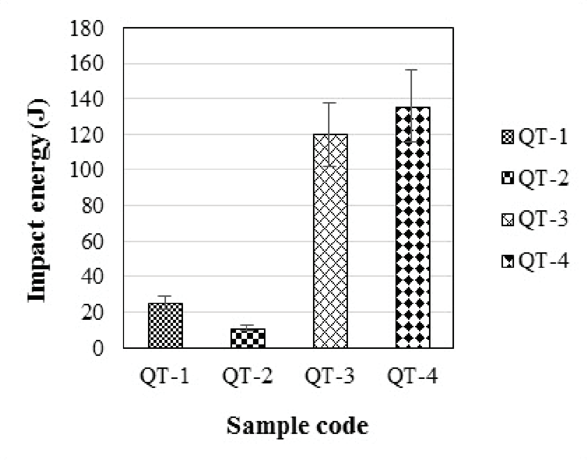

Fig. 7. The changing of impact energy under different tempering treatments.

As you can see, tempered samples at the temperature of 500 ºC (QT-1, QT-2) have far less impact energy than tempered samples at the temperature of 700 ºC (QT-3, QT-4,). This is due to the effects of two important parameters in tempering treatment: 1) precipitation and formation of alloy carbides Cr_7C_3 (Chromium-rich carbides) at 500 ºC, 2) the phenomenon of temper embrittlement in the temperature range of 375-575 ºC is due to the gradual penetration of impure elements such as phosphorus and tin into the austenite grain boundaries, which reduces the strength of the grain boundaries.

At 500 ºC, the impact energy decreases which is because of increasing in hardness caused by precipitation and formation of alloy carbides Cr_7C_3 (Chromium-rich carbides). Later on by increasing the temperature up to 700 ºC, due to softening of the structure and reduction in the hardness, impact energy increases. In a study performed by Amini et al. 12) on DIN 1.4057 martensitic stainless steel, increase in hardness and reduction of the impact energy in the temperature range of 350-420 ºC was due to precipitation of Cr_7C_3 carbides. The role of chromium in alloy steel embrittlement based on cooperation model in the grain boundary segregation of phosphorus atoms has been presented by Guttmann 15). According to this model, the chromium increases the grain boundary segregation of phosphorus atoms along with the primary austenite. This is done through reduction mechanism of carbon activities in solid solution as an impediment to the segregation of phosphorus atoms in primary austenite grain boundaries due to the formation of chromium-rich carbides. On the other hand, Suzuki and colleagues 16), proposed that increasing the carbon reduces the phosphorus atoms activity for the segregation along the primary austenite grain boundary which is attributed to the cooperation model between phosphorus and carbon atoms to occupy the place of the grain boundary. However, a group of researchers 17,18) believe that chromium plays an indirect role in the primary austenite grain boundary segregation of phosphorus atoms, so they believe that too much increasing chromium is harmful for high-alloy steels. In addition, it has been reported that 19), silicon is also able to reduce the carbon concentration in austenite grain boundaries because of its impact on the carbon activity, so excessive increasing of silicon is not recommended for alloy steels. In Fig. 8 the fracture surface of the heat treated samples after the impact test is shown.

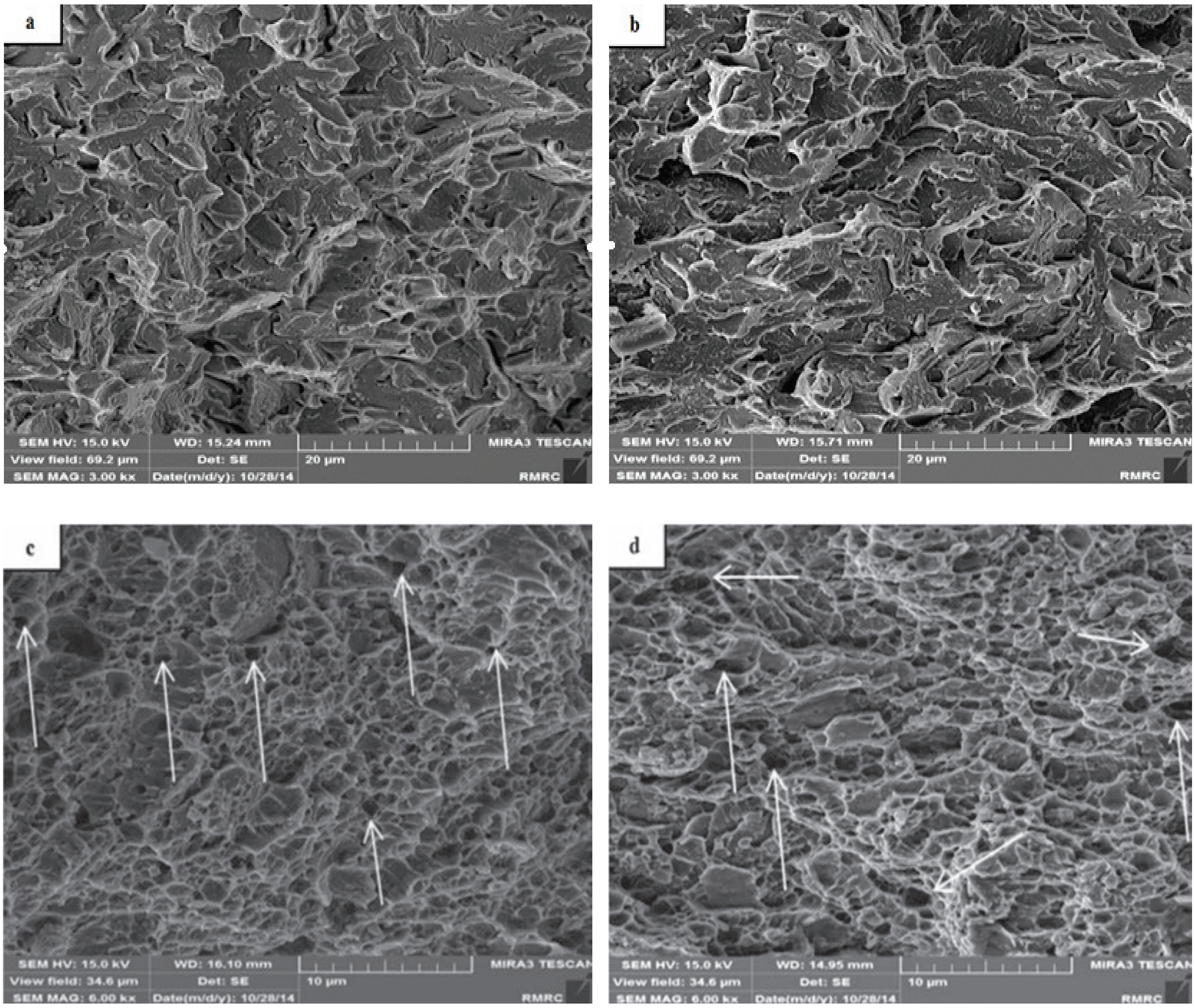

Fig. 8. The fracture surface of DIN 1.4021 martensitic stainless steel samples after heat treatment a) QT-1, b) QT-2, c) QT-3 and d) QT-4.

Spreading crack from the primary austenite grains indicates the brittle transgranular fracture for (QT-1, QT-2) samples. While for (QT-3, QT-4) samples, the fracture related to the presence of a void is more important which represents the ductile fracture. Significantly, however, the sizes of the voids in the samples (QT-3, QT-4) are different which shows big voids in the QT-4 sample in comparison with QT-3 sample. However, a group of researchers [20-22] believe that fracture toughness is determined by the width of the voids caused by the fracture surface, so an increase of the width of the void on the fracture surface represents higher impact energy. Increasing in the amount of impact energy for QT-4 sample in comparison with QT-3 sample may be considered due to an increase in the width of the void in the fracture surface of QT-4 sample in comparison with QT-3 sample. To investigate this type of behavior, X-ray Map analysis was performed on fracture surface of all the samples. The results for all samples are shown in Fig. 9.

As It can be seen, the distribution of impure phosphorus element (green dots) on the fracture surface of (QT-1, QT-2) samples is much higher than (QT-3, QT-4) samples. The reason for this is the phenomenon of temper embrittlement by heating DIN 1.4021 martensitic stainless steel in the temperature range of 375-575 ºC. Such a behavior can be caused by grain boundary segregation of impurity elements such as phosphorus atoms, tin and arsenic, which at the same time severely reduce the toughness. In DIN 1.4021 martensitic stainless steels and of all impure elements (phosphorus, tin, arsenic and antimony), phosphorus has shown the greatest influence on reducing the impact energy. Segregation of phosphorus atoms along with the primary austenite grain boundaries reduces grain boundary strength and sharply reduces toughness. Furthermore, it increases the ductile-brittle transition temperature to room temperature or even higher, provides intergranular fracture mode [23]. Because the atoms of the impure phosphorus migrate due to the phenomenon of influence toward the primary austenite grain boundaries, temper-embrittlement phenomenon is highly dependent upon the temperature and in the temperature range of 375-575 ºC. Incidence of this phenomenon will be faster. On the other hand, all diffusion phenomena highly depend on the time, so over time, the amount of temper embrittlement transformation will increase. As a result, it provides the conditions for an increase in segregation of impure phosphorus atoms in primary austenite grain boundaries along with a sharp reduction in impact energy for QT-2 sample in comparison with QT-1 sample (Fig.7), (Fig. 9 a and b). At the tempering temperature of 700 ºC, by increasing time from 2 to 5 h, a dramatic reduction in the distribution of impure phosphorus on fracture surface with an increase in impact energy level can be observed in the QT-4 sample. Guillou et al. [24] reported that in 13% Cr-martensitic stainless steel, impure phosphorus distribution on the fracture surface of the samples after 6 h tempering at 650 ºC falls to its lowest amount. One of the important reasons for considering the phenomenon of grain boundary impurities is the fact that segregation of impure elements atoms such as phosphorus along the primary austenite grain boundaries leads to intergranular brittle fracture with which a little plastic deformation can occur under macroscopic strain and yield stress.

The overall results of this study show that although the lion's share of flexibility and impact energy for QT-4 sample has been appeared by an increase in the amount of austenite in martensite laths in microstructure and increase of the width of the voids on fracture surface (Fig. 6 and Fig. 8-d) there is a significant reduction in the distribution of impure phosphorus atoms on the fracture surface (Fig. 9-d), which greatly improves flexibility and toughness.

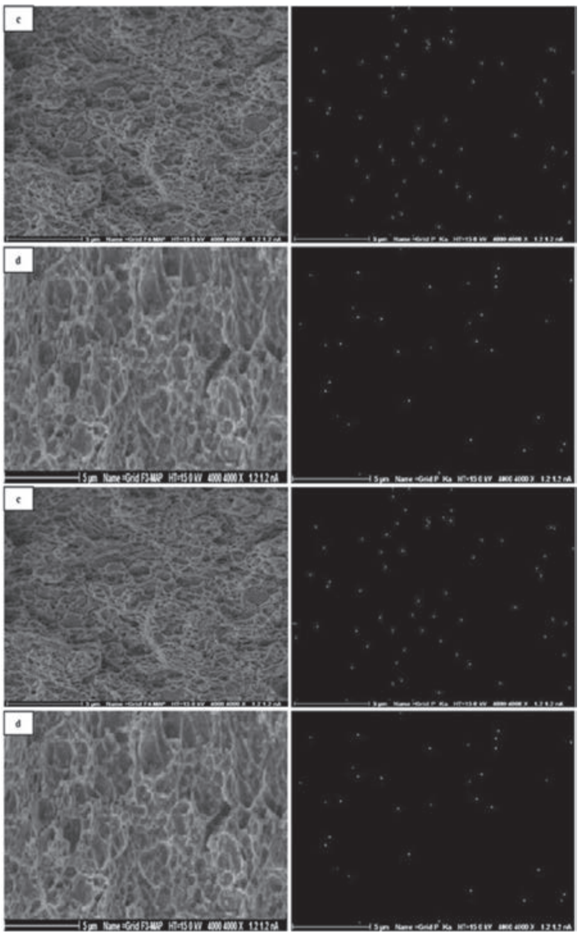

Fig. 9. Analysis of X-Ray Map on fracture surface of samples a) QT-1, b) QT-2, c) QT-3 and d) QT-4.

4. Conclusion

In this study the effects of tempering time and temperature of DIN 1.4021 martensitic stainless steel were investigated and the following results were obtained:

- Samples tempered at the temperature of 500 ºC have higher hardness, tensile strength and yield strength and lower levels of impact energy than the tempered samples at the temperature of 700 ºC. This is because of the precipitation and formation of alloy carbides Cr_7C_3at 500 ºC.

- At the temperature of 500 ºC, with increasing tempering time from 2 to 5 h (in QT-2 sample) levels of hardness, tensile strength and yield strength decrease. This is because of the increase in the size of the Cr_7C_3 carbide.

- At the temperature of 700 ºC, with increasing tempering time from 2 to 5 h (in QT-4 sample), transformation of martensite to austenite increased martensite between layers of austenite; and due to this transformation, mechanical properties of the sample (hardness, tensile strength and yield strength) reduced but the elongation percent increased.

- The amount of energy for the tempered samples at the temperature of 700 ºC (QT-3 and QT-4 samples), due to lower distribution of impure phosphorus element on the fracture surface of these samples after the impact test was significantly higher that tempered samples at the temperature of 500 ºC (QT-1 samples and QT-2).

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