The Influence of Microstructure on the Corrosion Rate of Carbon Steels

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Abstract

This paper presents the influence of carbon steel microstructure on the corrosion rates. Four types of microstructures have obtained by quenching and tempering and iso-thermal annealing. These microstructures are:

banded ferrite/pearlite microstructure, fine ferrite/pearlite microstructure, coarse ferrite/pearlite microstructure and tempered martensite microstructure.

General corrosion and localized corrosion (penetration rates) were determined via mass loss and optical microscopy. The different microstructures of steels investigated in this paper revealed corrosion rate variations of 0.8– 3.2 mm y^{-1} and 3.3–6.4 - mm y^{-1} for the general and localized forms, respectively. The corrosion stability of the various microstructures may arise from variations of phases within the steel. A banded ferrite/pearlite microstructures have worse general corrosion properties, while tempered martensite worse microstructures have localized pitting corrosion properties. Coarse ferrite/pearlite microstructures have better localized pitting corrosion resistances compared to others investigated microstructures This paper has demonstrated that, microstructure is an important consideration when selecting carbon steel for an industrial corrosion resistance application.

Keywords: general corrosion, localized corrosion, pitting corrosion resistance, carbon steel, microstructure, ferrite, pearlite, martensite, tempered martensite, phases.

تأثير البنية المجهرية على معدلات تأكل الفولاذ الكربوني

الخلاصة

يهدف البحث الحالي إلى دراسة تأثير بنية الفولاذ الكربوني على معدلات التآكل . تمت دراسة بنى مجهرية مختلفة, قسمت إلى أربعة مجاميع هي :حزم من الفرايت / البيرلايت ,المجموعة الثانية : الفرايت / البيرلايت الناعم ,الفرايت / البيرلايت الخشن , المارتنزايت المراجع.

تم كشف التآكل وحساب معدلاته بواسطة الفقدان بالوزن والمجهر الضوئي . بينت النتائج ان اختلاف البنى المجهرية يؤدي إلى تغير في معدلات التآكل من ٠,٨- ٣,٢ مم / سنة ومن ٣,٢ – ٦,٤ مم / سنة لكل من التآكل العام والتآكل الموضعي على التوالي. إن استقرارية التآكل تأتي من اختلاف

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البنى المجهرية . تمتلك حزم الفرايت / بيرلايت على مقاومة تأكل عام قليلة , بينما تمتلك بنية المارتنزايت المراجع مقاومة تأكل موضعي قليلة قيما تمتلك بنية الفرايت / البيرلايت الخشن على أفضل مقاومة تأكل موضعي مقارنة بالبني المجهرية المفحوصة الأخرى. أكدت نتائج البحث إن البنية المجهرية عامل مهم في اختيار الفولاذ الكربوني في التطبيقات الصناعية التي تتطلب مقاومة تأكل عالية .

INTRODUCTION

The importance of microstructure on corrosion of carbon and low alloy steels has been widely recognized, but different aspects are still uncertain and contradictory results can be found in the literature. This is mainly due to the complexity of the problem and the difficulty to describe the involved mechanisms. The chemical composition and the microstructure are not independent variables; the same microstructure can be obtained with different chemical compositions and vice versa. Some authors [1] report the effect of one of these parameters without taking into account that the other has been also modified.

The corrosion rate of carbon steel is not only governed by the electrolyte conditions, but can also be influenced by its chemical composition and microstructure. Furthermore, the driving force for corrosion in aqueous media is the difference in potential of small areas due to heterogeneities in the material [2]. It is important to note that these heterogeneities range from atomic to several hundred microns in scale, and can arise from various factors such as defects in the crystal structure of the metal, different phases, segregation of elements or phases, non-metallic inclusions, etc. [3]. It is reported that many of these heterogeneities are controlled by the elemental composition, thermal and mechanical history of the material [3]. In work [4] has found that, pitting was initiated almost exclusively at non-metallic inclusions. From the results of thermodynamic considerations, the sulfides themselves are not thermodynamically stable and tend to dissolve making a microcrevice at the periphery along the inclusion/metal interface.

Furthermore, the compositional and microstructural properties can vary significantly between steels of the same grade from different manufacturers, and these variations may lead to substantial differences in the corrosion resistance.

In study[5] revealed, that microstructure and chemical composition of carbon and low alloy steels are important factors and they have a significant influence on CO2 corrosion performance. If a low chromium alloy steel is to be selected, it is worth noting that even when the influence of steel microstructure seems of less importance than for carbon steels, it is recommended not to have a ferritic-perlitic microstructure[6].

The steel microstructure plays a significant role in terms of the corrosion rate and mechanism. Studies[4–6] undertaken recently revealed that the corrosion behaviour like mechanical properties is related to the alloy microstructure which is determined by heat treatment parameters (like austempering temperature, austempering time, austenitizing temperature and austenitizing time). The study[7] shows an increase in the corrosion resistance of the material due mainly to spheroidal annealing process.

The effect of temperature and time of annealing on hardness indicates that, the best time and temperature for spheroidal annealing is 740 °C over 60 min for hardness and 45 min for corrosion resistance for the same temperature[7]. In work [1] had been shown the change in the Icorr value as a function of the annealing temperature for specimens quenched in the different media. The lowest Icorr value was for the steel cooled in icy water, whereas the highest corrosion rate was for specimen cooled in hot water.

There are few studies that analyze the influence of heat treatment keeping the chemical composition constant. Some researchers [8] established that the solution-annealed specimens of DIN 1.4970 stainless steel and those aged at 1173 K did not present a susceptibility to intergranular attack. The specimens aged at temperatures in the range from 873 to 1073 K showed a small susceptibility to intergranular attack that decreased with aging temperature. The role of the microstructure in improving the steel corrosion resistance is not completely clear. The present study examines this effect and study the extent of metallurgical variations in microstructures of steel and their effect on corrosion performance.

Experimental

Materials

The preparing operation of the specimens involves cutting plates of steel with dimensions of (1000mm*1000mm*4mm) by hydraulic punch to obtain (20) pieces from each plate with dimensions of (100mm*200mm*4mm).

The steel used in this investigation is SA333 grade 6, which is used for the construction of piping for the primary heat transport system of pressurized heavy water reactors. The chemical composition and microstructure of the steel is shown in table 1.

Optical microscopic examination indicated that the steel contained ferrite and pearlite with prominent banding. **Banded ferrite-pearlite** microstructures can be clearly seen in the lower magnification micrographs as shown in fig.1. It can be seen also that, the microsegregation results in the banded microstructure of ferrite and pearlite.

Heat Treatment Processes

Heat Treatment: Heating and cooling procedure to manipulate structural changes (affect materials properties). In this work, isothermal annealing and quenching following by tempering are achieved as following:

Annealing

One of the popular heat treatment processes is annealing. The general purpose of annealing processes is to soften iron or steel materials and refine its grains [5]. Different temperatures and period of intermediate annealing was used in an attempt to get different microstructures. Slower cooling rates produce coarser microstructures, or holding at a temperature just below the eutectoid temperature, can result in fine microstructures.

The annealing process achieved (as shown in fig.2) at temperatures 760°C and holding time 60 min. The specimens after exposure time were rapidly cooled by water to:

A- 625 °C, which is T_{transf} way below T_E, and hold isothermally for small time, then cooling slowly in furnace after turn off the furnace and leave the door closed as indicated in fig.2.

The rate of a phase transformation is the product of the growth rate and nucleation rate contributions. The transformation is controlled by a rapid nucleation but slow atomic diffusion. Nucleation is controlled by supercooling. At these conditions, high nucleation rate and low growth rate occurred, therefore the transformation happens sooner (it is controlled by the rate of nucleation) and grain growth (that is controlled by diffusion) is reduced. The development of the microstructure is not instantaneously and is ruled by the diffusion of atoms. Slow diffusion at these temperatures leads to fine-grained microstructure with thin-layered structure of pearlite **(fine pearlite).**

B-675°C, which is T_{transf} just below T_E, then hold isothermally for 0^3 seconds, followed by a slow cooling process as shown in fig.2. At these conditions, the nucleation rate will be low, and the growth rate will be high, therefore the diffusion is faster than that in case (A). Grain growth is controlled by atomic diffusion. The high diffusion rates allow for larger grain growth and formation of thick layered structure of pearlite **(coarse pearlite).**

Quenching and Tempering

The specimens steel are heated to a temperature760°C at holding time 60 min. Then cooled rapidly by removing the specimens from the furnace and quenching in water to room temperature. A carbon steel quenched from these temperatures has a structure called **martensite**. Martensite is supersaturated solid solution of carbon in α-iron (greatly supersaturated ferrite). With the quenching-hardening process the speed of quenching can affect the amount of marteniste formed.

Martensite plates are hard and brittle that it needs to be modified for practical applications. To stabilize the structure, alleviate the brittleness and develop useful mechanical properties, quenching is always followed by **tempering**. This process allows carbon atoms to diffuse out of the distorted lattice structure associated with martensite, and thus relieve some of the internal stresses.

In this work tempering is done by heating the specimens to a temperature 500 C° for 45 minutes and air cooling. Tempering process results in the formation of **tempered martensite**, which consists of α- iron and many dispersed particles of cementite (i.e., iron carbide, Fe_3C).

Microstructure and metallography

The specimens were prepared for microstructure examination as the following steps:

1. Grinding process was carried out by using disk rotary instrument with different grades of emery paper (SiC) of (120,220, 320, 600, 800 and 1000). Then the samples were washed with water and alcohol and dried in the air.
2. Polishing process was carried out by using special polishing cloth and alumina (Al_2O_3) solution of grain size of (0.3µm). The polished specimens were washed with the water and alcohol and dried in oven.
3. After polishing the test pieces using a rotary polishing machine with the aid of diamond paste of 7 µm until achieving a mirror-like surface.
4. The polished surfaces are etched by immersing the each specimen in etching solution which consists of (5ml of HCl and 10ml of HNO_3) for (30) seconds. Then the specimen was washed with water and alcohol and dried in oven.
5. The specimens were then examined by using an Olympus PMG3 metallurgical microscope fitted with a 35 mm camera and computer.

Classification of the observed microstructures

According to heat treatment, which a achieved, it can be distinguished the obtained microstructures to four groups as following:

Group 1: banded ferrite/pearlite microstructure.
Group 2: fine ferrite/pearlite microstructure.
Group 3: coarse ferrite/pearlite microstructure.
Group 4: tempered martensite microstructure.

Corrosion test

Corrosion studies were carried out by weigh loss method to investigate the effect of intermediate annealing on corrosion in steel alloy. For this purpose, specimens with dimensions of (20mm*20mm*4mm) were polished up to 400 grit using polishing papers, accurately weighed, then immersed in 150mL of 3.5% NaCl solution for the desired exposure time. After each exposure time the samples were removed from its beakers, dried and reweighed to a constant weight using an analytical balance with accuracy of ±0.0001g. The weight loss was measured after each experiment and the corrosion rate was calculated in millimeters per year, whereas localized corrosion was measured by penetration depth using an Olympus PMG3 optical microscope. The latter method involved measuring the difference in focus (microns) between an un-corroded and a localized corroded area with the calibrated readings of the microscope. Five measurements were taken on each face of the specimen with the three deepest measurements, on each face, being averaged to obtain the penetration depth for that face. The in situmonitoring of pitting was also carried out using an optical microscope to identify the pitting initiation sites and to understand the pitting growth features.

RESULTS AND DISCUSSION

Two types of corrosion forms have been shown, the localized and general corrosion, which their rates vary slightly between different microstructures of carbon steels. Insignificant differences were observed in the corrosion performance of steels having fine-grained ferrite/pearlite, somewhat coarser ferrite /pearlite and tempered martensite microstructures as shown in fig.(3). In any event, the ferrite/coarser pearlite exhibited better in terms of general corrosion and worse in localized corrosion than fine ferrite/pearlite and tempered martensite.

Furthermore, the different microstructures of steels investigated in this paper revealed corrosion rate variations of 0.8– 3.2 mm y^{-1} and 3.3–6.4- mm y^{-1} for the general and localized forms, respectively as shown in table (2) and fig.(3).

It has been shown that variations in the general / localized corrosion occur partly due to differences in the microstructure. It was found that steels with a banded ferrite/pearlite structure perform poorly in terms of localized corrosion (pitting corrosion with penetration rate {5.7–6.4} mm y^{-1}) and relatively high general corrosion (1.0–2.2) mm y^{-1}. This could be a attributed to a segregated distribution of the iron carbide phase cementite (Fe_3C). This two - phase structure of α - iron and cementite sets up galvanic cells that accelerate the corrosion reaction in which cementite, acting as cathode. Narasaiah and Ray [10] had shown small crack formation in a commercial low carbon steel with banded ferrite–pearlite structure. It is reported that the angle between the direction of banding and the loading axis has pronounced effect on the orientation of such small cracks.

Fine ferrite/pearlite material performed better in terms of the average general corrosion than that for tempered martensite and a banded ferrite/pearlite structures, while the penetration rates of localized corrosion was the same as for tempered martensite. It is suggested [8] that, the corrosion rate of the steel decreases as the volume fraction of ferrite increases. This behavior has been attributed to the fact that ferrite, with more Fe contents than martensite, acts as anode whereas martensite, with a higher C contents than ferrite, acts as a cathode. It was found that the pitting in chloride solution took place preferentially in the ferrite phase rather than in the austenitic phase.

A fine ferrite/pearlite, and somewhat coarser ferrite/pearlite structure may be more suitable under the conditions investigated in this study compared to a banded ferrite/pearlite structure. In the banded ferrite/pearlite structure, the carbon-bearing phase (pearlite) is distributed in layers whereas in the other structures the carbon-bearing phases are much more evenly distributed [2].

The tempered martensitic specimens showed lower the average general corrosion rates than steels had different ferrite/pearlite microstructures, but suffered localized corrosion like fine ferrite/pearlite microstructures.

Ramirez-Arteaga etcl [1] reported that with increasing the martensite percentage in the specimen and the ferrite percentage decreases the corrosion rate decreased. For specimens quenched in water, the susceptibility to localized type of corrosion decreased by increasing the annealing temperature.

The good localized-corrosion resistance of the specimens had a ferrite/pearlite and a tempered martensitic microstructure steel was attributed to the presence of lamellar cementite for the first condition and quenching/ tempering microstructure steel have needle-like carbide structure provides a better anchoring surface for the $FeCO_3$ than large ferrite areas interdispersed by a few perlite grains.

In the ones a tempered martensitic one steel the cementite is homogeneously dispersed in the martensitic microstructure and due to the lack of anchoring, the corrosion products peel off partially. The annealed structure corrodes locally at a comparatively low rate because of the relatively massive form of cementite formed by decomposition of austenite compared with smaller - size cementite particles resulting from decomposition of martensite.

The primary iron carbonate scales formed on annealed specimens were thicker, less porous, more tenacious and better adhered than those formed on the quenching/tempering ones**.** i.e. The scale on the annealed steel specimens were found to be larger and more densely packed than those for the quenching/tempering specimens. The secondary scale has the same characteristics for both types of microstructures. The adherence of the corrosion product film was higher in the quenched samples. Consequently, any heterogeneous regions that are elongated in this direction may produce pitting corrosion, in which ridges corroded by one of the following mechanisms; (a) local anodes and cathodes may be formed due to electrochemical differences between matrix and secondary phases, and/or (b) scale may adhere preferentially to particular regions, due to factors such as carbide distribution, causing localized attack. (c)Presumably, galvanic couples form between carbon-rich phases and the bulk steel, noting that cementite is cathodic with respect to iron. This is consistent with suggestions made elsewhere that the shape and distribution of ferrite/Fe_3C plays an important role in influencing the corrosion rate and pits shapes. Recent studies have shown that corrosion rate increases as the size of iron carbide particles decreases.

For used carbon steels, the differences in pitting corrosion shapes (as shown in fig. 4) are assigned to the shape and distribution of ferrite and Fe_3C resulting from different heat treatment. The corrosion rate a banded ferrite/pearlite microstructure of used steel presented higher than the F/P microstructure in the annealing and quenching/tempering specimens. A banded ferrite/pearlite structures corrode (as general corrosion) faster than other structures, and steels containing coarse pearlite corrode more rapidly than those with fine pearlite. This results don't agree with the results obtained in work[8], who proposed a mechanism in which the cementite from the pearlite is left uncorroded as ferrite corrodes away, and then the local concentration of ferrous ions increases in the cavities between cementite platelets. Local flow stagnation and a higher local ferrous ion concentration allow the formation of an iron carbonate scale between the cementite platelets. Simultaneously, the cementite helps to anchor the scale.

Long exposure times lead to an increase in the corrosion rate (as shown in fig.5), and this was attributed to an elevated Fe_3C surface area. The corrosion rate increases with the presence of Fe_3C residues on the surface.

Alloying elements could reduce the corrosion rate by increasing the ferrite electrochemical resistance and/or preventing the formation of Fe_3C. In the case of Cr–Mo steel, the effect of the microstructure is less marked. Despite attributed a very important role to the Fe_3C content and its distribution. For pure iron, heat-treated samples corroded at rates far lower than any of the alloyed steel ones, screening the effect of carbon contents on the corrosion of the steel.

CONCLUSIONS

From the results, the following conclusions can be stated:
1-Two types of corrosion forms have resulted, the localized and general corrosion,
On the surfaces of the four groups of microstructures:
Group 1: banded ferrite/pearlite microstructure.
Group 2: fine ferrite/pearlite microstructure.
Group 3: coarse ferrite/pearlite microstructure.
Group 4: tempered martensite microstructure

2- The corrosion behavior of SA333 grade 6 steel was very dependent on the heat treatment. The different microstructures of steels investigated in this paper revealed corrosion rate variations of 0.8– 3.2 mm y^{-1} and 3.3–6.4 - mm y^{-1} for the general and localized forms, respectively.

3- The microstructure of the steel influences both localized and general corrosion properties. A banded ferrite/pearlite microstructures (group 1) have worse general corrosion properties compared to other groups.

4- Tempered martensite microstructures (group 4) have worse localized pitting corrosion properties compared to other groups.

5- Coarse ferrite/pearlite microstructures (group 3) have better localized pitting corrosion resistances compared to other groups.

6- Fine ferrite/pearlite microstructure have the same general corrosion properties as tempered martensite microstructure group (group 4).

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Table 1 : ***Chemical composition (wt.%) and microstructures of the investigated steel.***

Material	C	Mn	Si	S	P	Cr	Ni	Fe	Microstructure
SA333 grade 6	**0.14**	**0.9**	**0.25**	**0.018**	**0.016**	**0.08**	**0.05**	**Balance**	**F/P, M and TM**

Table 2. Corrosion resistances of the steel specimens grouped according to microstructure

Microstructural group	mean penetration rate (Range) mm y^{-1}	Mean average corrosion rate (Range) mm y^{-1}
Group 1	**6.0 (5.7–6.4)**	**1.7 (1.0–2.2)**
Group 2	**4.5 (3.9–5.2)**	**1.5 (1.0–3.2)**
Group 3	**4.7 (3.3–6.0)**	**1.2 (0.8–1.6)**
Group 4	**4.5 (4.4–4.6)**	**2.1 (2.0–2.2)**

Group 1: banded ferrite/pearlite microstructure.
Group 2: fine ferrite/pearlite microstructure.
Group 3: coarse ferrite/pearlite microstructure.
Group 4: tempered martensite microstructure.

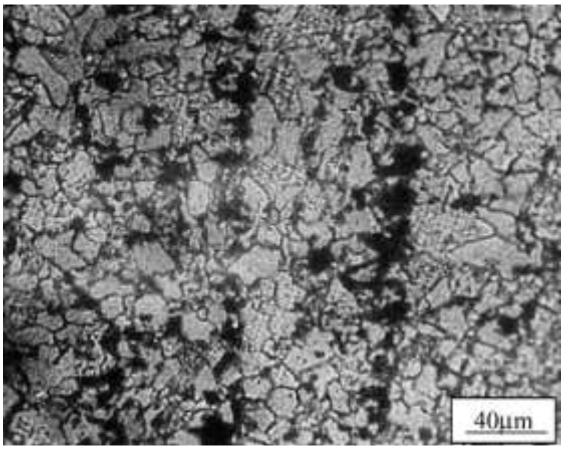
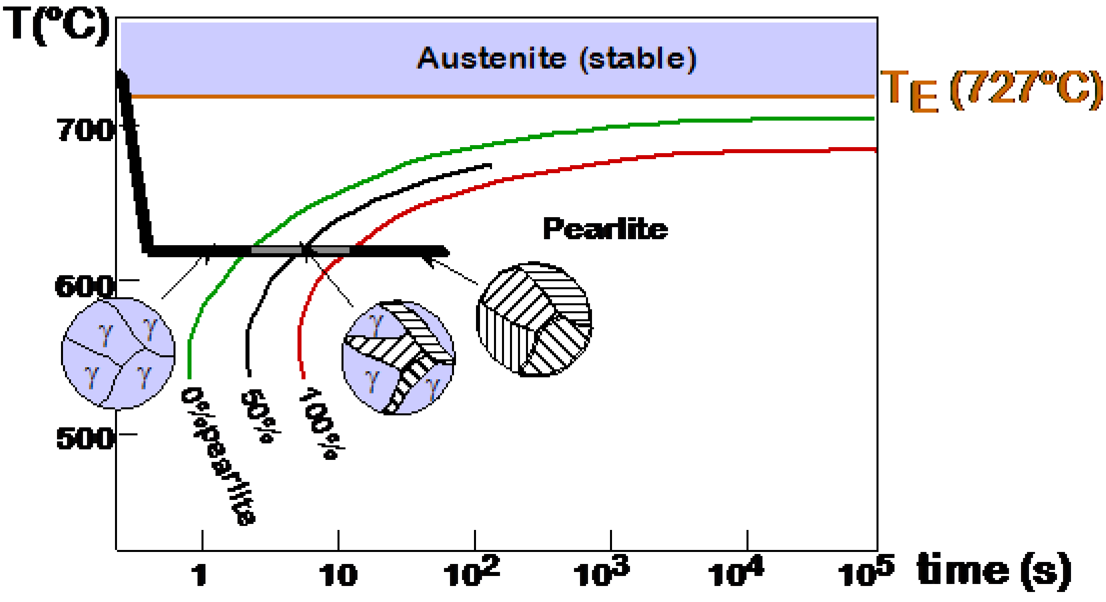
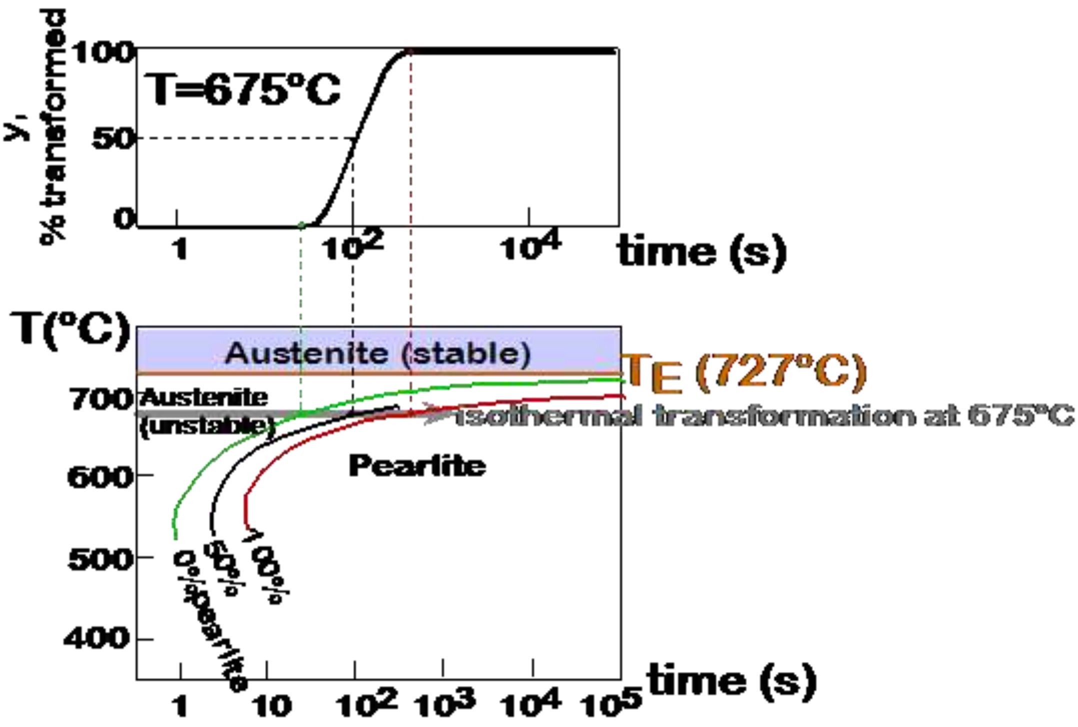


Figure 1: Typical banded ferrite/pearlite microstructure of the investigated material.



(A) Rapidly cool to 625 °C and hold isothermally



(B) Rapidly cool to 675 °C and hold isothermally

Figure 2: The heat transformation process to fine and coarse ferrite and pearlite.

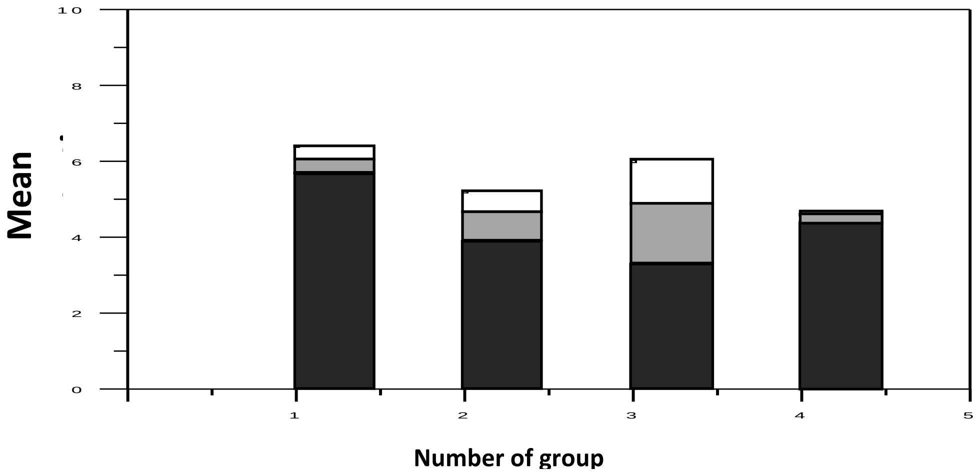
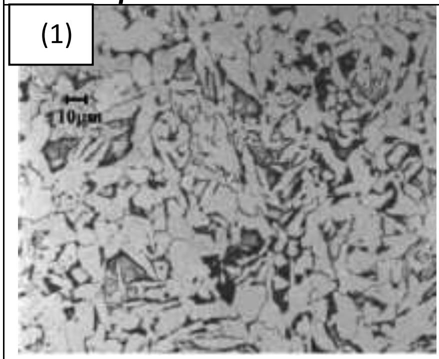
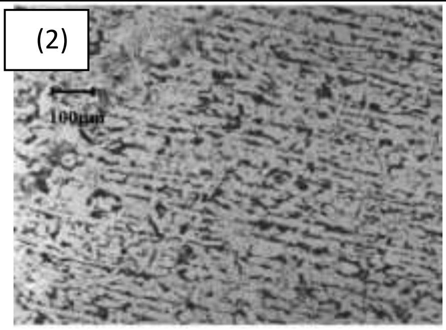
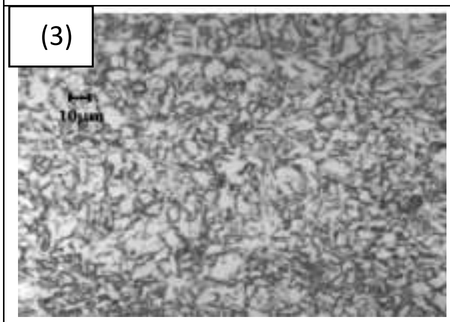
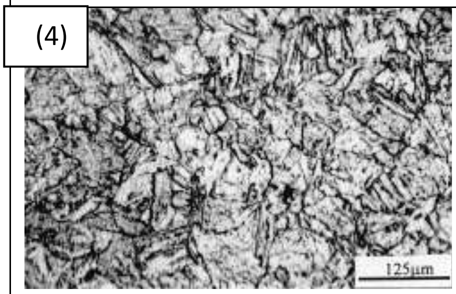
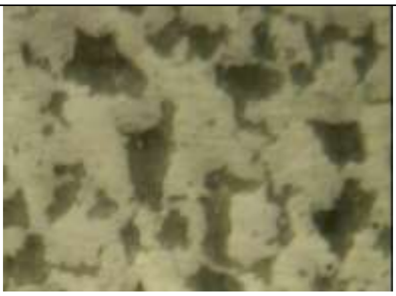


Figure 3: Corrosion penetration of the steel specimens grouped according to microstructure:

Group 1: banded ferrite/pearlite microstructure.
Group 2: fine ferrite/pearlite microstructure.
Group 3: coarse ferrite/pearlite microstructure.

After corrosion	*Before corrosion*
(1) 	
(2) 	
(3) 	
(4) 	

Group 4: tempered martensite microstructure.

Figure 4: Photographs taken of the various microstructures of carbon steel:

Group 1: banded ferrite/pearlite microstructure.

Group 2: fine ferrite/pearlite microstructure.

Group 3: coarse ferrite/pearlite microstructure.
Group 4: tempered martensite microstructure.

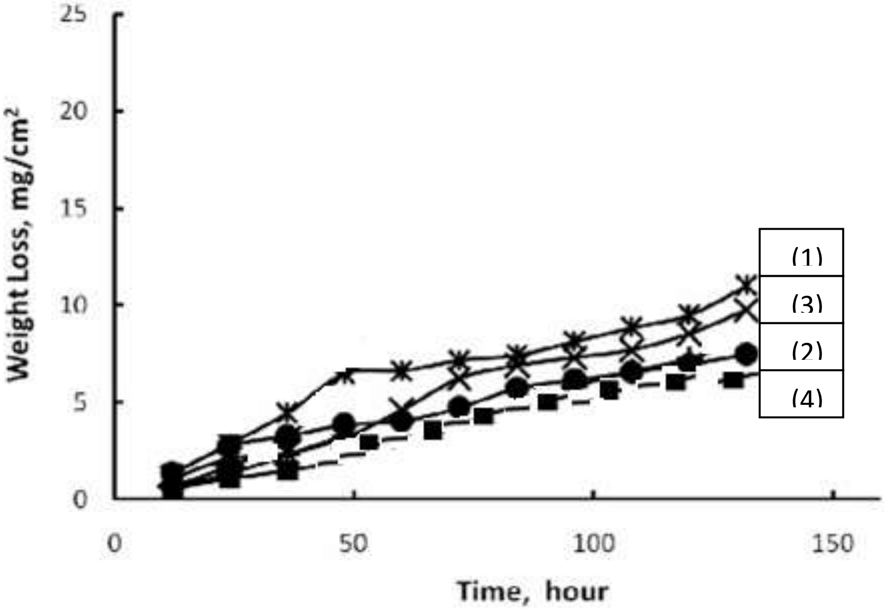


Figure 5: corrosion rate with time of the various microstructures of carbon steel:
Group 1: a banded ferrite/pearlite microstructure.
Group 2: fine ferrite/pearlite microstructure.
Group 3: coarse ferrite/pearlite microstructure.
Group 4: tempered martensite microstructure.