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EFFECT OF SOME HEAT TREATMENTS ON MICROSTRUCTURE AND MECHANICAL PROPERTIES OF A MICROALLOYED LOW CARBON STEEL AIMING TO ATTEND THE OIL AND GAS INDUSTRY

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Abstract. *The API linepipe steels have a great technological importance to oil and gas industry development around the world. Nowadays, the metallurgical challenge is to produce steels with high mechanical properties and low fraction of alloying elements. In this context, this work presents a study about the effect of some heat treatments on microstructure and mechanical properties of a microalloyed low carbon steel aiming to get the API X65 grade. Specimens were submitted to different heat treatments as normalization, quenching and tempering with different heat cycle combinations. In normalizing followed by tempering heat treatments, the material was cooled in air without agitation. In quenching heat treatments, the steel was heated until 920ºC, with a residence time of 15 minutes, and cooled in water at environment temperature. Specimens were submitted to tensile, Charpy impact and Vickers hardness tests. Microstructural and microfractographic analyses were conducted in optical and scanning electronic microscopes. The obtained results showed that the normalized (and variations) samples did not get the API X65 grade specifications, as well the quenched (without tempering). The other heat treated samples presented the mechanical properties predicted by API 5L standard, been a viable procedure.*

Keywords: *API X65, Heat Treatment, Mechanical Properties.*

1. INTRODUCTION

The petroleum is a raw material of vital importance for humanity. Thus, it becomes strategic to develop techniques that allow its extraction. Metallic materials that are employed in prospecting and conducting of oil and gas need to tolerate situations of extreme mechanical stresses, corrosion and critical work temperatures. The environment is increasingly severe as deep waters are explored (Morais, 2013).

The steels are extensively used by the oil and gas industry, but must meet a set of standards specified by the "American Petroleum Institute" - API. Those standards unify the requirements for the provision of such steels (Porto, 2010). In terms, expected properties of such materials are: high mechanical strength, significant fracture toughness at low temperatures, good weldability, high corrosion resistance and oxidation (Godefroid *et al*, 2012).

Aiming to reduce costs and increase productivity, several families of steels have been studied to reach good mechanical properties with lower concentrations of alloying elements. Aiming to adapt the material required properties, changes in the chemical composition or the application of heat treatments on steels have been extensively studied. The last mentioned are the most used due to its easy application on an industrial scale (Porto, 2010). It is known that the normalizing heat treatment produces a refinement of alloy microstructure, enabling the improvement of some mechanical properties, while quenching and tempering increase the hardness and mechanical strength of steel. (Godefroid *et al*, 2012; Lee *et al*, 2009; Chiaverini, 2008; ASM Metals Handbook, 1991).

These, among other possibilities of heat treatments have been studied in micro-alloyed steels aiming to reach properties that classify them according to API standards (Sami *et al*, 2014; Smirnov *et al*, 2012). For example, to achieve the API X65 grade, the steel must have the following properties: yield strength (YS) at least 450MPa, ultimate tensile strength (UTS) between 535MPa and 762MPa, maximum YS/UTS ratio of 0.90 and an elongation of 22% (American Petroleum Institute- API, 2005). These alloys are commonly employed in the high-pressure gas conducting (Hashemi 2011).

Usually these steels exhibit microstructure mainly composed of ferrite that can take different morphologies, such as acicular or polygonal. Besides to present bainite and possible MA constituent. The possibility of the presence of MA constituent is favored by the steel manganese content, due to that, the elevation of the steel yield strength may occur. This phase is detected with the aid of Le-Pera chemical etching (El-Danaf *et al*, 2013; Eilises *et al*, 2008).

In this context, the purpose of this study was to evaluate the effect of some heat treatments on the mechanical properties and the microstructure of a low carbon steel microalloyed, seeking to reach the API X65 level linepipe.

2. MATERIALS AND METHODS

2.1 Materials

Samples of a seamless pipe, manufactured of a microalloyed steel, were provided by an important Company for this work execution. The studied pipe had 273.1mm of diameter and 12.7mm of wall thickness. Tab. 1 shows the chemical specification of the steel in question.

Table 1. Chemical specification of the studied steel (weight %).

Element	Minimum	Maximum	Element	Minimum	Maximum
C	0.08	0.10	**Ni**	0.15	0.20
Si	0.25	0.35	**Al**	0.020	0.040
Mn	1.25	1.35	**Ti**	-	0.010
P	-	0.015	**V**	-	0.030
S	-	0.002	**B**	-	0.0008
Cu	0.15	0.20	**Nb**	0.020	0.030
Cr	-	0.20	**H(ppm)**	-	6
Mo	0.080	0.120			

2.2 Experimental Procedures

2.2.1 Heat treatments

The samples were removed in the longitudinal direction of the tube. They were machined in the proper geometry for mechanical tests, according to ASTM standards, and submitted to different combinations of heat treatments as normalizing treatments (N); normalizing and quenching (NT); quenching (T); quenching and tempering (TR), as highlighted in Tab. 2. The samples were austenitized in the Industrial Heating Oven model HAVE PERT 30 / N2. Some of them were cooled in water with gentle agitation in the Industrial Heating tank, model TOR / 180/500/500. For tempering and normalization an Industrial Oven Heating, model: TEMPER / R30 / N2 was used; all these equipment were used in VSB Company.

For each proposed heat treatment cycles, three specimens were tested in each mechanical test.

Table 2. Samples identification and heat treatments parameters.

Samples	Heat treatments	Temperatures (°C)	Soaking time (min)	Cooling Conditions
2NTR	Double normalizing	920	20	Calm air
	Quenching	920	15	Water
	Tempering	620	20	Calm air
NTR	Normalizing	920	20	Calm air
	Quenching	920	15	Water
	Tempering	620	20	Calm air
NT	Normalizing	920	20	Calm air
	Quenching	920	15	Water
NR	Normalizing	920	20	Calm air
	Tempering	620	20	Calm air
N	Normalizing	920	20	Calm air
TR	Quenching	920	15	Water
	Tempering	620	20	Calm air
T	Quenching	920	15	Water
2TR	Double quenching	920	15	Water
	Tempering	620	20	Calm air

2.2.2 Mechanical Tests

The tensile test was performed at room temperature according to ASTM E8 / 8M - 13th (2013) and ASTM A370 - 12a (2012). The used machine was the 1000kN EMIC, DL -100 000 model, equipped with software and an extensometer. The parameters yield strength (YS), ultimate tensile strength (UTS) and the percentage elongation (AL) were measured for each condition. Three representative specimens were tested and the average values were calculated.

The Vickers hardness test was performed according to ASTM E384 - 11e1 (2011). The measurements were executed on the transversal section of the pipe. The average values were calculated from the obtained results in nine measured points. The Charpy impact test was performed at 0°C according to ASTM E23 - 12c (2012). The specimens were machined from the longitudinal direction of the pipe. The notch was placed at pipe surface position. The average parameters were calculated from the tests performed in three specimens for each condition.

2.2.3 Microstructural characterization

Samples for microstructural analysis were taken from the ends of the tensile test or hardness specimens. Then they passed through the grinding and polishing metallographic standard procedures. After polishing, the specimens were etched by 2% Nital. The immersion time was from 5s to 15s. Some samples were submitted to etching by Le-Pera (1g of sodium metabissulfite, diluted with 100 ml of distilled water and picric acid diluted in 100 ml of ethanol) aiming to verify the presence of MA constituent (Eilises *et al*, 2008).

The microstructural analyses were performed in an optical microscope Olympus CX31 of the Heat Treatments and Optical Microscopy Laboratory (LTM) of DEMET-UFOP and in a scanning electron microscope VEGA 3 TESCAN with EDS OXFORD X-ACT which is in NanoLab - REDEMAT - Federal University of Ouro Preto (UFOP).

3. RESULTS AND DISCUSSIONS

3.1 Mechanical Tests

The yield strength (YS), the ultimate tensile strength (UTS) and yield ratio (YS/UTS) for each heat treated sample are presented in Fig. 1 and Fig. 2. The presented results are the average values obtained for the three tested specimens for each condition of heat treatment with their respective standard deviations. Fig. 1 refers to the procedures started with the normalizing heat treatment, while Fig. 2 to those that started with quenching.

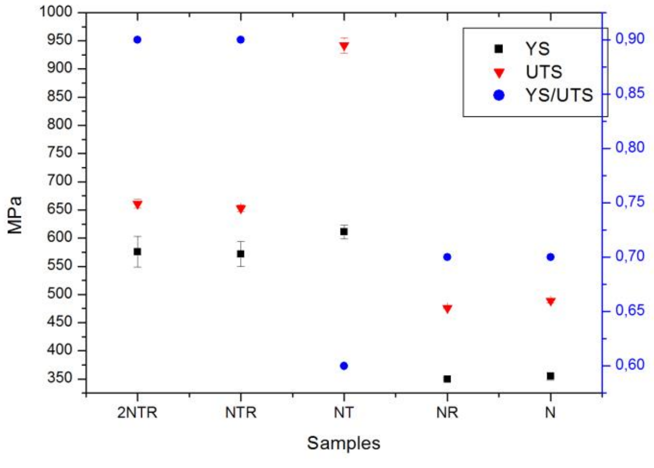


Figure 1. Comparison between YS (Yield strength), UTS (Ultimate tensile strength) and YS/UTS of heat treatments started with normalizing procedure.

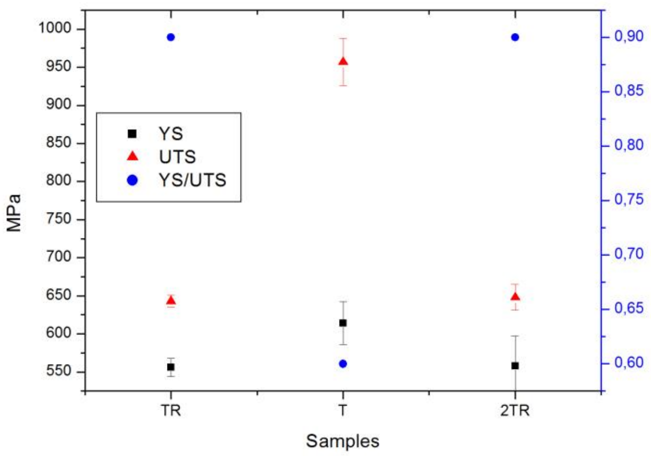


Figure 2. Comparison between YS (Yield strength), UTS (Ultimate tensile strength) and YS/UTS of heat treatments started with quenching procedure.

It is observed that the performed heat treatments influenced significantly the mechanical properties assessed on tensile test. It was found that the NR and N samples showed lower and very close values for YS and UTS, and are therefore rejected by API X65 grade. The NT and T conditions violate the standard specification by exhibiting UTS values greater than specified, beyond the highest YS values. The T condition also presented the ratio YS/UTS lower than requested.

By comparing the samples 2NTR and NTR it is noticeable that the mechanical property values were very similar. This leads to discarding the viability of performing double normalizing, because there would involve a high energy expenditure without significant improvement in the steel properties. The same idea is plausible for the TR and 2TR samples which would discard the last one.

All tested samples meet the API X65 requirements in terms of elongation. All of them showed values greater than 22%. The NR and N specimens exhibited the highest elongations compared with other samples that were, respectively, 57% and 44%. Such behavior is explained by the combination of heat treatment that had performed a notoriously soft condition compared to the others (Godefroid *et al*, 2012; ASM Metals Handbook, 1991).

Thus, the samples that met the API X65 standard specifications were simultaneously NTR, 2NTR, 2TR and TR. For these samples, the Vickers hardness and Charpy impact toughness (absorbed energy) are represented in Fig. 3.

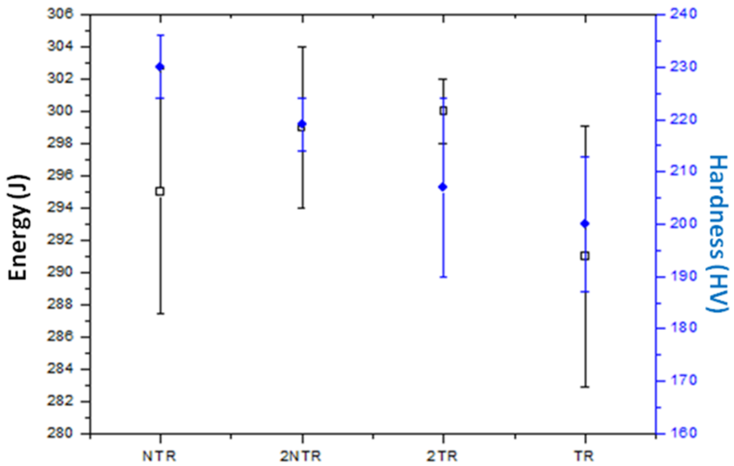


Figure 3. Vickers hardness and impact toughness (absorbed energy) of heat-treated steels.

It is important to highlight that the 2NTR sample simultaneously showed high values for toughness and hardness. Such behavior can be explained by the effect of the combination of the double normalizing and the quenching heat treatments. The first had prepared the steel for subsequent heat treatment, refining prior austenite grain, increasing its toughness, and homogenizing the distribution of alloying elements in the microstructure. The final tempering relieves internal stresses by the steel phase transformation during quenching, promoting the precipitation of carbides and decreasing the dislocation density in the structure (Chiaverini, 2008; Zhang *et al*, 2011; Zhou et al, 2015). According to Zhou et al (2015), for low carbon microalloyed steels, at tempering temperature around 600ºC, a significant amount of iron and microalloying carbides precipitate and partially compensate the loss of strength mainly due to the decomposition of M-A constituents (quenching product). The decomposition of M-A constituents and softening of bainitic-ferrite matrix, after tempering, result in higher density of microvoids and substantial plastic deformation before impact failure, increasing the absorbed energy (Zhou et al, 2015).

3.2 Microstructural characterization

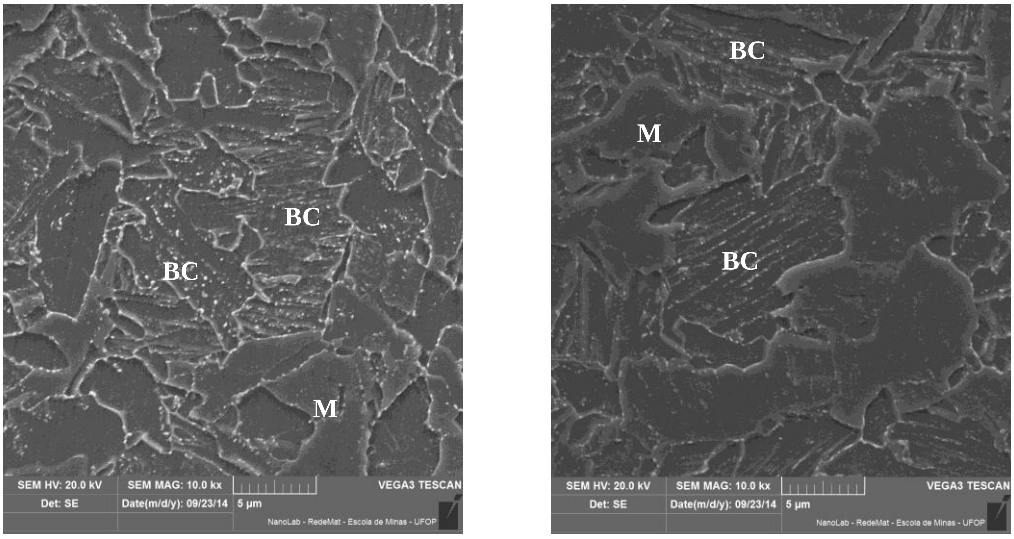
The Fig. 4 shows the analyzed microstructures with the aid of scanning electron microscopy, for samples that met the API X65 level. The samples 2NTR and NTR, Fig. 4 (a) and (b) have similar microstructures consisting mainly of bainite and tempered martensite. The formation of carbide globules is noticed, some of them aligned. The structure of 2NTR is significantly more refined than the NTR. This refined microstructure is the fact that increases simultaneously the material mechanical strength and impact toughness due to its submission to the double normalizing (Lee *et al*, 2009).

The 2TR sample is shown in Fig. 4 (c). Its microstructure is homogeneous and consists of tempered martensite and bainite, and a fraction of ferrite due to the precipitation of carbides finely dispersed throughout the structure. The TR condition shown in Fig 4 (d) is very similar to 2TR, thus confirming the validity of the very close mechanical property values. However, it is noted in Fig. 3 that the sample 2TR has largest value of the impact toughness when compared to TR. One hypothesis that would justify this observation is that the double quenching tends to reduce the formation of MA constituent and decrease the prior austenite grain size. The region of such constituent usually has high dislocation density. Whereas the conditions of tempering were similar for the two samples, the 2TR specimen would have smaller fraction of MA constituent. Thus, present enhanced mobility of dislocations and structure locally absorb larger amount of energy on impact. These results are in accordance with Lan *et al* (2014), Zhang et al (2011), Gao (2010), Lee *et al* (2009), and Hwang et al (2005).

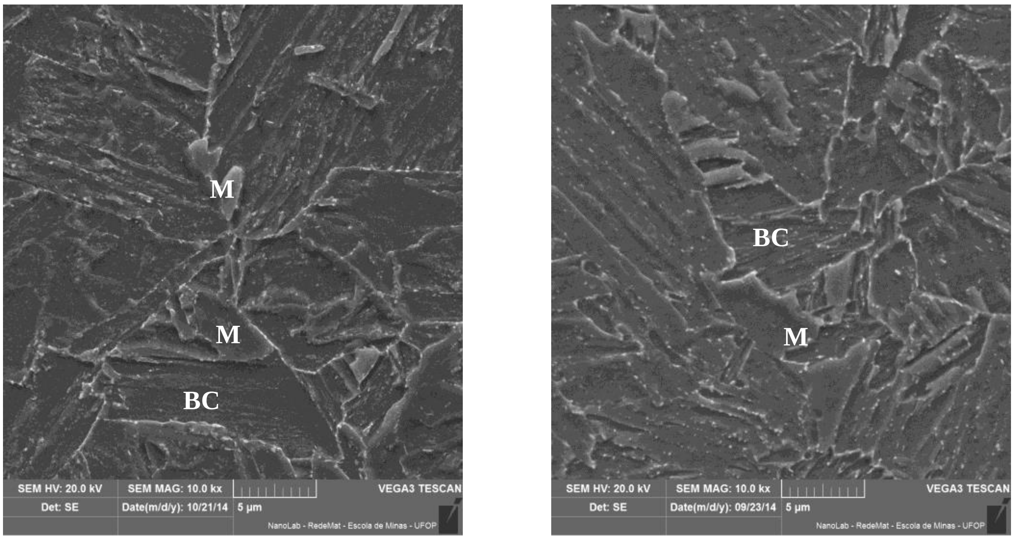
Lan *et al* (2014) also verified, for a microalloyed steel, that the tensile strength was increased with increase in the volume fraction of bainite (B) and MA constituent, while the yield strength increased with increase in the volume fraction of bainite, and was not sensitive to the volume fraction of MA constituent. They showed that large blocky MA constituent facilitate initiation of cracks at the MA constituent/matrix interface, while small MA constituent of size was helpful in improving toughness.

The effect of the volume fraction of bainite on the mechanical properties of the dual-phase pipeline steel was investigated by microscopic analysis and testing of mechanical properties. Results indicate that both the yield strength and ultimate tensile strength of the steel increases almost linearly with the increasing volume fraction of bainite, whilst ductility, work hardening exponent, and impact absorption energy decrease (Zhang *et al*, 2011).

Gao (2010) reported that amongst many strengthening mechanism, such as dislocation strengthening, fine-grain strengthening, solid-solution strengthening, deposition strengthening, the first two mechanisms increase the tensile strength more than they do the yield strength, leading to an increased YS/UST. Considering that the strengthening mechanisms of bainite are mainly dislocation and fine-grain strengthening, the strengthening effect of these mechanisms is enhanced with increasing of bainite fraction and prior austenite grain size decreasing. Thus, this implies in the increase of YS/UST parameter.



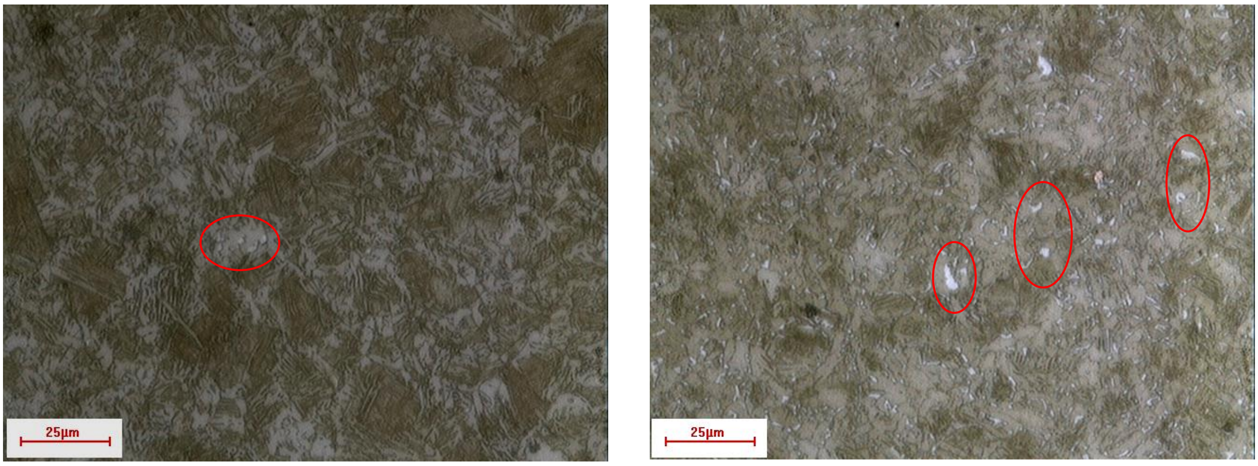
(a) (b)



(c) (d)

Figure 4. Microstructures of (a) 2NTR; (b) NTR; (c) 2TR and (d) TR samples. SEM - Nital 2% (M – tempered martensite, BC - bainite-carbides).

Aiming to check the existence of MA constituent (martensite-retained austenite) in quenched samples, they were etched with Le-Pera and observed in an optical microscope. The obtained results for T and NT samples are shown in Fig. 5. It is observed that both samples have MA constituent (small and whit constituent), but the NT species presented the highest fraction of it. The two specimens presented very similar values of mechanical properties, except hardness. The NT sample presented approximately 300HV, while T reached 200HV. The larges tamount of MA constituents in the sample NT explain this difference. Its high hardness is conferred by the presence of high dislocation density or twinning in the MA constituent substructure (Eilises *et al*, 2008).



(a) (b)

Figure 5. Microstructures of (a) T and (b) NT samples. OM – Le-Pera.

4. CONCLUSIONS

It is observed that the studied steel was greatly influenced by the applied heat treatments.

The NR and N samples showed low yield strength (YS) and tensile strength (UTS) values, while NT and T exhibited high values of UTS values. So, they did not meet the requirements of API X65 linepipe.

The specimens that have reached the standard specifications were 2NTR, NTR, 2TR and TR. Their microstructures are constituted, in general, by bainite, tempered martensite, ferrite and carbides. Furthermore, it was observed that those samples had a fine prior austenitic grain influencing significantly the impact toughness of the studied steel.

In general, the sample yield strengths and ultimate tensile strengths increase with the increasing volume fraction of bainite whilst ductility and impact absorption energy decrease. The increasing of bainite fraction and the prior austenite grain size decreasing implied in the increase of YS/UST parameter.

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