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RESEARCH ARTICLE OPEN ACCESS

REHEAT TREATMENT: EFFECTS IN SUPERMARTENSITIC STAINLESS STELL

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ABSTRACT

Reheat treatment of metals to obtain a specific hardness is a common industrial practice. Hardness, sometimes, is the only parameter on quality control to approve the reheat treatment, efficacy. This investigation analyses a sequence from one to seven heat re-treatment, and its influence on the microstructure and mechanical properties of the 13Cr supermartensitic stainless steel. Metallographic analysis, tensile and Charpy impact tests were conducted in specimens reprocessed seven times by quenching and tempering. Microstructure examinations showed the grain refinement and nonlinear variation of the volume fraction of retained austenite. Mechanical resistance was improved until the fifth reheat. The best relation between all properties was available in the fourth cycle.

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INTRODUCTION

Heat treatment is one of the most required processes used to obtain desired properties on metal products. Industry practices, commonly, use hardness tests to evaluate heat treatment efficacy. It is a cheap possibility to make relationships between this property to the others by graphics and tables available in guidelines, as well in the literature. When the expected hardness is not achieved, usually, the heat treatment is carried out again, until it reaches the desired value. This practice is used to avoid discarding the metal to the scrap. In consequence, we investigated the reprocessing of heat treatment in 13Cr supermartensitic stainless steel (SMSS) to check changes in properties, other than hardness. This alloy containing 13% of chromium (Cr) has been the largest used in the oil and gas industry due to their excellent corrosion resistance in aggressive environments, such as which contain CO_2 (Zhao *et al*, 2005; Ma *et al*, 2012), as well as excellent mechanical properties when quenched and tempered (De Andrés *et al*, 1998). Those companies are very exigent with applications involving materials due to high risks of accidents. Most of the time it is necessary to check the minimum and maximum range of the limit values of the properties.

Therefore, this study opens one problem of interest verifying if the technique of reprocessing heat treatment is well suited for its requirements. Based on the observation of reprocessing the heat treatment, previous studies have pointed investigations with another emphasis: cyclic heat treatment is purposefully applied as a good option for the improvement of the properties (Lv *et al*, 2015; Singh and Nath, 2020; Saha *et al*, 2010; Nakazawa *et al*, 1978; Fan *et al*, 2016). A recent study about cyclic heat treatment for SMSS investigated thermal cycles of heating to 850, 950 and 1050 ºC with fast cooling (Singh and Nath, 2020). The best relationship among ultimate tensile strength, hardness and ductility was found in cycling with a temperature of 950 °C.

Studies using a heat cycling of just heating (generally austenitization temperature) and cooling is usual; therefore, the effect of a cycle of quenching followed by tempering is open in literature. Quenching and tempering is a typical heat treatment of SMSS steels, which includes austenitizing − to ensure the full transformation into the austenitic phase and carbides dissolution− followed by cooling. This route, called quenching, promotes the martensite transformation. Besides, the tempering of martensite improves toughness and ductility

(Barlow, 2009; Nakagawa and Miyazaki, 1999), The high alloy elements content gives good hardenability for the martensitic lath microstructure, which could be obtained in quenching heat treatment even by air cooling, since the material does not have over-thick sections (Ma *et al*, 2012; Barlow, 2009). The microstructure of SMSS quenched and tempered is generally composed of a martensitic matrix with at least 15% of the austenite phase (Leem *et al*, 2001), which keeps relatively stable at room temperature after cooling (Bilmes *et al*, 2001). It is virtually impossible to obtain the total transformation of the austenite to martensite in industrial quenching practice (Dutta, 2014). This phenomenon occurs because of the high nickel content in solid solution stabilizes austenite, even at room temperature (Wang *et al*, 2013). It is well accepted that retained austenite improves toughness and ductility, but in contrast, reduces the hardness (Galindo-Nava and Miyazaki, 2016).

To recognize the effect of the reheat treatment on SMSS utilization, we detailed its effects on the morphological characteristics of the microstructure and mechanical properties intending to find a favorable number of heat treatment cycles that promote the best combination between the properties.

Experimental procedure: The chemical composition of the alloy used in the work is listed in Table 1. This steel comes from commercial tubes used in petroleum companies to tap into deep wells and aggressive environments. Seven samples from the tube of 13Cr SMSS were supplied for the investigation. The heat treatment cycle is shown in Fig. 1.

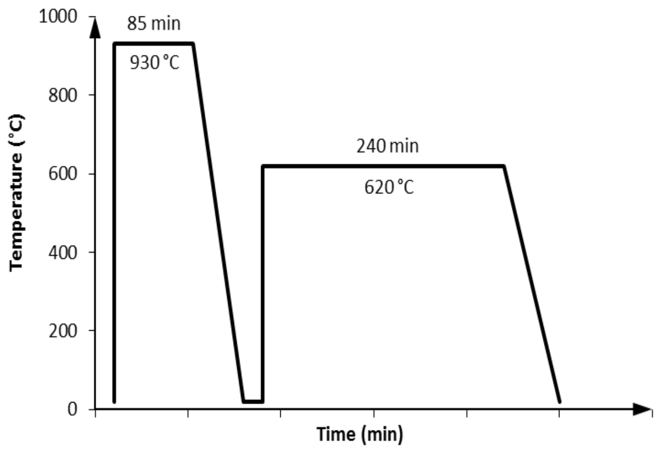


Figure 1. Heat treatment cycle, composed by quenching and tempering, applied to the 13Cr supermartensitic stainless steel

Quenching was conducted by the samples austenitization in a muffle furnace at 930 °C for 85 min, followed by air-cooling to room temperature. Tempering was held for 240 min at 620 °C, after that the samples were left cooling in air.

The heat treatment cycle was repeated seven times, taking off one sample at a time. After that, specimens were prepared for microstructural observation and mechanical tests. The microstructure was revealed using Vilella metallographic etchant (1 g picric acid, 10 mL hydrochloric acid and 100 mL ethanol) (Vander Voort, 1985). The morphology and dispersion were examined using an optical microscope and scanning electron microscope (SEM). The microchemical dispersion of nickel, chromium and iron were analyzed using an energy dispersive spectrometer (EDS) equipped to SEM to show the distribution of chemical elements by elemental mapping. The grain size was evaluated by the lineal intercept method (ASTM E112, 2013) and the volume fraction of retained austenite was estimated by the systematic manual point count (ASTM E562, 2019). Rockwell C hardness measurements with an applied preload of 10 kgf and the load of 150 kgf were performed on all the heat-treated samples according to the standard method (ASTM E92, 2017). The results were reported as the average of five tests per sample. Tensile tests were performed on a tensile testing machine as per the standard method (ASTM E8, 2016). Impact tests were performed on Charpy V-notch impact specimens (10 mm x 10 mm x 55 mm) at room temperature according to specification on the standard method (ASTM A370, 2019). Every mechanical property value reported in the results is the average of three tests.

RESULTS AND DISCUSSION

Table 2 shows the microstructure evolution as a function of the number of heat treatment cycles. The more times the material was reheated, the more the reduction of the grain size. Looking at the SEM images, in the first cycle one can see only the grain boundary, while in the seventh cycle, one can see the whole grain (see the arrows). The large grain of 27 µm in the initial structure becomes fine-grain about 13 µm in the last cycle. In accordance with other studies, the grain size reduction is expected (Lv *et al*, 2015; Saha *et al*, 2010; Nakazawa *et al*, 1978; Fan *et al*, 2016; Tavares *et al*, 2017; Syn *et al*, 1976; Kumar *et al*, 2015). The refinement is explained by the nucleation of new austenitic grains in the middle of pre-existing grains of each new heating (Nakazawa, 1978). The effect observed is more pronounced in the first cycle because after the second cycle, the new grains size approximates more and more to the new nucleated austenitic grain size (Lv, 2015; Kumar, 2015).

The volume fraction of retained austenite presented nonlinear variation, reducing until the fourth cycle and increasing again after the fifth cycle. This phase has been previously identified in SMSS by other authors in their investigations (Bilmes, 2001; Al Dawood, 2004). It has been reported that the austenite phase causes dimensional change and would be one important parameter to control (Dutta, 2014). It is known that tempering favors the transformation of retained austenite into martensite in high alloy steels and it had happened until the fourth cycle. On the other side, the grain refinement shifts the TTT diagram (Time-Temperature-Transformation) towards left. Therefore, the critical cooling rate increases and more retained austenite is possible to be present at room temperature (Al Dawood *et al*, 2004; Yang and Bhadeshia, 2009). Through the SEM analyses, it was possible to evidence those carbides precipitation did not occur over grain boundaries. The elements distribution maps show that the concentration of elements nickel, chromium and iron elements are homogeneously dispersed throughout the structure. Table 3 summarizes all analyzed properties. It is noticeable that the best relationship, among all specimens, can be achieved in four cycles of heat treatment. Higher hardness values were observed for three and four cycles, coincidently in specimens with a lower amount of retained austenite. Moreover, the grain refinement even increases the hardness because more grain boundary areas act hindering dislocation movements, acting as a barrier to that movement, increasing the material resistance (Callister and Rethwisch, 2018).

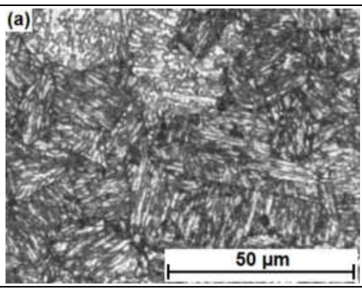
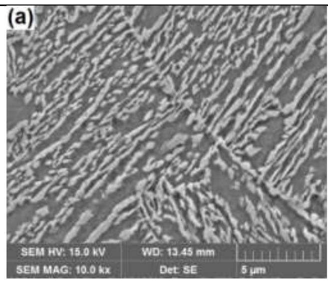
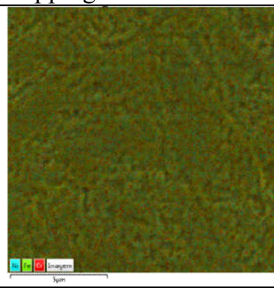
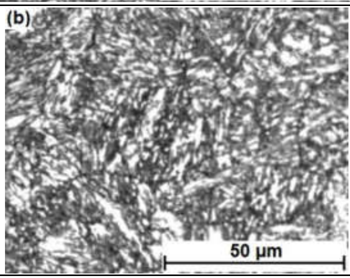
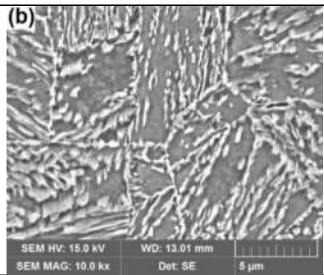
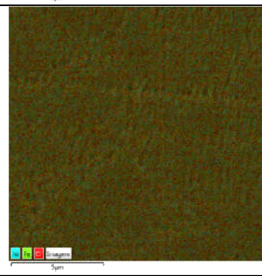
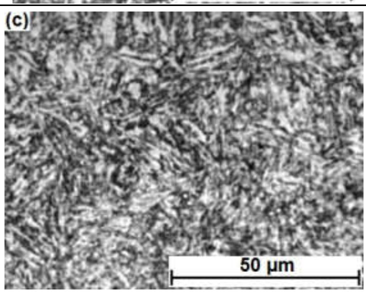
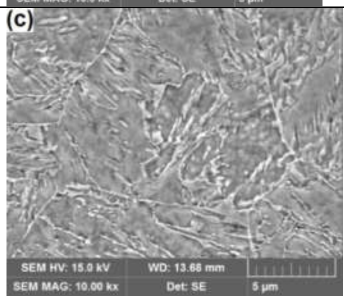
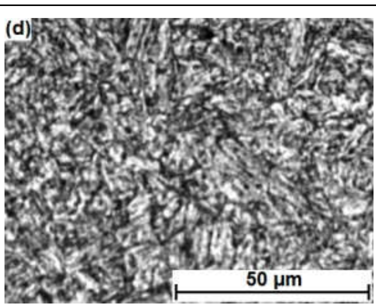
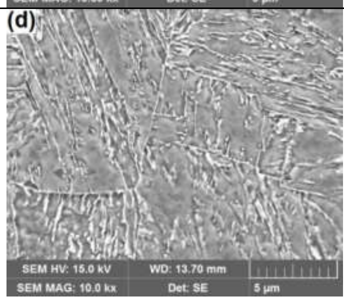
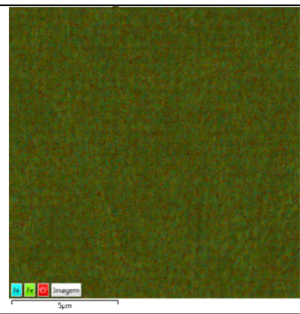
Table 1. Chemical composition of 13Cr supermartensitic stainless steel (ASTM A276/UNS S41425)

Chemical Composition (wt%)										
C	Mn	Si	Cr	Ni	Mo	S	P	Cu	N	V
0.02	0.75	0.29	13.50	4.90	1.65	0.0002	0.017	0.13	0.07	0.03

Table 2. Evaluated proprieties as a function of the number of heat treatment cyclesby quenching and tempering

N°	Grain Size (µm)	Retained Austenite (%)	Rockwell C Hardness (HRC)	Tensile Strenght (MPa)	Yield Strength (MPa)	Toughness (J)
One cycle	27 ± 0.25 (7.5 ASTM)	28.43 ± 1.90	28 ± 0.32	883 ± 6.8	688 ± 11	126 ± 4.6
Two cycles	19 ± 0.29(8 ASTM)	22.95 ± 0.81	29 ± 0.32	886 ± 8.2	676 ± 13	143 ± 1.5
Three cycles	18 ± 0.13(8 ASTM)	9.94 ± 1.78	31 ± 0.48	904 ± 1.7	853 ± 5	147 ± 2.4
Four cycles	17 ± 0.10 (8.5 ASTM)	15.75 ± 1.51	32 ± 0.40	999 ± 1.7	855 ± 11	156 ± 5.3
Five cycles	15 ± 0.23 (8.5 ASTM)	21.26 ± 0.58	29 ± 0.40	950 ± 0.4	767 ± 6	175 ± 0.4
Six cycles	14 ± 0.08(9 ASTM)	23.38 ± 0.93	28 ± 0.32	916 ± 1.5	630 ± 27	174 ± 4.8
Seven cycles	13 ± 0.17(9 ASTM)	26.69 ± 2.10	31 ± 0.48	900 ± 1.7	653 ± 20	153 ± 2.6

Table 2. Evolution of the microstructure as a function of the number of heat treatment cycles by quenching and tempering.Martensite (dark region) and retained austenite (light region) can be observed. Arrows indicate the grain boundary.

N°	Optical micrographs magnification 500 x	SEM micrographs magnification 1000 x	EDS chemical elements mapping
One cycle			
Two cycles			
Three cycles			
Four cycles			

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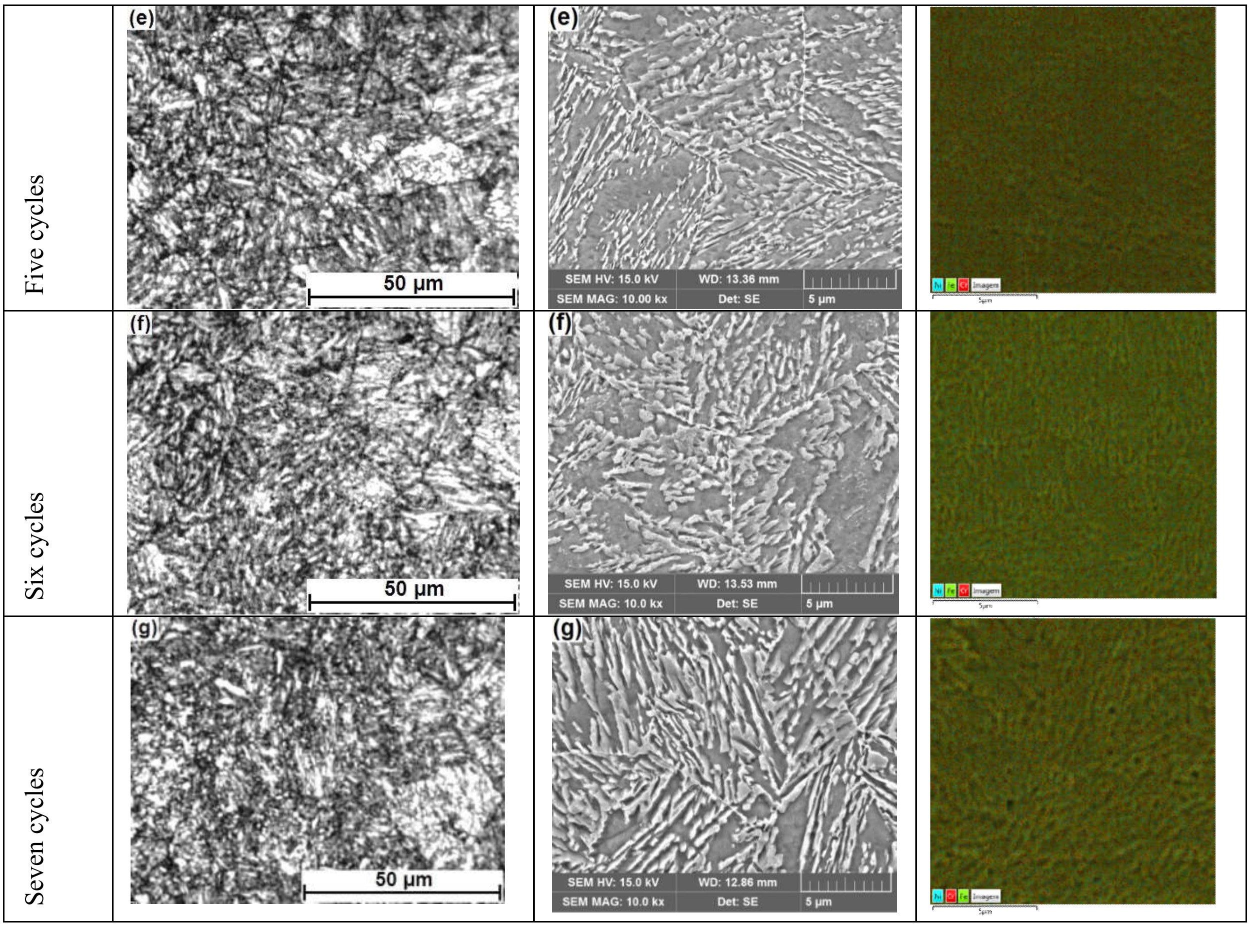

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Higher toughness values were observed for five and six cycles, coincidentally in specimens with more retained austenite and smaller grains (good conditions for high toughness). After six cycles, the toughness decreased, because a severe grain refinement could reduce toughness (Callister and Rethwisch, 2018). The highest tensile and yield strength are observed in the fourth cycle, coincidently in the specimen with the higher hardness. Here, the same effect acts as explained for hardness.

Conclusion

The conclusions obtained in this study are summarized as follow:

- Reheat treatment alters significantly the properties of supermartensitic stainless steel.
- The favorable number of heat re-treatment to maintain good properties is four.
- Reheat treatment conduct to grain size refinement.
- The cyclic heat treatment did not interfere in the alloy elements distribution over the matrix structure.
- The volume fraction of retained austenite reduces until the fourth reheat; and starts raising again after the fifth re-treatment.
- Toughness demonstrated a nonlinear behavior; the combination with small grain size and a higher amount of retained austenite gives the best results, including fifth and sixth reheat.

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