Low-temperature tempering reactions in a high nitrogen martensitic stainless steel by magnetic saturation measurements

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Abstract

Tempering behavior in the temperature range 150-500 °C of a Fe-15Cr-1Mo-0.3C-0.38N (mass-%) martensitic-austenitic stainless steel, commercially known as Cronidur® 30, was studied by means of dilatometry, magnetic saturation, and hardness measurements. The first stage of tempering, centered around 150 °C, was characterized by an increase in the hardness and magnetic flux density. In the second stage of tempering centered around 350 °C, the hardness continuously decreased. Magnetic saturation studies indicated an initial decrease in the magnetic flux density which changed to an increase in the upper temperature range for the second stage. The occurrence of secondary hardening was the main characteristic of the third stage of tempering and it is thought to mark the end of precipitation reactions under paraequilibrium conditions.

Keywords: Cronidur® 30, tempering reactions, magnetic saturation, dilatometry

1. Introduction

Much work has been done in the past to study the tempering behavior of martensitic steels with carbon and/or nitrogen as interstitial atoms [1-5]. Although remarkable advances have been made in making the general reactions of the tempering process clear, a comprehensive and widely-accepted mechanism is still lacking. For example, Ferguson and Jack [2] proposed the formation of initial clusters of carbon-nitrogen atoms (GP zones) in supersaturated solid solution of C and N in α-Fe which evolve to body-centered tetragonal α′-Fe4C(N)2 and finally to γ′-Fe2N and ε-Fe3(C,N) precipitates. On the contrary, Cheng et al. [5] believe that during tempering of Fe-C-N martensite, the carbon and nitrogen atoms precipitate separately at least mainly as ε-Fe23C carbide and α′-Fe16N2 nitride, respectively.

In addition to binary and ternary alloys, tempering reactions of alloyed martensites have been studied by many investigators [6-12]. According to the data presented by Berns et al. [6-8], the sequence of precipitation for Fe-Cr-Mo-C-N stainless steels is totally different from those reported for the simple Fe-C-N steels. In the case of stainless steels, tempering at 200 °C caused the precipitation of (Fe,Cr)2C ε-carbide and (Fe,Cr)2N ε-nitride with hexagonal close packed (hcp) crystal structures. The transformation of transition carbides and nitrides to stable precipitates was found to start at 500 °C where cementite and CrN precipitates formed from ε-carbides and ε-nitrides, respectively. The suppression of α′-Fe4C2 and γ′-Fe2N nitrides and the formation of ε-(Fe,Cr)2N and ξ-(Fe,Cr)2N nitrides were concluded to be the major differences between binary and high-alloy martensites. Furthermore, no carbonitride was reported after tempering [6-8]. A summary of the transformation sequences during tempering of C- and/or N-alloyed martensitic steels, extracted from the literature data, is shown in Table 1.

The addition of interstitials to ferritic steels brings about two competing effects whose balance determines the average magnetic moment of the material. The first is a volume expansion which increases the magnetic moment and the second is an increased valence electron concentration which weakens the magnetic moment. Formation of tempering products causes a decrease in the martensite lattice parameter and the number of valence electrons in the martensite. This might cause a change in the magnetic moment of the matrix [13]. The net change in the magnetic moment after tempering of steels additionally depends on the magnetic properties and the fraction of tempering precipitates. Accordingly, variations in the type and magnetic properties of the microstructural constituents can form the basis for a novel method of studying the structural evolutions upon tempering of martensite.

This work aims to study the low temperature tempering reactions of a high nitrogen martensitic stainless steel with various methods in particular magnetic saturation measurements. The martensitic steel Cronidur® 30 used for this purpose was patented in 1989 by G. Stein et al. [14] and has been used in the high duty service components ever since [15]. This material possesses an excellent combination of hardness, impact bending energy and corrosion resistance in the quenched and tempered condition [15].
2. Experimental details

Table 2 shows the chemical composition of the as-received bar of the Cronidur® 30 stainless steel. The alloy was supplied in the annealed condition. Austenitization treatments were carried out using 3.5 × 3.5 × 10 mm dilatometry simulations at 1150 °C for 5 minutes in a nitrogen protective atmosphere. Subsequently, the samples were quenched in water held at 25 °C. To obtain a high fraction of martensite for the study of tempering reactions, the water-quenched specimens were cooled in liquid nitrogen (-196 °C). The samples were then tempered at various temperatures from 150 to 500 °C in a resistance heating furnace. One sample was used for tempering studies at each temperature. Cumulative holding time varied between 2 and 35 minutes and the ferromagnetic phase content after each holding time was determined by magnetic flux density measurements after magnetizing specimens up to saturation. Tempering reactions were also studied by continuous heating in a BÄHR-DIL805 dilatometer. Light optical micrographs were taken using a Neophot 30 microscope. A Wolpert 430SVD-type hardness tester was used for Vickers hardness measurements. Specimens for hardness measurements were the ones used for magnetic saturation studies with a cumulative tempering time of 35 minutes.

3. Results and discussion

3.1. Austenitization and martensitic transformation

In order to strengthen the signals in magnetic and dilatometric studies, it was necessary to have a high fraction of high-Interstitial martensite with as little auto-tempering as possible. This also ensures that the relative ratio of interstitial elements in the martensite remains close to this ratio in the nominal chemical composition of the alloy. To choose the solution annealing temperature, different annealing temperatures in the range of 900-1150 °C were examined by dilatometry. Variation of the martensite start (Mₐ) temperature then reflects the dissolution behavior of precipitates. Dilatometry curves in Figure 1

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Phase transformation sequences for various interstitially-alloyed steels during tempering</th>
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<tbody>
<tr>
<td>Alloy</td>
<td>Transformation sequence</td>
</tr>
<tr>
<td>Fe-1.13C (wt%)</td>
<td>Redistribution of carbon atoms below 100 °C → Precipitation of Fe₃C, hcp, transition ε/η-carbide between 80 °C and 200 °C → Decomposition of retained austenite between 240 and 320 °C → Conversion of ε/η carbide into cementite between 260 °C and 350 °C</td>
</tr>
<tr>
<td>Fe-1.5N (wt%)</td>
<td>Precipitation of tetragonal, α'-nitride (Fe₂N₃) below 270 °C → Formation of stable Fe₃N, fcc, γ'-nitride above 200 °C</td>
</tr>
<tr>
<td>Fe-(0.8-7)N (at%)</td>
<td>Redistribution of nitrogen atoms below 100 °C → Precipitation of incoherent, Fe₅N₇ bct, α''-nitride between 100 °C and 220 °C → Decomposition of retained austenite above 240 °C</td>
</tr>
<tr>
<td>Fe-0.2C-1.29N (wt%)</td>
<td>Formation of ordered α' from α martensite at 23 °C → Formation of α' expanded martensite and α'-Fe₅N₇ at 80 °C → Formation of ε-Fe₅,C₃N + γ'-nitride Fe₃N at 195 °C → Conversion of ε-Fe₅,C₃N into cementite at 300 °C</td>
</tr>
<tr>
<td>Fe-C-N C₄N=5.5 (at%)</td>
<td>Redistibution of interstitials up to 97 °C → Precipitation of Fe₅N₇, transition bct, α''-nitride and Fe₃C, hcp, transition ε/η-carbide between 97 °C and 177 °C → Conversion of α'' into Fe₃N, s, fcc, γ'-nitride between 177 °C and 287 °C</td>
</tr>
<tr>
<td>Fe-15Cr-1Mo-0.6C (wt%)</td>
<td>Precipitation of Fe₅C₃, hexagonal, transition ε-carbide between 90 and 200 °C → Conversion of ε into cementite between 250 and 300 °C → Formation of Cr₇C₃ carbide at 600 °C</td>
</tr>
<tr>
<td>Fe-15Cr-1Mo-0.6N (wt%)</td>
<td>Precipitation of (Fe, Cr)₃N, hexagonal, ε-nitride between 80 and 200 °C → Formation of (Fe,Cr)₃N, orthorhombic, ε-nitride between 300 °C and 500 °C → Formation of hexagonal, Cr₃N at 700 °C</td>
</tr>
<tr>
<td>Fe-15Cr-1Mo-0.29C-0.35N (wt%)</td>
<td>Precipitation of hcp, ε-carbide and ε-nitride at 200 °C → Transformation of transition phases into cementite and cubic Cr₃N at 500 °C → Transformation of Cr₃N into Cr₇N at 650 °C</td>
</tr>
</tbody>
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<th>Table 2</th>
<th>Chemical composition of the as-received Cronidur® 30</th>
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<tbody>
<tr>
<td>Element</td>
<td>C</td>
</tr>
<tr>
<td>Weight %</td>
<td>0.30</td>
</tr>
</tbody>
</table>
demonstrate that the Mₜ temperature decreases from around 325 °C to room temperature by increasing the annealing temperature from 900 to 1150 °C. Thermodynamically, a higher fraction of precipitates dissolve at higher temperatures and the increased concentration of alloying elements stabilizes the austenite with respect to the martensitic transformation thereby increasing the fraction of retained austenite.

According to Beneteau et al. [16] for a Fe-16Cr-1.5Mo-0.3V-0.2N-0.4C alloy, whereas the dissolution of M₃C₆ carbides (M mainly denoting Cr and Fe) begins between 700 and 750 °C, it happens between 850 and 900 °C for the M₂N nitrides. It was also claimed that the dissolution of M₃C₆ started in the ferrite and continued during the ferrite to austenite transformation. On the other hand, the dissolution of Cr₃N started during austenite formation and continued in the fully austenitic matrix. During the investigations on the Cronidur® 30 by Kaluba et al. [17] the austenitization was proposed to take place at two temperature levels corresponding to the dissolution of M₃C₆ and M₂N. They suggested that the higher diffusivity of carbon with respect to that of nitrogen was responsible for the earlier dissolution of carbides.

The microstructure of the as-received material as well as specimens after austenitization and subzero quenching in liquid nitrogen are shown in Figure 2. As can be seen in the Figure 2a, the initial microstructure consists of ferrite and precipitates. The precipitates are likely a mixture of M₃C₆ and M₂N [17]. After holding at 1150 °C for 2 minutes, the microstructure is almost fully austenitized with annealing twins visible in some grains (Figure 2b). The presence of undissolved precipitates is apparent in the matrix. Partial dissolution of precipitates after annealing at 1100 °C of this alloy has been reported before [18]. The micrograph shown in Figure 2c represents the microstructure of a specimen annealed at 1150 °C and quenched to -196 °C. The microstructure consists of martensite laths, retained austenite, and undissolved precipitates.

The amount of retained austenite after austenitization at temperatures in the range of 900-1150 °C was measured by magnetic saturation measurements and dilatometry. Figure 3 also includes the data extracted from the work done by El Mehtedi et al. [10] and those from the material datasheet of Cronidur® 30 [15].

![Figure 1](image1.png)

**Figure 1.** Dilatometry curves obtained after annealing at various temperatures for 2 minutes. Heating and cooling rates were 50 and 20 °C/s, respectively.

![Figure 2](image2.png)

**Figure 2.** Microstructure of Cronidur® 30 in various conditions (a) as-received material; (b) sample austenitized at 1150 °C for 2 minutes, (heating and cooling rates were 50 and 20 °C/S, respectively); (c) austenitized as in (b) and quenched to -196 °C.

As shown in Figure 3, the fraction of retained austenite increases by increasing the annealing temperature. However, there is a pronounced difference in the fractions, especially between the present work and Ref. [10] where El Mehtedi et al. report an austenite content of only about 40% after 2 hours of holding at 1150 °C. Our observations indicate an austenite fraction of 98%
after austenitization at this temperature. It is particularly clear from Figure 1 that no substantial fraction of martensite has formed after annealing at 1150 °C. The methods used by El Mehtedi et al. for the quantification of retained austenite were metallography and hardness testing [10]. In both cases, the samples were subjected to mechanical stresses at surface during specimen preparation and therefore the formation of deformation induced martensite is quite likely. Given that $M_s$ of the alloy in this condition is about room temperature, it is logical to assume that the deformation-induced martensite has been responsible for the overestimated martensite fractions in Ref. [10].

Our experiments show that this alloy is prone to decarburization and denitriding upon exposure to high temperatures. Prolonged holding (2 hours) at 1150 °C is thought to be another possible reason for obtaining high fractions of martensite in Ref. [10] as the carbon and nitrogen depletion rises the $M_s$ temperature.

The martensite fractions obtained by subzero cooling of the specimens austenitized at 1150 °C are shown in Figure 4. The martensite fraction increases at temperatures immediately below the $M_s$ temperature. The martensitic transformation rate decreases substantially below -100 °C and finally reaches a plateau below -150 °C. A martensite content of the order of 46% was achieved by cooling to -196 °C.

3.2. Dimensional changes during continuous heating

Tempering reactions during continuous heating were studied using dilatometry at a heating rate of 0.5 °C/s in vacuum. The dilatometry curve (solid line) and its corresponding first derivative denoted incremental CTE (coefficient of thermal expansion) and marked by square symbols are depicted in Figure 5. The derivative curve in Figure 5 is very similar to the curves obtained during dilatometry heating of Fe-11Cr-0.05C-0.24N and Fe-11Cr-0.8Mo-0.05C-0.23N martensitic alloys at a rate of 50 °C/hr [9]. As the derivative curve suggests, there is a decrease in the slope beginning at approximately 70 °C. A clear minimum in the derivative curve occurs at around 150 °C. Based on the TEM studies of the Fe-15Cr-1Mo-0.6N alloy by Berns et al. [8], tempering at this temperature range leads to the precipitation of hcp $M_2$(N,C) precipitates and is associated with a small contraction.

Liu Cheng et al. [5] observed a contraction between 97 °C and 177 °C during tempering of a ternary Fe-C-N martensite. The contraction in that work was ascribed to the formation of transition $\alpha''$-nitrides and $\varepsilon$-carbides. The similarity of tempering reactions in binary Fe-C steels [3] and ternary Fe-Cr-C steels [19] means that a possible correlation between the tempering reactions in Fe-C-N steels and the steel used in this work cannot be excluded.

Figure 3. Fraction of retained austenite after holding at different temperatures for 2 minutes. The magnetic saturation and dilatometry results obtained in this research are compared with literature data.

Figure 4. Martensite fraction as a function of subzero cooling temperature. Specimens were initially solution heat treated at 1150 °C.

Figure 5. Dilatometry curve (solid line) and its first derivative (squares) during heating of the Fe-15.5Cr-1Mo-0.3C-0.4N steel at a rate of 0.5 °C/s. CTE denotes the coefficient of thermal expansion.

The derivative curve in Figure 5 indicates that after the first minimum in the CTE as discussed above, a second minimum, although much smaller than the first one, occurs at a temperature of approximately 325 °C. This minimum whose position depends on the heating rate
is expected to mark the formation of stable carbides and nitrides e.g. \( \text{M}_{x}\text{C}_{y} \) and \( \text{M}_{z}\text{N}_{t} \) (\( \text{M} \) denoting Fe and substitutional atoms) precipitates. Yet a third decrease in the CTE begins at almost 440 °C which could mark the temperature for the heating rate used, at which the diffusivity of substitutional alloying elements in martensite becomes significant. The third CTE decrease is therefore expected to correspond to the start of the temperature regime where equilibrium precipitation or pre-precipitation reactions are allowed. This issue is further discussed in section 3.4.

3.3. Magnetic saturation measurements

Precipitation reactions which occur upon tempering of martensite can change its magnetic properties. Such possible changes are due to the reduction of the solute interstitials content of martensite and the partial replacement of a fraction of martensite by tempering precipitates which might, depending on the ordering of interstitials atoms, exhibit magnetic properties different from that of the martensite. The lattice expansion due to the ordering of nitrogen atoms in common types of iron nitrides is the primary reason behind their being often ferromagnetic. In terms of the positioning of the iron atoms, the \( \varepsilon \)-\( \text{Fe}_{x}\text{N} \) and \( \gamma'\text{-Fe}_{4}\text{N} \) structures are equivalent to the hcp \( \varepsilon \)-Fe and fcc \( \gamma \)-Fe structures, respectively. The \( \gamma \)-Fe and \( \varepsilon \)-Fe structures are nonferromagnetic in the ground state but they become ferromagnetic at sufficiently large volumes, i.e. by the introduction of interstitials. The introduction of interstitials at the same time increases the number of valence electrons which tends to weaken the magnetic moment. As a result, the magnetic moment of \( \text{Fe}_{x}\text{N} \) \( (2 \leq x \leq 3) \) decreases as the value of \( x \) decreases [13]. The \( \alpha''\text{-Fe}_{4}\text{N} \) is the nitride with the least nitrogen concentration and has the largest magnetic moment [20]. In contrast, the orthorhombic \( \xi \)-\( \text{Fe}_{2}\text{N} \) nitride shows a paramagnetic doublet in Mössbauer spectrum at room temperature and is antiferromagnetic below 10 K [21]. \( \text{FeN} \) thin films deposited by dc magnetron sputtering were reported to be nonmagnetic [22]. The carbide types \( \varepsilon \)-\( \text{Fe}_{2}\text{C} \) \( (2 \leq x < 3) \), \( \text{Fe}_{5}\text{C} \), and \( \text{Fe}_{7}\text{C} \) are known to be ferromagnetic at room temperature [13, 23]. The presence of \( \text{Cr} \) in carbides has been found to decrease their Curie temperature and magnetic moment [13]. Accordingly, cememite containing more than about 9 wt% \( \text{Cr} \) becomes paramagnetic at room temperature. Magnetic moment values for various iron nitrides and carbides are given in Table 3.

Figures 6 and 7 show changes in the magnetic flux density with tempering time and temperature of the Cronidur® 30 and an X46Cr13 type stainless steel used for the purpose of comparison. The latter N-free alloy contains 13 wt% \( \text{Cr} \) and 0.46 wt% \( \text{C} \) and forms only carbides during tempering. In the following discussion, the Cronidur® 30 and X46Cr13 alloys will be referred to as (C+N)- and C-steel, respectively. Comparison of the magnetic behavior of these two alloys can help understand the effect of nitrogen on the tempering response of (C+N)-containing martensitic steels.

Owing to the difference in the martensite content after quenching to -196 °C of \( \text{C} \)- and (C+N)-steels \( (\approx 96\% \) and \( \approx 46\% \), respectively), the measured magnetic flux densities were normalized with respect to the value before tempering.

As shown in Figures 6 and 7, changes in the magnetic flux density due to tempering of these two alloys follow different trends. For the C-steel, magnetic flux density decreases with respect to the untempered state for almost all tempering times and temperatures. Only the specimen tempered for 35 minutes at 500 °C showed a higher magnetic induction with respect to the untempered state. In contrast, the (C+N)-steel showed an almost constant increase in the magnetic flux density as the tempering time and temperature increased.

![Figure 6. Magnetic flux density as a function of cumulative tempering time for the (C+N)- and the C-stainless steels.](image)

According to the literature data, tempering of binary \( \text{Fe}-\text{C} \) [3] and high-alloy C-containing [7] martensitic steels leads to the precipitation of transition \( \varepsilon/\eta \) carbides between 80 °C and 200 °C followed by their conversion into cementite between 260 °C and 350 °C. According to Table 3, magnetic moment of the carbides is always lower than that of iron. At low tempering temperatures, carbides form under paraequilibrium condition, a thermodynamic condition in which only interstitial alloying elements have sufficient mobility to equilibrate their chemical potential across a moving interface. Nevertheless, due to the limited diffusivity of substitutional elements, the chemical potential of substitutional alloying elements may remain unequal across the transformation front. As a result, low-temperature tempering precipitates formed in the C-steel used in this study will inherit the Cr concentration of the martensitic matrix, i.e. they will also contain
almost 13 wt% Cr. The Curie temperature of hcp ε-Fe₃C carbide and orthorhombic 0-Fe₃C carbide in binary Fe-C alloys are approximately 380 °C and 215 °C, respectively [24]. For the cementite, this amount of Cr is sufficient to depress its Curie temperature to below room temperature and a similar shift to lower temperatures is expected for the Curie temperature of transition carbides. Nevertheless, the higher Curie temperature of transition carbides means that a higher amount of Cr would be needed in order to make these carbides paramagnetic at room temperature. Therefore, apart from the possible changes in the magnetic moment of the martensitic matrix upon the formation of tempering carbides, a larger reduction in the magnetic flux density is expected for the C-steel when tempering is associated with the cementite formation than when epsilon carbides form. This seems to be responsible for the small decrease in the magnetic flux density of the C-steel upon tempering at temperatures up to 200 °C as well as after short holding times at 250 °C and 300 °C. A holding time of 35 minutes at 250 °C, holding times in excess of 2 minutes at 300 °C, and all holding times at 350 °C seem to have led to completion of M₆C formation under paraequilibrium conditions.

After completion of the M₆C formation at 350 °C, a gradual increase occurs in the magnetic flux density of the C-steel as the tempering temperature increases to 500 °C. Possible reasons for this increase are the changes in the composition, lattice parameter, and valence electron density of the martensitic matrix due to the recovery of martensite. Alternatively, this may have been caused by the changes in the chemical composition of the existing M₆C carbides due to the removal of the paraequilibrium constraint. For instance, a reduction in the Cr content of cementite may have turned it ferromagnetic leading to a higher magnetic flux density. In this case, the concurrent decrease in the magnetic moment of the martensitic matrix due to its Cr enrichment should have been of secondary importance.

Prolonged tempering at 500 °C which enables Cr diffusion even in the austenite phase leads to the formation of Cr-rich stable carbides, most likely M₆C₃ and M₂₃C₆, in the microstructure. This raises the Ms temperature of retained austenite and the fresh martensite formation in the subsequent cooling step increases the magnetic flux density. Dilatometry studies confirmed this for the C-steel tempered 35 minutes at 500 °C.

Another factor which can increase the magnetic flux density of high carbon martensitic stainless steels after tempering at temperatures where the Cr-rich precipitates such as M₆C₃ and M₂₃C₆ replace the cementite is the reduced solute Cr content of the martensitic matrix. Addition of Cr in concentrations up to 40 at%Cr has been found to almost linearly decrease the magnetic moment of iron from 2.22 μB/atom for pure iron to almost 1.23 μB/atom for an Fe₀.9Cr₀.1 alloy [13]. Cr-depletion of martensite upon formation of Cr-rich precipitates will then increase the magnetic flux density.

In contrast to the C-steel, tempering of the (C+N)-steel was invariably associated with an increase in the magnetic flux density which implies a difference in the type of tempering precipitates formed in this alloy. According to Berns et al. [7], ε-carbides and ε-nitrides form upon low-temperature tempering of (C+N)-containing martensitic stainless steels. Magnetic moment of the ε-Fe₃N phase is very low in comparison with α-iron (Table 3) and it might even be paramagnetic due to the presence of about 15%Cr and 1%Mo in the (C+N)-steel. Formation of this phase as the only type of nitride at 200 °C therefore seems unlikely. The α′′- and γ'-nitrides, on the other hand, possess a high magnetic moment and their high Curie temperature makes it very likely that they remain ferromagnetic even after dissolving the nominal Cr and Mo content of the alloy. The observed increase in the magnetic flux density of the (C+N)-steel might therefore be related to the precipitation of these phases.

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**Figure 7.** Magnetic flux density as a function of tempering temperature for the (C+N)- and the C-stainless steels (reproduced from Figure 6). Average initial martensite contents for the (C+N)- and the C-steels specimens were 46% and 96%, respectively. Vertical axis shows values after normalization with respect to the magnetic flux density of the initial (γ+fresh α′) microstructure.
Nevertheless, the possible formation of other types of carbides and nitrides and a change in the magnetic properties of the martensitic matrix due to changes in the number of valence electrons and in the atomic volume of martensite cannot be excluded.

By analogy with the C-steel, tempering at 500 °C might have led to the formation of equilibrium Cr-rich carbides and nitrides in both martensite and austenite phases. Clearly, magnetic flux density is then influenced by the type and magnetic properties of such precipitates whose formation becomes possible at temperatures where the substitutional diffusion becomes significant. Besides, these precipitation reactions can influence magnetic flux density by altering the solute Cr concentration of the alloy and by the formation of fresh martensite during cooling from the tempering temperature. No clear dilatometry indication for the latter process was found during cooling to room temperature of a dilatometry specimen of the (C+N)-steel after 45 minutes of tempering at 500 °C. This observation is in agreement with the well-known effect of nitrogen on the deceleration of precipitation reactions in interstitially-alloyed austenitic stainless steels [18].

3.4. Hardness test

Effect of tempering on the hardness of the Cronidur® 30 alloy is shown in Figure 8. Tempering at 150 °C caused a slight increase in the hardness with respect to the untempered state. This initial hardening is very likely related to the processes leading to the first minimum in the dilatometry derivative curve of Figure 5 and the slight increase in the magnetic flux density after tempering at 150 °C and after a two-minute tempering at 200 °C (see Figures 6 and 7). The increased hardness at 150 °C is therefore thought to be due to the formation of coherent transition carbides and nitrides. It should be noted that, at least as long as tempering reactions are involved, short holding time at a given temperature has the same effect as prolonged holding at a higher temperature. This has been demonstrated by dilatometry heating of an AISI 420-type martensitic stainless steel at various heating rates where the tempering contractions corresponding to the formation of transition and stable carbides displaced to lower temperatures as the heating rate decreased [19]. A temperature shift is therefore required to make the dilatometry curve during continuous heating of Figure 5 (heating rate of 0.5 °C/s) comparable with the magnetic saturation and hardness results.

![Figure 8. Hardness of Cronidur® 30 as a function of tempering temperature. Initial martensite content of each specimen was approximately 54%. Cumulative tempering time at each temperature was 35 minutes.](image)

The subsequent decrease of the hardness might be due to the coarsening of transition phases attended by a reduction of coherency strains [3]. The softening behavior at temperatures up to 350 °C could also have been caused by changes in the type and fraction of precipitates. Evidence for such microstructural changes is the decrease in the instantaneous CTE beginning at almost 300 °C (see Figure 5).

Above 350 °C, the hardness starts to increase and reaches a maximum at 500 °C. This secondary hardening is almost always observed during tempering of high-nitrogen martensitic steels in the temperature range of 450-500 °C, regardless of the chemical composition [25]. Using small-angle neutron and X-ray scattering studies, Ojima et al. [25] observed the formation of N-enriched regions at the secondary hardness peak of an Fe-16Cr-1.1Mo-0.2V-0.1C-0.6N alloy, without commenting on the type of precipitates. The enhanced hardness was attributed to the shearing of N-enriched regions and/or interactions between dislocations and stress fields around the N-enriched regions.

Comparison of the hardness and dilatometry results suggests that there is a correlation between the hardness increase at and above 400 °C and the microstructural changes which lead to the decrease in the instantaneous CTE beginning at almost 430 °C during continuous heating at a rate of 0.5 °C/s. A similar decrease in the instantaneous CTE has been observed to begin at approximately 400 °C during continuous heating of a nitrogen-containing Fe-10Cr alloy at a rate of 50 °C/hr (0.014 °C/s) [9]. Identification of the mechanism

<table>
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<tr>
<td>Magnetic moments for nitride and carbides [13 and 24]</td>
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<tr>
<td>Phase</td>
</tr>
<tr>
<td>Magnetic moment (μₚ/Fe atom)</td>
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behind the above-mentioned decrease in the CTE can help clarify the secondary hardening of high N martensitic stainless steels.

Tempering at 600 °C caused significant softening in spite of the formation of some fresh martensite in the cooling step. The softening is thought to be related to the formation of equilibrium chromium carbides and nitrides in both martensite and austenite and the significant recovery of martensite. Furthermore, the fresh martensite formed in the cooling step has a low interstitial content and is therefore softer than the original martensite.

4. Conclusions

Low temperature tempering reactions in a Fe-15.5Cr-1Mo-0.3C-0.38N martensitic-austenitic stainless steel were studied in the temperature range of 150-500 °C. The following conclusions were drawn:

1. Increasing the solution annealing temperature from 900 °C to 1150 °C reduced the M, temperature from 325 °C to RT so that a fully austenitic alloy was achieved at RT. Further cooling to -196 °C of the austenite phase then led to the formation of 45% virgin martensite, i.e. martensite without auto-tempering. This microstructure serves as a good starting microstructure for the study of tempering reactions.

2. Continuous dilatometry heating up to 550 °C of the alloy indicated the occurrence of three reactions associated with a length contraction. These contractions became noticeable only after differentiation of the dilatation data with respect to temperature. In the derivative curves obtained in this manner, any reaction associated with a length change will lead to the deviation of the derivative curve from the expected temperature dependent CTE of the alloy. During continuous heating at a rate of 0.5 °C/s, the first contraction, likely corresponding to the formation of transition carbides and nitrides, was found to begin at 70 °C. The second contraction started at 300 °C and is thought to be related to the formation of more stable paraequilibrium carbides and nitrides. The third contraction beginning at almost 430 °C is thought to be due to a mechanism which simultaneously leads to the secondary hardening of the alloy.

3. Magnetic surveys indicate that the magnetic flux density of the steel initially increases after two minutes of tempering at 150 and 200 °C, consistent with the high magnetic moment and high Curie temperature of transition nitrides and carbides. The subsequent decrease in the magnetic flux density could be related to the formation of precipitates with a lower magnetic moment. Higher tempering temperature caused a continuous increase in the magnetic flux density. This behavior differs from that of N-free high carbon martensitic stainless steel where the initial formation of paraequilibrium ferromagnetic transition carbides causes a slight decrease in the magnetic flux density. This slight decrease is followed at higher temperatures by a sharp decrease in the magnetic flux density as transition carbides are replaced by paramagnetic M_C-type precipitates formed under paraequilibrium conditions.

5. References


