Original Article

Developing high-strength, ductile Ni-free Fe–Cr–Mn–C–N stainless steels by interstitial-alloying and thermomechanical processing

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ABSTRACT

Microstructures and mechanical properties of a new grade of Fe–18Cr–12Mn–CN (wt%) austenitic stainless steels interstitial-alloyed with 0.3–0.48 wt% C+N at 0.22–1.06 C/N ratios were investigated after thermomechanical processing. Appropriate thermomechanical treatment was designed to obtain good combination of strength and elongation. The developed steel possessed ultimate tensile strength of 1 GPa, yield strength of 450 MPa, and elongation up to 83%. It was found that strength and ductility of the studied steels were affected by strain-hardening behavior and decreasing the strain-hardening rate resulted in lower ultimate tensile strength. Addition of C to N-containing Ni-free steels deteriorated mechanical properties. The best combination of strength and elongation was obtained in steel with lowest C+N (0.3 wt%) and C/N ratio (0.22).

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1. Introduction

Austenitic stainless steels (ASSs) are frequently utilized in many industries because of their easy processing, suitable mechanical properties, high corrosion resistance and adequate biocompatibility [1,2]. Due to the high cost of nickel and the well-known probability of causing allergies in the human body, Ni-free high N ASSs with better strength, ductility, and corrosion resistance are believed to be a suitable alternate for the conventional CrNi ASSs which are extensively utilized in orthopedic implants [3].

Although N enhances the strength and ductility of these steels but deteriorates toughness at low temperatures [4]. N also has low solubility in molten iron and increases production problems by utilizing the high pressure metallurgy [5]. To solve these problems, recently a new alloying system is introduced in which C is used as austenite stabilizer in associated with N to obtain excellent properties in economic way [6]. Fe–Cr–Mn–C–N stainless steels alloyed with C+N, investigated by several authors [7–9]. The new stainless steels have shown higher strength, ductility and impact toughness in comparison to the conventional CrNi stainless steels [6,7], elongated fatigue life [10], and better corrosion resistance [9].
The synergetic influence of C + N alloying has been introduced as responsible to improved properties [10]. It is reported that stabilizing the austenite with C + N may enhance concentration of free electrons compared to alloying solely with N and promotes metallic nature of inter-atomic bonding and short range ordering rather than atomic clustering [11]. This could lead to strengthening the binding between stagnant interstitial atoms and dislocations, and consequently higher strength, ductility and impact toughness [6,11]. The replacement of Ni by Mn results in a higher interstitial solubility of C and N [12]. Simultaneous alloying by C and N increases the solubility of N and reduces the production difficulties [16].

It is clearly evident that addition of C + N has strong effect on crystal lattice parameter of austenite and among the alloying elements C and N have most effect on yield strength [14]. In most studies the C and N content up to 1 wt% is used to influence strength but this amount of C + N retards strain-induced δ-martensite transformation. The effect of C + N on ASSs at amounts greater than 0.5 wt% is investigated by several authors but there is a few studies at low level of C + N (below 0.5 wt%). Also there is a limited investigation on the effect of C/N ratio on properties of developed steels. In this work, microstructures and mechanical properties of metastable ASSs containing different amounts of C + N (less than ~0.50 wt%) are investigated and the effects of C + N and C/N ratio on microstructure, deformation mechanism, mechanical properties and strain hardening behavior is studied.

2. Chemical composition design

At least 12 wt% Cr is required for corrosion resistance properties in ASS and generally chemical composition of ASS composed of 18 wt% Cr [15]. In design a Ni-free ASS, considering Cr content equal to 18 wt%, the next step is selection of austenite stabilizing elements i.e. Mn, N and C and their concentration in the alloy in order to maintain the austenitic structure to room temperature. These elements strongly affect mechanical and corrosion properties by influencing on stacking fault energy (SFE), deformation mechanisms and precipitations [16,17]. Since low SFE (lower than 15 mJ/m²) enhances the formation of strain-induced δ-martensite in the course of deformation and activates the TRIP mechanism, the amount of these alloying elements should be selected so that prevent from increasing the SFE. It is shown that SFE in Fe–Mn phase system reaches to its minimum at 12 wt% Mn [18]. Therefore the Mn content of alloying system was selected to be 12 wt%. When Cr content is above 13 wt%, it is necessary to utilize other austenite stabilizing element besides Mn [19]. Generally C and N are utilized as austenite stabilizing elements. In a study by Lee et al. on Fe–18Cr–10Mn–(N or N + C) alloys, a linear relation was found between the SFE and C + N [20]. It is shown that at SFES below 15 mJ/m² the prominent deformation mechanism is TRIP. By increasing the interstitial-alloying elements and increasing the SFE (SFE ≈ 15–20 mJ/m²), correspondingly, deformation mechanism changes to mixed mode of TWIP and TRIP and at SFES above 20 mJ/m², TWIP is the governing mechanism. Therefore C + N content must be selected so that SFE remains as low as possible to minimize SFE and austenitic structure is provided simultaneously. Considering Cr content equal to 18 wt% and using the approach proposed by Hsiao [21] to calculate the minimum C + N required for obtaining full austenitic structure in alloys, at least 0.43 wt% C + N is required to obtain a fully austenitic structure.

To determine the proper C + N range and C/N ratio, thermodynamic calculations by Thermo-Calc using TCFE7 database in temperature range of 673–1873 K (400–1600 °C) were performed to investigate austenite stability and phase fractions. Fig. 1 shows equilibrium phase diagrams as a function of C wt% by varying N. It can be seen that by increasing C + N, austenite stability region expands and ferrite stability region shrinks. Also by increasing C content, precipitation temperature of M23C6 carbides shifts to higher temperatures. Same trends can be seen in precipitation temperature of M2N nitrides by increasing N content. Regarding to phase diagrams, maximum C + N of 0.5 wt% at two levels of C/N ratio (0.25 and 1) was selected for chemical composition of steels. Finally, chemical composition of steels was selected as Fe–18Cr–12Mn–X(C, N).

3. Material and methods

The steel samples were prepared in a 10 kg vacuum induction melting furnace with N atmosphere under the partial pressure of 100–300 mbar depending on the required N content followed by electro-slag remelting technique to purify the ingots. Chemical composition of the samples is shown in Table 1. The alloy concentrations were measured by optical emission spectroscopy (OES). The first and second numbers in coding the samples is illustration of C and N content, respectively.

Formation of precipitates in ASSs deteriorates mechanical and corrosion properties. The most common precipitate in ASSs is M23C6 and in high nitrogen ASSs, M2N that precipitate at grain boundaries [22]. Therefore, in order to prevent from precipitation of nitrides and carbides, deformation temperature should be selected appropriately. Based on Thermo-Calc calculations, temperature of 1273 K (1000 °C) was selected for hot rolling temperature. At 1273 K in all test materials the only stable phase is austenite and thermodynamically, the probability of precipitates formation is very low.

The formation of precipitates from kinetics point of view was also investigated using the approach suggested by Dai [23]. It was found that if deformation is occurred at temperature of 1273 K (1000 °C) and above, kinetically, the formation time of precipitates is long enough for deformation of steels.

The as-cast ingots were cut into specimens with size of 30(width) × 15(thickness) × 70(length) mm ground blocks. The homogenization of specimens was performed at 1473 K (1200 °C) for 5 h followed by water-quenching. Multi-pass hot rolling was conducted in a single stand rolling mill at 1273 K (1000 °C) to convert the specimens to sheets of 1.2 mm thickness. Followed by rolling, specimens were water-quenched to avert nitride/carbide precipitation. In order to eliminate the share of dislocation hardening mechanism to strength, samples were annealed at 1273 K (1000 °C) for 1 h followed by water-quenching.

The X-ray diffraction (XRD; Phillips Expert (MPD) equipment) with Cu-Kα radiation at room temperature in the angle range of 30–120 was used to study of microstructures
of the samples. The Volume percentage of strain-induced ε-martensite was determined using a Ferritescope (model FMP30, Helmut Fischer GmbH). To calibrate the measurement of ε-martensite in ASSs, the Ferritescope readings are converted to the actual martensite contents using a calibration curve. In the present study, the actual ε-martensite values were calculated by the following equation [24]:

\[
\text{ε-martensite content} = 1.71 \times \text{Ferritescope reading}
\]  

(1)

The microstructure of samples was studied by a Nikon optical microscope (LV100ND). The specimens were first mechanically polished followed by electrolytic polishing in a solution containing 25 g CrO₃, 133 ml acetic acid and 7 ml water at temperature range of 17–19 °C and at an operating voltage of 20–22 V for 4–6 min. Then, specimens were electro-etched by lowering the voltage to 2 V. Tensile test specimens were machined from the samples based on the ASTM E8 standard technique with the 25 mm gauge length at rolling direction. An Instron tensile testing machine was utilized to perform the uniaxial tensile tests (three times for each test material) at 298 K (25 °C) with the engineering strain rate of 0.001 s⁻¹.

C13-N17 sample with C+N of 0.30 wt% has maximum δ-ferrite content and C23-N25 with C+N of 0.48 wt% has no δ-ferrite content. Austenite stability can be discussed from three points of view: C/N ratio, precipitates and SFE. Based on the Thermo-Calc calculations, the fully-austenitic structure in the designed steels is between 900 and 1200 °C and the stability region grows by increasing C+N. It was found that by decreasing the C+N, δ-ferrite phase fraction increases and temperature of formation shifts to lower temperatures. Therefore increasing C+N increases austenite stability. In addition, the austenite stability is influenced by carbides and nitrides. By decreasing the C/N ratio, formation of carbides occurs at lower temperatures and transient region to Mₗ(C, N) becomes narrower. Calculations also showed that increasing C/N ratio leads to increasing volume fraction of carbides and in some steels this fraction is higher than MₗN volume fraction.

Fig. 2 shows OM micrographs of investigated steels after hot rolling and annealing. A recrystallized microstructure can be seen in all samples. The annealing twins, as the characteristic aspect of the low-SFE alloys, were readily observed within some grains.

Table 2 shows mean grain size of investigated steels. In samples with lower C+N amount, grain size was smaller. Generally average grain size of samples with C+N greater than 0.4 wt% was higher than samples with lower C+N. This can be related to SFE of steels. In fact, keeping all others variables constant, the lower is the SFE, the larger will be the stored energy during deformation and the corresponding driving force for recrystallization. Therefore, the final grain size of steels with lower SFE will be finer. In samples with higher C+N and higher C/N ratio, SFE is higher, therefore during hot rolling recovery of

### Table 1 – Chemical composition of the investigated steels (in wt%)

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Cr</th>
<th>Mn</th>
<th>C</th>
<th>N</th>
<th>Mo</th>
<th>Si</th>
<th>Fe</th>
<th>C+N</th>
<th>C/N</th>
</tr>
</thead>
<tbody>
<tr>
<td>C23-N25</td>
<td>16.00</td>
<td>10.10</td>
<td>0.23</td>
<td>0.250</td>
<td>0.010</td>
<td>0.33</td>
<td>Base</td>
<td>0.48</td>
<td>0.92</td>
</tr>
<tr>
<td>C22-N21</td>
<td>17.00</td>
<td>11.00</td>
<td>0.22</td>
<td>0.205</td>
<td>0.004</td>
<td>0.4</td>
<td>Base</td>
<td>0.43</td>
<td>1.07</td>
</tr>
<tr>
<td>C10-N30</td>
<td>17.20</td>
<td>10.80</td>
<td>0.10</td>
<td>0.305</td>
<td>0.004</td>
<td>0.35</td>
<td>Base</td>
<td>0.40</td>
<td>0.33</td>
</tr>
<tr>
<td>C06-N27</td>
<td>17.10</td>
<td>11.30</td>
<td>0.06</td>
<td>0.275</td>
<td>0.004</td>
<td>0.27</td>
<td>Base</td>
<td>0.33</td>
<td>0.22</td>
</tr>
<tr>
<td>C08-N24</td>
<td>17.10</td>
<td>11.40</td>
<td>0.08</td>
<td>0.245</td>
<td>0.004</td>
<td>0.36</td>
<td>Base</td>
<td>0.32</td>
<td>0.33</td>
</tr>
<tr>
<td>C13-N17</td>
<td>17.60</td>
<td>12.00</td>
<td>0.13</td>
<td>0.170</td>
<td>0.003</td>
<td>0.32</td>
<td>Base</td>
<td>0.30</td>
<td>0.76</td>
</tr>
</tbody>
</table>

4. Results and discussion

Similar dendritic microstructure was seen in all samples in the as-cast condition. The only difference was the formation of δ-ferrite in test materials with low amount of C+N. Table 2 shows δ-ferrite content of samples measured by Ferritescope.
dislocations occurs easily and leads to coarser microstructure after annealing [25]. The SFE of steels was calculated using Eq. (2) obtained by Lee et al. [20] and listed in Table 2:

\[
SFE = -5.79 + 39.94(C + N) + 3.81(C/N)
\]  

(2)

The XRD pattern of the samples showed that, except for C13–N17 sample, a fully-austenitic structure is formed. In C13–N17 sample (with C/N = 0.76 and C + N = 0.3 wt%) some δ-ferrite was also formed. The δ-ferrite content was measured by Ferritescope and was about 5.2 vol.%. In this sample annealing temperature was close to the formation temperature of δ-ferrite. Therefore, some δ-ferrite was formed. C08–N24 sample also has C + N of 0.32 wt% but at these samples no δ-ferrite was formed. This can be related to differences of C/N ratio in samples. In fact, at the same C + N level, by increasing the C/N ratio, the stability of austenite is decreased.

Fig. 3 shows the true stress–strain and engineering stress–strain curves of all test materials. Relatively, stress–strain curves of samples follow a similar regime. The yield strength of all test materials was almost equal and was about 450MPa. The UTS of steels was very high and varied between 900 and 1000MPa. All steels showed considerable elongation to fracture which was varied between 75 and 83% in different test materials. It can be seen all test materials showed excellent combination of strength and ductility. Best combination of mechanical properties was found in C06–N27 material (C + N = 0.33 wt% and C/N = 0.22).

To investigate the effect of C/N ratio and C + N on strength and ductility, the variation of elongation and ultimate tensile strength (UTS) of steels were plotted as a function of C + N and C/N ratio in Fig. 4(a) and (b) and Fig. 4(c) and (d), respectively. It can be seen by increasing C/N and C + N elongation was decreased. Noticing Fig. 4(a), it seems that by increasing C + N elongation firstly increases then decreases. But noticing the C + N content of materials, it was revealed that C + N content of first three test materials in diagram was very close together and was about 0.3 wt%. Therefore observed variation in elongation was related to effect of C/N ratio on elongation (Fig. 4(c)). With some little differences same trend can be found in the effect of C + N and C/N ratio on UTS of test materials i.e. by increasing C/N and C + N, UTS was decreased. It can

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>C/N</th>
<th>C + N wt%</th>
<th>δ-ferrite vol. %</th>
<th>Δ-Martensite after tensile (vol.%)</th>
<th>Mean grain size (µm)</th>
<th>δ-Ferrite of as-cast samples (vol.%)</th>
<th>Calculated SFE (mJ/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C23-N25</td>
<td>0.32</td>
<td>0.36</td>
<td>0</td>
<td>4.6</td>
<td>40 ± 3</td>
<td>0</td>
<td>17</td>
</tr>
<tr>
<td>C22-N21</td>
<td>0.33</td>
<td>0.38</td>
<td>0.3</td>
<td>7.9</td>
<td>59 ± 4</td>
<td>0.3</td>
<td>15</td>
</tr>
<tr>
<td>C10-N30</td>
<td>0.34</td>
<td>0.39</td>
<td>1.7</td>
<td>10.9</td>
<td>39 ± 5</td>
<td>1.7</td>
<td>12</td>
</tr>
<tr>
<td>C06-N27</td>
<td>0.35</td>
<td>0.40</td>
<td>5.1</td>
<td>21.8</td>
<td>30 ± 6</td>
<td>5.1</td>
<td>8</td>
</tr>
<tr>
<td>C08-N24</td>
<td>0.36</td>
<td>0.41</td>
<td>7.5</td>
<td>25.5</td>
<td>25 ± 8</td>
<td>7.5</td>
<td>8</td>
</tr>
<tr>
<td>C13-N17</td>
<td>0.37</td>
<td>0.42</td>
<td>10.6</td>
<td>22.7</td>
<td>23 ± 10</td>
<td>10.6</td>
<td>9</td>
</tr>
<tr>
<td>C10-N30</td>
<td>0.38</td>
<td>0.43</td>
<td>0</td>
<td>4.6</td>
<td>40 ± 3</td>
<td>0</td>
<td>17</td>
</tr>
<tr>
<td>C22-N21</td>
<td>0.39</td>
<td>0.44</td>
<td>0.3</td>
<td>7.9</td>
<td>59 ± 4</td>
<td>0.3</td>
<td>15</td>
</tr>
<tr>
<td>C10-N30</td>
<td>0.40</td>
<td>0.45</td>
<td>1.7</td>
<td>10.9</td>
<td>39 ± 5</td>
<td>1.7</td>
<td>12</td>
</tr>
<tr>
<td>C06-N27</td>
<td>0.41</td>
<td>0.46</td>
<td>5.1</td>
<td>21.8</td>
<td>30 ± 6</td>
<td>5.1</td>
<td>8</td>
</tr>
<tr>
<td>C08-N24</td>
<td>0.42</td>
<td>0.47</td>
<td>7.5</td>
<td>25.5</td>
<td>25 ± 8</td>
<td>7.5</td>
<td>8</td>
</tr>
<tr>
<td>C13-N17</td>
<td>0.43</td>
<td>0.48</td>
<td>10.6</td>
<td>22.7</td>
<td>23 ± 10</td>
<td>10.6</td>
<td>9</td>
</tr>
</tbody>
</table>
be concluded that C has detrimental effects on mechanical properties of test materials. Also by increasing the C+N the stability of austenite increased.

Table 2 shows the α-martensite content of test materials after tensile testing. The results of tensile tests and phase identification showed the direct connection between mechanical behavior of the steels and strain-induced α-martensitic transformation.

The variation of strain-hardening rate (SHR) as a function of true strain is drawn in Fig. 5, to study the role of α-martensite phase in mechanical response. The SHR curves of test materials had same trend at strains below 0.4. At strains above 0.4, SHR curves of low C+N steels (with C+N ~ 0.3 wt%) showed higher values compared to steel with C+N above 0.4 wt%. SHR of low C+N steels showed a multistage behavior with rapid increase in SHR at strain of ~0.5.

The strain hardening sequence of test materials may be divided in four stages as illustrated in Fig. 5. At stage I that was occurred at small strains below 0.1, a sharply falling of the hardening rate was observed. At this stage the minimum SHR was below 1700 MPa. The minimum SHR in stage I was followed by mild increase of SHR at stage II and reaches to
about 2500 MPa at the true strain of 0.45. The third stage begins at the strain of 0.45, with increasing SHR that reaches to value of 3000 MPa at the true strain of about 0.7.

Different mechanisms such as deformation twinning [26,27], deformation-induced martensitic transformation [28,29] and planar dislocation glide [30] have been suggested for the different hardening stages. Talonen showed that minimum SHR depends on deformation temperature and amount of martensitic transformation [24]. Lowest SHR were found at the lowest deformation temperatures where the kinetics of a-martensite phase transformation is the highest. Sharply falling of SHR at stage I has been related to the fast formation of e-martensite [31]. But Talonen believes that this is in conflict with elementary dislocation theory [24]. The formation of e-martensite is directly interlinked to the formation of stacking faults and Shockly partial dislocations which are not able to cross slip. Moreover, the e-martensite and stacking faults should operate as barriers for the slip instead of enhancing it. Therefore, the formation of e-martensite and stacking faults should increase SHR rather than decrease it. Suzuki [32] by in situ TEM study on AISI 304 steel suggested that low SHR is related to a-martensite nucleation at the junctions of shear bands. In this mechanism two shear bands which may lock each other, can intersect easily. In more generally terms, it has been suggested that nucleation of a-martensite brings dynamic softening as a result of a-martensite transformation strain [33]. The shift from stage I to stage II corresponds to increase of SHR from the minimum point. Therefore by starting the stage II, strengthening effect of a-martensite phase dominates in strain hardening process. Talonen suggested two mechanisms for increasing effect of a-martensite on strain hardening [24]. When volume fraction of a-martensite is lower than a threshold level, the microstructure is composed of hard a-martensite clusters at soft austenite matrix that leads to non-homogeneous deformation and results in enhanced generation of dislocations in austenite. Intensification of dislocation generation leads to increase in the flow stress and SHR. At stage III when the volume fraction of a-martensite exceed a threshold level, percolating cluster of a-martensite forms which is extended thorough the whole aggregate, leading to further increase in SHR. After a threshold level, flow stress is not dependent only on dislocations density [24]. In this stage, the plastic deformation of aggregate cannot totally be accommodated by austenite plasticity and a-martensite must also deform. Due to high strength and high dislocation density of a-martensite compared to austenite, it is reasonable that external load required for deformation is increased steeply. Furthermore, by increasing the volume fraction of a-martensite, the strength of a-martensite clusters increases and therefore SHR increases by increasing the amount of a-martensite [34]. At stage IV, SHR begins to decrease. Controlling parameters of deformation of aggregate at this stage are plasticity and recovery of a-martensite phase, and behavior of aggregate is similar to a single phase material [24]. Therefore SHR begins to decrease. This stage depends on amount of a-martensite and when only little a-martensite is formed, the stage IV does not occurs at all due to occurring plastic instability before decreasing SHR [24].

Noticing the SHR curves of samples it can be found that in test materials with C+N higher than 0.4 wt%, stage III which is corresponding to rapid increase of SHR was not occurred. This means that in these steels, amount of strain-induced a-martensite was below the threshold level. It can be seen in Table 2 that maximum 10 vol.% a-martensite was formed at these materials. Therefore, the formation of a-martensite has considerable effect on mechanical properties of steels such that in test materials with exhibition of all stage of SHR, excellent mechanical properties were obtained. The formation of a-martensite depends on SFE of steel [20,35]. It can be seen from calculated SFE for studied test materials in Table 2 that in samples with C + N = 0.3 wt%, SFE is lower compared to samples with C+N higher than 0.4 wt%. Relation between SFE and deformation mechanisms in interstitially-alloyed ASSs is studied by Lee et al. [20]. The results of the present study have good agreement with those obtained by Lee.

5. Conclusions

- High-strength up to 1 GPa with high ductility up to 83% can be obtained by alloying the Ni-free ASSs with C+N.
- Elongation and UTS decreases by increasing C/N ratio and C+N content. Therefore in comparison to alloying with N, C has detrimental effects on mechanical properties.
- In constant level of C+N, by decreasing the C/N ratio (decreasing C), strain-induced a-martensitic transformation is retarded. C postpones TRIP effect by increasing SFE and stability of austenite.
- The UTS and ductility of the investigated steels is affected by strain-hardening behavior. Decrease in the SHR resulted in a lower UTS. The shift of the strain-hardening peaks to the higher strains improved the ductility.
- Addition of C to N containing Ni-free steels deteriorated mechanical properties by retardation of the strain-induced \( \alpha \)-martensite phase transformation. Best results were obtained in test material with the lowest C + N and C/N ratio.

**Conflicts of interest**

The authors declare no conflicts of interest.

**Uncited references**

[13].

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