Effect of Manganese on Microstructure and Mechanical Properties of Cast High Alloiyed CrMnNi-N Steels**

By Marco Wendler,* Andreas Weiβ, Lutz Krüger, Javad Mola, Armin Franke, Alexander Kovalev and Steffen Wolf

Within the Collaborative Research Center 799 novel composite materials which consist of a highly alloyed TRansformation-Induced Plasticity/Twinning-Induced Plasticity (TRIP/TWIP) CrMnNi cast steel matrix and a partially stabilized zirconium dioxide (Mg-PSZ) ceramic, referred to as TRIP-Matrix-Composites, are developed.[1] By applying an external load larger than the yield strength, the TRIP steel matrix shows a strain-induced phase transformation from metastable austenite to \( \alpha' \)-martensite which leads to a concurrent increase of strength and ductility. By contrast, stress-induced formation of \( \alpha' \)-martensite occurs at stresses below the yield strength, i.e., during elastic deformation.[2] The stress-induced transformation of the partially stabilized ZrO\(_2\) from tetragonal phase to monoclinic modification can result in a further increase of the strength. Currently the interstitial-free austenitic CrMnNi cast stainless steels with TRIP/TWIP effect are in use. Representative alloys are 16Cr–7Mn–3Ni, 16Cr–7Mn–6Ni, and 16Cr–7Mn–9Ni.[3,4] These austenitic steel grades typically show low yield strengths of the order of 180–200 MPa. As a result of the low stress levels, only small fractions of the ceramic phase can transform to the monoclinic structure. In order to assist the phase transformation of the ceramic phase from tetragonal to monoclinic, the current steel research in the CRC 799 is focused on the increase of strength, especially the yield strength of the austenitic TRIP/TWIP CrMnNi cast steels by solid solution strengthening due to the addition of nitrogen and manganese as well as phase hardening by as-quenched martensite.

The effect of the manganese content (0–11%) on the transformation temperatures, the mechanical properties and microstructure development of five highly alloyed 14Cr–X Mn–6Ni cast stainless steels with 0.1% nitrogen was studied. The examinations reveal that the \( M_s, A_s, \) and \( A_f \) temperatures decrease with increasing manganese contents. As a result of low austenite stability, room temperature austenitic-martensitic as-cast microstructure was formed at manganese contents between 0 and 3%. At manganese levels of 6% and higher a fully austenitic as-cast microstructure was observed. The temperature dependence of tensile properties in alloys was explained on the basis of varying contributions to the strength and ductility of deformation-induced martensite and twin formation mechanisms. All investigated cast steel alloys achieved yield strengths above 200 MPa at room temperature. The increased proof stress is caused by solid solution strengthening due to the addition of nitrogen and manganese as well as phase hardening by as-quenched martensite.

Within the Collaborative Research Center 799 novel composite materials which consist of a highly alloyed TRIP/TWIP CrMnNi cast steel matrix and a partially stabilized zirconium dioxide (Mg-PSZ) ceramic, referred to as TRIP-Matrix-Composites, are developed.[1] By applying an external load larger than the yield strength, the TRIP steel matrix shows a strain-induced phase transformation from metastable austenite to \( \alpha' \)-martensite which leads to a concurrent increase of strength and ductility. By contrast, stress-induced formation of \( \alpha' \)-martensite occurs at stresses below the yield strength, i.e., during elastic deformation.[2] The stress-induced transformation of the partially stabilized ZrO\(_2\) from tetragonal phase to monoclinic modification can result in a further increase of the strength. Currently the interstitial-free austenitic CrMnNi cast stainless steels with TRIP/TWIP effect are in use. Representative alloys are 16Cr–7Mn–3Ni, 16Cr–7Mn–6Ni, and 16Cr–7Mn–9Ni.[3,4] These austenitic steel grades typically show low yield strengths of the order of 180–200 MPa. As a result of the low stress levels, only small fractions of the ceramic phase can transform to the monoclinic structure. In order to assist the phase transformation of the ceramic phase from tetragonal to monoclinic, the current steel research in the CRC 799 is focused on the increase of strength, especially the yield strength of the austenitic TRIP/TWIP CrMnNi cast steels by solid solution strengthening due to the addition of nitrogen and manganese as well as phase hardening by as-quenched martensite.

The longest known FeMnC steels are characterized by manganese contents between 15 and 30% and an austenitic...
microstructure. The FeMnC steels with low carbon mass contents of maximum 600 ppm and Al and Si contents between 2 and 4\%, exhibit excellent ductility with elongations up to 95\% combined with high tensile strengths up to 1100 MPa.[11,12] These impressive mechanical properties are due to the strain-induced microstructural changes under load.

Depending on the SFE, even a sequence of martensitic transformations in the form of $\gamma \rightarrow \varepsilon \rightarrow \alpha'$ could occur. Reduced austenite stability in TWIP or TRIP steels can be adjusted by low contents of the austenite stabilizing elements such as C, N, Ni, and Mn. The well-known Schaeffler diagram provides an opportunity for the description of the resistance such as C, N, Ni, and Mn. The well-known Schaeffler diagram provides an opportunity for the description of the resistance against the $\gamma \rightarrow \alpha'$ formation of high-alloy stainless steels. This constitutional diagram was originally developed for the prediction of the microstructure in high-alloy steels after welding. Nevertheless, it can also be used for characterization of the as-cast structure.[4] The austenite stability was calculated with the following Ni- and Cr-equivalent equations proposed by Weiß[13]:

$$\text{Ni}_{eq} = \%\text{Ni} + 30\%\text{C} + 18\%\text{N} + 0.5\%\text{Mn}$$
$$+ 0.3\%\text{Co} + 0.2\%\text{Cu} - 0.2\%\text{Al}$$

(1)

$$\text{Cr}_{eq} = \%\text{Cr} + \%\text{Mo} + 4\%\text{Ti} + 4\%\text{Al} + 1.5\%\text{Si}$$
$$+ 1.5\%\text{V} + 0.9\%\text{Nb} + 0.9\%\text{Ta} + 0.5\%\text{W}$$

(2)

The increase of the austenite stabilizing elements leads to an enhanced Ni-equivalent, thereby to a higher austenite stability.

Some investigations have treated the strengthening effects of increased carbon content in FeMnC steels. In the steel Fe–18Mn–0.6C–1.5Al which shows dynamic strain aging (DSA), a yield strength of above 400 MPa was achieved due to solid solution hardening by carbon.[14] Nevertheless, carbon contents over 1.2\% are not recommended because of the possibility of cementite precipitation in austenite.[7]

The development of novel corrosion resistant, high-manganese CrMnC TWIP steels is an active area of research. Besides the passivation effect imparted by Cr, alloying with chromium and manganese allows a higher solubility of nitrogen in the melt and thus the development of high-strength steels. Furthermore, with the increase of the austenite stabilizing elements Mn, Ni, C, and N the solidification mode changes from ferritic to austenitic. When the solidification of the melt proceeds austenitic, a higher nitrogen content can be dissolved. Gavriliuk et al.[15] examined the influence of an increased carbon plus nitrogen content, in a high-manganese TWIP steel. It has been shown that the alloy 19Cr–19Mn–0.49C–0.58N exhibits superior mechanical properties, e.g., a proof stress of 604 MPa, a tensile strength of 1075 MPa, and a fracture elongation of 80\% at a strain rate of $4 \times 10^{-4}$ s$^{-1}$. Due to the combined C + N alloying concept, the resistance to impact wear is comparable to that of the 12Mn–1.2C Hadfield steel. Moreover, values exceeding 400J were reached in the notch-impact test because of intensive twinning. Weber et al.[16] developed a high alloyed corrosion resistant hot rolled TWIP-steel (Fe–20Mn–12Cr–0.25C–0.3N) with a yield strength of 430 MPa, a tensile strength of 840 MPa, and a uniform elongation in excess of 90\%. Lee et al.[17] developed a deformation-induced plasticity steel grade with a nitrogen content of 0.5\% in a pressurized vacuum induction melting furnace. The chemical composition of their austenitic TWIP/(TRIP) steel was Fe–18Cr–10Mn–0.5N. Due to the occurrence of deformation-induced $\varepsilon$- and $\alpha'$-martensite transformations a yield strength of 449 MPa, a tensile strength of 952 MPa, and a uniform elongation of 60\% were obtained. Kim et al.[18] studied the influence of varying nitrogen contents on the deformation behavior of an Fe–18Cr–10Mn–N steel. It was shown that the deformation-induced martensite transformation and the deformation-induced twinning depended on the nitrogen content. The TRIP effect was reduced and finally suppressed by the increase of the nitrogen content which favored the TWIP effect. In the steel Fe–18Cr–10Mn–N only deformation-induced twinning occurred at nitrogen levels above 0.5\%.

The SFE in high-manganese hot rolled FeMnC and CrMnC steels with increased carbon content was thoroughly investigated. Allain et al.[19] found out that the $\gamma \rightarrow \varepsilon$ martensite transformation can occur during plastic deformation at SFE values below 18 mJ m$^{-2}$. For the mechanical twinning a range of the SFE between 12 and 35 mJ m$^{-2}$ was given. Hamada[20] and Vercaemmen[21] provided larger ranges of SFE for twinning, i.e., 25–60 mJ m$^{-2}$ and 15–80 mJ m$^{-2}$, respectively. Akbari et al.[22] developed SFE maps based on thermodynamic calculations for high-manganese contents (10–35 wt\% pct) and 0–1.2 wt\% pct carbon. The upper SFE limit for a strain-induced martensite transformation was defined at 20 mJ m$^{-2}$. Furthermore, the SFE increases due to a grain refinement of austenite, which restricts the martensitic transformation. Dumay et al.[9] examined the influence of the alloying elements Cu, Si, Al, and Cr on the steel Fe–22Mn–0.6C. It was shown that only Cr decreases the SFE. The largest increase of the SFE was achieved through Al followed by Cu and finally Si.

Recent investigations on high alloyed TRIP steels are focused on the system CrMnNi with additions of the main alloying elements C, N, Al, and Si which emerged from the considerations and findings of the research in the field of CrNi stainless steels.[23–26] Pozuelo et al.[27] studied the dominating temperature dependent deformation mechanisms of the TRIP/TWIP steel 16.5Cr–8Mn–3Ni–2Si–1Cu–0.25N–0.08Ti in the temperature range from –196 to 400 °C. A yield strength of 400 MPa, a tensile strength of 700 MPa and a fracture elongation in excess of 70\% was obtained for solution annealed steel at room temperature.

In the field of steel castings, however, reports on high plasticity steels are rather rare. Berns et al.[28] published results about the development of Fe–20Cr–18Mn–0.5C steels with an impressive nitrogen content of 0.6\%. An ingot without nitrogen porosity was achieved through centrifugal casting under atmospheric pressure. The solution annealed and quenched specimen exhibited a yield strength of 554 MPa, a tensile strength of 1040 MPa, and 58\% uniform elongation.
In this paper, the effect of Mn on the austenite start (\(A_s\)), austenite finish (\(A_f\)), and martensite start (\(M_s\)) temperatures as well as the microstructure and temperature dependent stress–strain behavior is investigated using new CrMnNi-N cast steels with 0.1% nitrogen and manganese contents between 0 and 11%. The low nitrogen content is intended to prevent the pore formation during the ferritic-austenitic solidification. The chemical composition is adjusted to ensure low austenite stabilities and SFEs compatible with the TRIP and TWIP effects. The requirement for the strain-induced \(\gamma \rightarrow \alpha'\) martensite transformation is the creation of metastable austenite, which is formed at Ni-equivalent values near the line which separates the austenite phase region and the austenite + martensite phase region at the corresponding Cr-equivalent in the Schaeffler diagram by Weiß.\(^{[13]}\) The well-known Schaeffler diagram has been used in the past for the prediction of the microstructure in high-alloy corrosion resistant CrMnNi steels.\(^{[4]}\) In order to trigger the TWIP effect it is further necessary to combine low austenite stabilities with relatively low stacking fault energies. Previous studies on CrMnNi cast steels have pointed out that deformation twins are formed when the SFE is in the range of 20–40 mJ m\(^{-2}\).\(^{[29]}\) At stacking fault energies below approximately 20 mJ m\(^{-2}\), the strain-induced \(\varepsilon\) martensite transformation is expected. The aim of this development is the creation of strengthened steel with a low delta ferrite content through the use of solid solution strengthening by nitrogen, phase strengthening by as-quenched \(\alpha'\)-martensite, and the increase of strain-hardening potential by TRIP and TWIP effects.

1. Experimental

1.1. Fabrication of the Cast Steels

The steels used in this study were melted in a vacuum induction furnace under a pressure of 800 mbar. Initially an argon partial pressure of 400 mbar was used to melt down the feedstock. Afterwards nitrogen gas with a partial pressure of 400 mbar was added for nitriding. The steels were subsequently cast into a water cooled copper mould placed in the furnace chamber. Two ingots of each melt with the dimensions of 220 × 50 × 50 mm\(^3\) were produced and then machined to round tensile specimens with a diameter of 6 mm. Because of the possibility of martensite formation during machining, heat treatments were performed after final machining of the tensile specimens. The chemical composition of produced steels is given in Table 1.

1.2. Heat Treatment and Tensile Test

The solution annealing was done in a vacuum furnace at 1050 °C for 30 min. Cooling to room temperature of tensile specimens was done by nitrogen gas flow into the furnace.

Heat-treated specimens were tensile tested at different temperatures in the range of –50 to 220 °C. To characterize the as-cast and deformed microstructures Light Optical Microscopy (LOM) and magnetic scale measurements were performed. The tensile tests were carried out at a strain rate of 0.0004 s\(^{-1}\). The austenite start (\(A_s\)), austenite finish (\(A_f\)), and martensite start (\(M_s\)) temperatures were determined by a BAHR 805A/D quenching and deformation dilatometer. To determine the \(M_s\) temperature, the dilatometry specimens were heated up with a heating rate of 10 °C s\(^{-1}\) to the austenitization temperature of 1050 °C and held for 10 min followed by cooling to –130 °C at a cooling rate of 10 °C s\(^{-1}\). \(A_s\) and \(A_f\) temperatures were determined using a heating rate of 2 °C min\(^{-1}\).

1.3. Magnetic Scale Measurements

The magnetic scale allows to quantify the ferromagnetic phase contents based on the following principle: when a ferromagnetic material is exposed to a magnetic field, polarization occurs as the Weiss domains align themselves with the external magnetic field direction. As a result, the specimen becomes magnetic. This results in a force which acts to move the sample in the magnetic field. Therefore, the scale arm of the magnetic scale is displaced. With a magnetic field on the other side of the scale arm, in the opposite direction, the displacement is compensated. The ferromagnetic phase content is proportional to the current that creates the compensating magnetic field. By calibration using standard specimens of known ferromagnetic phase contents, the ferromagnetic phase fraction can be determined. The error associated with the ferromagnetic phase fraction determination with magnetic scale is limited to ±5%. The amount of martensite was measured in the as-heated treated condition and in fractured tensile specimen in the area of uniform elongation. For the quantification of the delta ferrite fractions through LOM, specimens etched by the Murakami reagent were used.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>C (wt.%)</th>
<th>N (wt.%)</th>
<th>Cr (wt.%)</th>
<th>Ni (wt.%)</th>
<th>Mn (wt.%)</th>
<th>Si (wt.%)</th>
<th>Fe + others (wt.%)</th>
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<td>MnN1</td>
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<td>0.121</td>
<td>13.90</td>
<td>5.90</td>
<td>0.17</td>
<td>0.54</td>
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<tr>
<td>MnN2</td>
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<td>0.108</td>
<td>14.20</td>
<td>5.84</td>
<td>2.96</td>
<td>0.52</td>
<td>Bal.</td>
</tr>
<tr>
<td>MnN3</td>
<td>0.032</td>
<td>0.106</td>
<td>13.90</td>
<td>5.87</td>
<td>5.87</td>
<td>0.51</td>
<td>Bal.</td>
</tr>
<tr>
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<td>0.106</td>
<td>14.20</td>
<td>5.85</td>
<td>7.77</td>
<td>0.52</td>
<td>Bal.</td>
</tr>
<tr>
<td>MnN5</td>
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<td>0.129</td>
<td>14.20</td>
<td>5.79</td>
<td>10.70</td>
<td>0.49</td>
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<table>
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<tr>
<th>Alloy</th>
<th>Cr-equivalent</th>
<th>Ni-equivalent</th>
<th>SFE(_{\text{Ni}}) [mJ m(^{-2})]</th>
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<td>14.71</td>
<td>9.11</td>
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<td>MnN4</td>
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<td>12.42</td>
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<tr>
<td>MnN5</td>
<td>14.94</td>
<td>14.56</td>
<td>20.6</td>
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2. Results and Discussion

2.1. SFE and Austenite Stability

For the estimation of SFE at room temperature, an empirical equation applicable to high-alloy stainless steels was used.\cite{30} Based on the calculated SFE values, the likelihood of the deformation-induced twin formation can be evaluated:

\[
\gamma_{SFE} = 39 + 1.59\% \text{Ni} - 1.34\% \text{Mn} + 0.06\% \text{Mn}^2 - 1.75\% \text{Cr} + 0.01\% \text{Cr}^2 + 15.21\% \text{Mo} - 5.59\% \text{Si} + 26.27(\% \text{C} + 1.2\% \text{N})(\% \text{Cr} + \% \text{Mn}) + \% \text{Mo}^{0.5} + 0.61[\% \text{Ni}(\% \text{Cr} + \% \text{Mn})]^{0.5} - 60.69(\% \text{C} + 1.2\% \text{N})^{0.5}
\]

The calculated Ni- and Cr-equivalents using Equations 1 and 2 as well as the stacking fault energies for the steels are shown in Table 2. The calculated SFE values in the order of 8–130 \text{mJ m}^{-2} shown in Table 2. The calculated SFE values in the order of 8–130 \text{mJ m}^{-2} and 2 as well as the stacking fault energies for the steels are indicated. Moreover, the position of the cast steels MnN1–MnN5 in the Schaeffler-diagram are indicated. However, Figure 1 represents only a portion of the complete Schaeffler-diagram with Ni-equivalents in the range of 6–16 and Cr-equivalents ranging from 10 to 20. According to this constitutional diagram, the alloy MnN5 should have a fully austenitic microstructure without delta ferrite. The cast steels MnN4–MnN1, on the other hand, should exhibit an austenitic-martensitic microstructure, still free of delta ferrite.

2.2. Dilatometry

Table 3 presents the \(M_s\), \(A_s\), and \(A_t\) temperatures obtained from the dilatometry. The cast steel alloys MnN1–MnN4 show as-quenched martensite formation during cooling down to –130°C. In contrast, the alloy MnN5 exhibits no thermal martensite formation due to the increased austenite stability caused by the addition of 11% Mn. Cooling to temperatures lower than –130°C is required to determine a possible \(M_s\) temperature for the \(\alpha\)-martensite formation in the MnN5 steel. Due to the absence of thermal martensite, \(A_s\) and \(A_t\) temperatures could not be specified. Table 3 reveals that the \(M_s\) temperature decreases with increasing Ni-equivalent. This effect can be explained by the increased austenite stability because of the rising manganese content. Furthermore, a high Ni-equivalent, for example that of the cast steel MnN4 (\(\text{Ni}_{eq,MnN4} = 12.42\)), reduces the Gibbs free energy of the austenite–martensite transformation. The following relationship was found between the \(M_s\) temperature and the Ni-equivalent.

\[
M_s = -18.6\frac{\text{Ni}_{eq}^2}{\text{C}^2} + 302.7\text{Ni}_{eq} - 1002.6
\]

This equation was verified for a fixed nitrogen content of 0.1% and manganese contents up to 11%. Using regression analysis, a similar relationship can be found to express the relationship between the \(A_s\) and \(A_t\) temperatures and the Ni-equivalent. For the alloys MnN1–MnN4 both temperatures could be measured. As with the \(M_s\) temperature, the \(A_s\) and \(A_t\) temperatures decrease with the increase of manganese. In this case, however, the relationship between these temperatures and the Ni-equivalent was found to be linear.

\[
A_s = -23.5\frac{\text{Ni}_{eq}}{\text{C}} + 802.4
\]

\[
A_t = -31.2\frac{\text{Ni}_{eq}}{\text{C}} + 1005.8
\]

Using Equations 4–6 which are also plotted in Figure 2, it is possible to estimate the \(M_s\), \(A_s\), and \(A_t\) temperatures as a function of manganese contents in the range of 0–11%. It must be noted that the above equations are only valid when the concentrations of the other austenite stabilizing alloying elements such as C, N, and Ni are constant.

![Schaeffler-diagram](image1.png)

Fig. 1. Positions of the cast steels in the Schaeffler diagram adapted from ref.\cite{31}.

![Correlation diagram](image2.png)

Fig. 2. Correlation between \(M_s\), \(A_s\), and \(A_t\) temperatures and the Ni-equivalent.
2.3. Microstructure of the Cast State

Depending on the manganese content the microstructure of the investigated CrMnNi-N cast steels is either fully or partially austenitic at room temperature. A maximum delta ferrite fraction of 1% was detected in MnN3-MnN5 steels. The cast steel without manganese (MnN1) had a mainly martensitic microstructure with only 15% austenite. With the increase of the Ni-equivalent by 3% manganese addition to MnN1, the austenite fraction rises sharply from 15% in MnN1 to 94% in MnN2. For the alloys MnN3–MnN5 (6–11% Mn) an almost fully austenitic microstructure, without as-quenched martensite, was observed. Figure 3 shows the microstructures of the as-cast steels. The as-cast austenitic microstructure of steels MN3–MN5 is represented by the MnN4 steel. Furthermore, the developed cast steels exhibited a coarse-grained dendritic microstructure with grain sizes of up to 2 mm. The martensite volume fractions determined experimentally were found not to agree with the predictions in the Schaeffler-diagram (Figure 1). An austenitic-martensitic microstructure was only observed in MnN1 and MnN2 steels. Only in the case of the MnN1 steel did the martensite phase fraction closely coincide with the predicted position in the Schaeffler diagram. When MnN1 is alloyed with manganese, the austenite stability rises sharply and accordingly, the martensite content decreases. Therefore, it seems that manganese has a greater austenite stabilizing effect than assumed in the Schaeffler diagram. For the same reason, almost 100% austenite was obtained in the cast steels MnN3–MnN5 while according to the Schaeffler diagram, only the alloy MnN5 should be fully austenitic.

2.4. Microstructure Evolution During Tensile Test

To trigger the martensitic transformation the sum of the Gibbs free energy for the $\gamma \rightarrow \alpha'$ transformation and the external mechanical work must be equal or higher than the martensite nucleation threshold. With falling temperatures the available Gibbs free energy increases. As a consequence a higher martensite volume fraction is formed by a given mechanical work. For the investigated CrMnNi-N cast steels, this material behavior is clearly shown in Figure 4. Due to the presence of as-quenched martensite in steels MnN1 and MnN2, the fraction of strain-induced martensite which can form at room temperature is limited to 15% for MnN1 and 94% for MnN2. The TRIP effect was observed in all of the tested cast steels. The MnN2 steel reaches the highest deformation-induced martensite content at room temperature of about 85% followed by the steel MnN3 at 72%. The lowest deformation-induced martensite phase fraction of 15% was measured in the MnN1 cast steel after the complete transformation of the existing retained austenite. Therefore, a fully martensitic microstructure was obtained after tensile testing of the MnN1 steel. Further tensile tests were carried out at $-50$, $-20$, 80, and 220 °C. The alloys MnN1 and MnN2 show a fully martensitic microstructure after tensile testing at $-20$ and $-50$ °C. On the other hand, the other alloys only partially transform to $\alpha'$-martensite at temperatures as low as $-50$ °C. It can be noted that even MnN5 forms some deformation-induced martensite at room temperature in spite of the high austenite stability. Figure 4 clearly shows that an increased manganese content leads to a lower strain-induced martensite amount after tensile test.

2.5. Mechanical Properties

Figure 5 shows the engineering stress–strain behavior of the investigated steels at room temperature. Conventional austenitic cast steels possess yield strengths of approximately 150–175 MPa at room temperature, whereas the newly developed steels exhibit yield strengths in the range of 200–334 MPa. This increase is caused by the alloying with nitrogen and the presence of as-quenched $\alpha'$-martensite in the MnN1 and MnN2 alloys. Furthermore, fracture elongations of up to 66% were achieved in the case of the MnN5 alloy. The highest tensile strength value of 1233 MPa was measured in the cast steel MnN1 with a high fraction of as-quenched martensite. At a room temperature, the strength decreases and the elongation increases with rising manganese contents. In other words, the chemical driving force for the austenite to $\alpha'$-martensite transformation decreases from MnN1 to MnN5. MnN1 shows an engineering stress–strain curve typical of a martensitic steel, with a high strength and a low elongation. MnN2 shows a pronounced TRIP effect at room temperature.

Fig. 3. As-cast microstructure at RT: (a) MnN1, white = austenite, gray and black = martensite; (b) MnN2, white and gray = austenite, black = martensite; (c) MnN4, gray and black = austenite.
This type of microstructure formation is associated with a characteristic s-shaped curve progression of the stress–strain curve. In the steel MnN3, both TRIP and TWIP effects occur during tensile loading at room temperature. This resulted in an excellent fracture elongation of 53% and a tensile strength of 820 MPa. The high strains obtained in the case of MnN4 and MnN5 were caused by martensite formation and twinning.

Considering the mechanical properties of the alloys over the entire temperature range in Figure 6, it is clearly shown that the steel MnN1 without manganese exhibits the highest strength and the lowest strain levels. Because of its martensite volume fraction of higher than 85%, the tensile strength of MnN1 remains above 1100 MPa and its yield strength remains at a high level of 280 MPa even at 200 °C. The austenitic-martensitic cast steel MnN2 with 3% manganese reached its maximum fracture elongation of 40% at 80 °C. For this alloy, a remarkable increase of the tensile strength from 380 MPa at 220 °C to 1280 MPa at 1280 MPa at −50 °C was observed, which can be attributed to the TRIP effect. It can also be noted that the elongations in the studied temperature range are lower for the MnN2 than those for the austenitic steels MnN3–MnN5. This can be explained by the presence of as-quenched martensite and the associated reduction of austenite fraction. The cast steel MnN3 with 6% manganese has the highest uniform and
fracture elongation of all alloys at 80 °C, where the fracture elongation reached 79%. This can be attributed to the combined effect of TRIP and TWIP. When the test temperature decreases the thermodynamic driving force for the γ→α'-martensite formation increases. This results in a preferred occurrence of the TRIP effect at the expense of the TWIP effect which leads to an abrupt rise of the tensile strength. The temperature dependence of the mechanical properties is very similar for the alloys MnN4 (8% manganese) and MnN5 (11% manganese). Similar to the as-cast steel MnN3, these steels too exhibit an increased strain-induced martensite formation at temperatures below 80 °C leading to a significant increase in tensile strength. The alloy MnN1 reveals the largest 0.2% proof stresses in the examined temperature range due to the large amount of as-quenched martensite and solid solution strengthening by nitrogen. The yield strength of the alloys MnN2–MnN5 with no or very small fractions of as-quenched α'-martensite was significantly lower. In these specimens, the yield strength was primarily controlled by the solid solution strengthening effect of Mn and N. Accordingly, the steel MnN5 with the highest Mn and N concentrations of all alloys showed the highest yield strength among steels MnN2–MnN5 at temperatures below 80 °C. The results however do not allow to evaluate the possible influence of stress-induced α'-formation on the yield strength. Furthermore, the largest elongations in the temperature range of ~50 to 20 °C, assisted by the TRIP effect, were achieved in the steels MnN4 and MnN5. The elongation maximum for these steels was shifted to lower temperatures relative to the MnN3 alloy which can be explained by the increase of manganese. The mechanical properties are also influenced by the TWIP effect. The fully austenitic alloy MnN5 at 80 and 220 °C should serve as an example of plasticity accommodated by dislocation glide and twinning. The normal material behavior for metals is characterized by an increase of the ductility at elevated temperatures. The occurrence of deformation-induced twinning can, however, reverse the temperature dependence of elongation. The TWIP effect is for instance responsible for the increase in the fracture elongation of MnN5 alloy by decreasing the tensile test temperature from 220 to 80 °C. At 220 °C, the twinning activity is expected to be low and deformation is primarily accommodated by dislocation glide.

3. Conclusions

The influence, on the microstructure formation processes and the mechanical properties, of varying Mn contents and deformation temperatures was studied in five high-alloy 14Cr-XMn-6Ni-0.1N cast steels. It was found that the increase of the manganese content leads to a decrease of the $M_s$, $A_s$, and $A_f$ temperatures and additionally to a rise of austenite stability. As a result, cast steels with 6–11% manganese exhibited a fully austenitic as-cast microstructure, but those with <6% manganese have an austenitic-martensitic as-cast microstructure. Furthermore, empirical equations for the transformation temperatures $M_s$, $A_s$, and $A_f$ in dependence of the Ni-equivalent were established. Comparison of the tensile test results at a constant temperature indicated that in most cases the tensile strength decreases and the elongation increases with increasing manganese content. The austenitic-martensitic steel grades exhibited higher strengths and lower strains in comparison to the fully austenitic steel grades. This can be explained by the presence of as-quenched martensite which on the one hand leads to a significant strengthening but on the other hand reduces the fraction of metastable austenite which is essential for the TRIP and TWIP effects. With the development of these novel nitrogen alloyed TRIP/TWIP CrMnNi cast steels, δ-ferrite amounts below 1% and yield strengths at room temperature in the range of 200–352 MPa were achieved.

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