

Review

Research Progress on Ultra-Low Temperature Steels: A Review on Their Composition, Microstructure, and Mechanical Properties

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Abstract: To address global environmental concerns and reduce carbon dioxide emissions, countries worldwide are prioritizing the development of green, eco-friendly, and low-carbon energy sources. This emphasis has led to the growing importance of promoting clean energy industries like hydrogen energy and natural gas. These gases are typically stored and transported at cryogenic temperatures, making ultra-low temperature alloys indispensable as essential materials for the storage and transportation of liquid gas energy. With the temperature decreasing from room temperature (RT) to liquid nitrogen temperature (LNT), the dominant deformation mechanism in high-manganese steels undergoes a transformation from dislocation slip to deformation twinning, resulting in exceptional cryogenic mechanical properties. Consequently, high-manganese steel has emerged as an excellent material candidate for cryogenic applications. This report focuses on establishing the composition of high-manganese steel suitable for cryogenic applications and provides a comprehensive review of its microstructure and mechanical properties at both RT and LNT. Furthermore, it offers a prospective outlook on the future development of cryogenic high-manganese steels.

Keywords: high-manganese steel; cryogenic temperatures; low-temperature metals; mechanical properties; deformation mechanisms; microstructure



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1. Introduction

With the growing severity of global environmental issues, countries worldwide are prioritizing energy reform, clean energy development, and carbon dioxide emissions reduction as strategic objectives. In April 2021, the European Union passed the European Climate Law, mandating EU institutions and Member States to achieve net-zero emissions by 2050. In the future, the energy structure will gradually change to green, low-carbon, efficient, safe, sustainable, and intelligent. As a result, significant attention has been focused on clean energy sources such as hydrogen and liquefied natural gas [1,2]. Hydrogen energy is considered a core energy source to replace traditional fossil fuels, with broad application prospects in aerospace, military and civil fields [2]. The boiling points of liquid hydrogen and liquefied natural gas are $-253\text{ }^{\circ}\text{C}$ and $-163\text{ }^{\circ}\text{C}$, respectively. Therefore, they must be stored and transported at ultra-low temperatures. In addition, the consumption of liquid oxygen ($-183\text{ }^{\circ}\text{C}$), liquid nitrogen ($-196\text{ }^{\circ}\text{C}$), and liquid helium ($-269\text{ }^{\circ}\text{C}$) is gradually increasing in aerospace, medical transportation, and advanced scientific research industries. Thus, there is a growing demand for ultra-low temperature alloys as critical materials for storage and transportation facilities. Currently, ultra-low temperature alloys mainly include high-nickel (Ni) steels, medium/high entropy alloys, and high-manganese steels.

High-nickel steels are the earliest cryogenic steels, predominantly comprising 5% Ni, 7% Ni, and 9% Ni steels [3]. Among them, 9% Ni steel was first utilized in liquid oxygen storage tanks in 1952 [4]. Currently, most large cryogenic storage tanks are manufactured with 9% Ni steel due to its sufficient strength and resistance to crack growth. It is worth

noting, however, that Ni is an expensive and rare metal, which has spurred demand for alternatives to 9% Ni steel.

Medium/high entropy alloys have emerged as promising cryogenic alloys in recent years [5–8]. The FCC-structured high entropy alloys exhibit an excellent combination of strength, ductility, and high toughness at cryogenic temperatures. CoCrFeMnNi is a typical representative of high entropy alloys for potential cryogenic applications [6,7,9], in which yield strength, tensile strength, and elongation could simultaneously increase with a decrease in temperature due to the formation of large stacking faults and extensive nano-deformation twins during deformation at cryogenic temperatures [6]. When the tensile strength of CrMnFeCoNi reaches 1 GPa, the fracture toughness can exceed $200 \text{ MPa}\cdot\text{m}^{-1/2}$, thus demonstrating their excellent mechanical properties [7]. However, it should be noted that high entropy alloys are primarily synthesized in the laboratory, and their industrial-scale applications are still in the early stage of development. Moreover, the production cost of high-nickel alloys and medium/high entropy alloys is notably high due to the high content of expensive alloy elements such as Ni, Cr, and Ti. Figure 1 shows the Ni/Mn and Co/Mn price ratios from 2011 to 2022 [10], highlighting the significant price differences. The average price of Ni and Co is approximately ten times higher than that of Mn, underscoring the economic challenges associated with these alloys. Therefore, future ultra-low temperature alloys should prioritize high performance and resource-saving approaches in order to overcome these challenges and facilitate their practical applications.

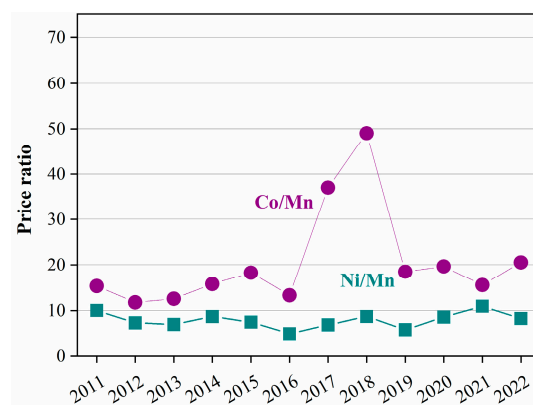


Figure 1. Ni/Mn and Co/Mn price ratios from 2011 to 2022 [10]. Data from [10].

High-manganese steels have gained significant recognition in the automotive industry due to their exceptional properties such as high ultimate tensile strength, large uniform elongation, and excellent work-hardening ability [11]. In recent years, the interest on these steels has expanded to include their remarkable cryogenic mechanical properties [12,13]. By deliberate composition and microstructure design, the dominant deformation mechanism in high-manganese steels can be transformed from dislocation slip to deformation twinning as the temperature decreases from RT to LNT, leading to an inverse temperature dependence of their mechanical properties. Another advantage of high manganese steels is their cost-effectiveness, as the price of manganese is approximately one-tenth that of nickel [12]. These distinctive attributes position high manganese steel as an appealing alternative for cryogenic applications. Notably, in 2015, POSCO successfully developed ultra-low temperature high-manganese steel for LNG storage tanks, demonstrating comparable cryogenic toughness, fatigue resistance, and corrosion resistance to the widely used 9% Ni steel. Moreover, the high manganese steel exhibited superior ductility, approximately three times that of the 9% Ni steel [14]. Additionally, high-manganese steels offer better weldability and lower production costs, further enhancing their attractiveness for applications involving the storage and transportation of liquid gas energy [12].

2. High Manganese Steel

2.1. Fe-Mn-C

Fe-Mn-C steel offers a cost-effective alternative to other high-manganese steels that incorporate additional alloying elements such as Al or Cr. Typically, high-manganese steels contain Mn in the range of 18–26 wt.%. The excellent mechanical properties of high-manganese steel are closely associated with various deformation mechanisms, including dislocation slip, stacking faults, deformation twinning, and deformation-induced martensitic transformation [15]. The plastic deformation mechanisms in high-manganese steels are strongly dependent on the SFE [16], which is affected by several factors including composition [17–19], temperature [15,20], and grain size [21,22]. To prevent deformation-induced martensitic transformation, increasing the Mn content in Fe-Mn-C steel is necessary. Mn acts as an austenite stabilizer, significantly lowering the austenite transformation temperature.

Fe-Mn binary alloys containing 30–40 wt.% Mn have been identified as exhibiting exceptional cryogenic toughness [23]. However, the comprehensive investigation of cryogenic mechanical properties in Fe-Mn-C steels remains incomplete. While certain high-manganese steels and high/medium-entropy alloys have shown an inverse temperature dependence of strength and ductility in previous studies, the majority of metals and alloys exhibit a decrease in impact toughness as temperature decreases.

Notably, Fe-30Mn-0.11C steel, characterized by an average grain size of 5.6 μm , displayed enhanced strength, ductility, and toughness at low temperatures, with a cryogenic toughness exceeding 450 J [24,25]. This behavior can be attributed to the presence of manganese and carbon as austenite stabilizing elements, along with a reduction in grain size to the near-micrometer scale. These factors inhibit martensitic transformation while promoting dislocation slip and deformation twinning as the dominant deformation mechanisms. The findings from the above studies offer a novel approach for designing high-manganese steels tailored for cryogenic applications. Moreover, Fe-34.5Mn-0.04C steel exhibited exceptional tensile properties at $-180\text{ }^{\circ}\text{C}$, including a yield strength of 612 MPa, a tensile strength of 983 MPa, and a total elongation of 52.5% [26]. These results further highlight the potential of Fe-Mn-C steels for demanding low-temperature environments. However, it is noteworthy that the carbon content has a significant impact on the deformation mechanism and mechanical properties of high-manganese steel [27]. Increasing carbon content can promote the transition of the deformation mechanism from dislocation slip to deformation twinning. It has been reported that increasing the carbon content to 0.6 wt.% results in a reduction in the low-temperature plasticity of Fe-Mn-C steel, attributed to the plastic instability caused by the rapid activation of deformation twins [28,29].

2.2. Fe-Mn-Al-C

The incorporation of aluminum (Al) into high-manganese steels has shown potential in improving strength and reducing density, resulting in mass reduction and reduced emissions of polluting gases [30]. Research on Fe-Mn-Al-C steels for cryogenic applications has primarily focused on investigating the influence of Mn and Al contents on microstructure, deformation mechanisms, and mechanical properties. The SFE of high-manganese steels can be increased by increasing the Mn or Al content, as Mn acts as a FCC stabilizer and Al acts as a BCC stabilizer [31]. It has been reported that the SFE increases by approximately 8 mJ/m² with a 1 wt.% increase in Al content [32]. Consequently, the addition of Al to high-manganese steels can facilitate deformation twinning or dislocation slip while suppressing deformation-induced martensitic transformation.

In the Fe-(17–22)Mn-(0–2)Al-0.45C steels, it has been observed that as the temperature decreases from RT to LNT, the strength of the steels increases, while the ductility and toughness decrease, particularly in the case of the Fe-19/22Mn-0.45C and Fe-17Mn-2Al-0.45C steels [32,33]. The Fe-22Mn-2Al-0.45C steel exhibits excellent comprehensive mechanical properties due to the prevalence of deformation twinning and dislocation slip during cryogenic plastic deformation. However, reducing the Mn or Al content based on the Fe-22Mn-2Al-0.45C steel leads to the activation of deformation-induced ϵ -hcp or α' -bcc

martensitic transformation, which significantly reduces the cryogenic ductility and Charpy impact energy. The transformed ϵ/α' -martensite in the notch-trip region can act as crack initiation sites, resulting in a transition from ductile-dimpled fracture to quasi-cleavage fracture mode, as shown in Figure 2. In addition, α' -martensite (BCT) is more detrimental to ductility and toughness compared to ϵ -martensite (HCP) due to its increased brittleness. It is noteworthy that α' -martensite is more likely to be induced than ϵ -martensite in Fe-Mn-Al-C steel, as Al acts as a BCC stabilizer.

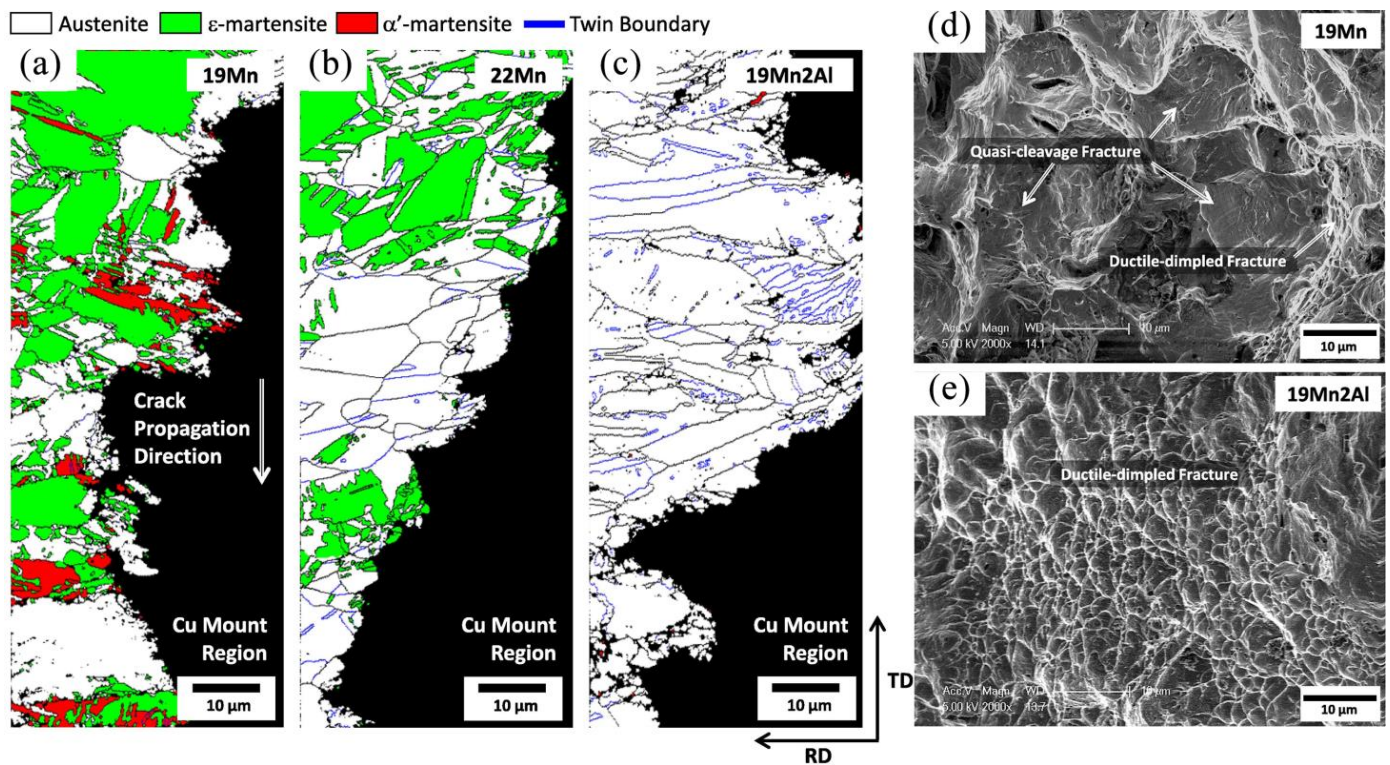


Figure 2. EBSD phase maps of the fracture initiation region and SEM fractographs of the cryogenic-temperature Charpy impact specimen of the (a,d) Fe-19Mn-0.45C, (b) Fe-22Mn-0.45C, (c,e) Fe-19Mn-2Al-0.45C [32]. Adapted from [32].

Li et al. [34,35] reported that the strength and elongation increased simultaneously as the temperature decreased from RT to LNT for the Fe-20Mn-4Al-0.3C and Fe-27Mn-4Al-0.3C steels, while the Charpy impact energy generally decreased. The RT yield strength and LNT Charpy impact energy of the Fe-27Mn-4Al-0.3C steel are 419 MPa and ~180 J, respectively, which are similar to those of the Fe-22Mn-2Al-0.45C steel [33]. The Fe-20Mn-4Al-0.3C steel showed deformation-induced martensite and twins after the tensile test at LNT, while only deformation twins formed in the Fe-27Mn-4Al-0.3C steel. In contrast, Sohn and Lee et al. [32] suggested that the TRIP effect was beneficial to the cryogenic work-hardening rate, leading to a higher elongation. The different conclusions may be related to the composition which determines the SFE. It should be noted that, after the tensile test at LNT, the volume fractions of ϵ -martensite and α' -martensite in the Fe-19Mn-0.45C steel were 39% and 18%, respectively. However, the volume fraction of α' -martensite in the Fe-20Mn-4Al-0.3C steel was only 3.88% when the true strain is 0.5. Moreover, the cryogenic impact toughness of the Fe-27Mn-4Al-0.3C steel was significantly higher than that of the Fe-20Mn-4Al-0.3C steel (~100 J). It was suggested that the formation of martensite may have a more significant effect on cryogenic impact toughness than on elongation, due to high strain rate in the impact test. However, Li et al. [35] did not analyze the microstructure of specimens after the impact test at LNT.

When the Al content in Fe-Mn-Al-C steels exceeds 5 wt.%, δ -ferrites tend to form. In general, the hard and brittle δ -ferrite can contribute to a strong strengthening effect but deteriorates cryogenic toughness. The Fe-18Mn-xAl-0.6C-0.5Si ($x = 3, 5, 8$) steels exhibit an increase in the RT yield strength from 406 to 588 MPa as the Al content increases from 3 to 8 wt.%, attributed to solid-solution, grain-refinement and δ -ferrite strengthening [36]. However, the presence of δ -ferrite (~25%) results in a significant decrease in the cryogenic toughness from 120 J to 18 J. Microcracks tend to nucleate and propagate along the γ/δ interface or within δ -ferrite colonies, ultimately resulting in brittle fracture [36].

The volume fraction and morphology of δ -ferrites in Fe-Mn-Al-C steels can be adjusted through the manipulation of alloy composition and solid solution treatment parameters. It has been reported that the volume fraction of δ -ferrite increases with the increase in Al content and decreases with the increase in C content for the Fe-23Mn-(3.97–5.31)Al-(0.22–0.41)C steels [37]. According to Xu et al. [38], the austenite content in dual-phase Fe-26Mn-6.2Al-0.05C steel decreases from 78.9% to 36.7% with the increase in solid solution temperature from 700 to 1200 °C. After the solid solution treatment at 1000 °C for 1 h, a homogeneous microstructure was obtained, which can be attributed to the separation of banded δ -ferrites by recrystallized austenite grains, resulting in an optimal combination of a RT yield strength of 362.4 MPa and a cryogenic impact energy of 129.7 J.

The deformation behavior and mechanical properties of Fe-Mn-Al-C steels could be controlled by the addition of other alloying elements such as V, Ni, and Cu. Chen et al. [39] investigated the role of V in Fe-24Mn-2Al-0.5Si-0.6C steel and found that the addition of 0.6 wt.% V significantly enhances the RT yield strength by approximately 113 MPa, while only slightly decreasing the cryogenic toughness by 34 J, resulting in a value of 121 J. The improved yield strength is attributed to the precipitation strengthening from VC carbides and the presence of high-density dislocations, resulting from the strong retardation effect of high V addition on recrystallization and recovery. The effect of V addition on grain-refinement strengthening and solid-solution strengthening is relatively weak. Kim et al. [17] analyzed the effect of 1 wt.% Ni or Cu content on cryogenic mechanical properties in the Fe-22Mn-1Al-0.45C steel, indicating that the main effect of Ni or Cu addition is to improve the SFE and suppress the martensitic transformation during deformation at LNT. Furthermore, the yield strength of high-manganese steels can be enhanced by alloying with C element. In comparison to Fe-24Mn-2Al-0.6V-0.5Si-0.6C steel, the RT yield strength of Fe-24Mn-2Al-0.6V-0.5Si-0.8C steel is increased by 120 MPa, reaching 624 MPa, while both steels exhibit similar cryogenic toughness of approximately 120 J [40]. The enhanced yield strength is mainly attributed to the solid-solution strengthening of interstitial C atoms and precipitation strengthening from fine nanoscale VC carbides. It is noteworthy that the addition of high C content facilitates recrystallization and recovery, leading to a decrease in dislocation density, which is essential for maintaining high cryogenic toughness of Fe-24Mn-2Al-0.6V-0.5Si-0.8C steel.

2.3. Fe-Mn-Cr-C

Fe-Mn-Cr-C steel is another typical representative composition of high-manganese candidate steels for cryogenic applications. In the Fe-24Mn-0.45C-xCr ($x = 0, 3$, and 6 wt.%) steels, it was observed that the RT yield strength and cryogenic toughness increased with the increasing in Cr content, while the elongation decreased [18]. The enhancement in yield strength is primarily attributed to the solid-solution strengthening from Cr, and the increased cryogenic toughness is a result of the higher Cr content increasing the SFE, which inhibits martensitic transformation. Among the investigated steels, the Fe-24Mn-6Cr-0.45C steel exhibits a good combination of strength and toughness, with an RT yield strength of 479 MPa and an LNT impact energy of 146 J. Luo et al. [41] reported the mechanical properties of Fe-25Mn-4Cr-0.5C steel with the RT yield strength and LNT impact energy of 350 MPa and 201 J, respectively. The higher Charpy impact energy was primarily due to the transformation of only ~2.5% ϵ -martensite from austenite and the presence of a greater number of mechanical twins formed after the impact test at LNT. Wang et al. [42] studied

the effect of Cr/N alloying on the mechanical properties of cryogenic high-manganese steel and indicated that the addition of 6.3 wt.% Cr and 0.2 wt.% N to Fe-24Mn-0.48C steel enhanced the yield strength while maintaining good cryogenic toughness.

It is worth noting that carbides and grain boundary segregation are common occurrences in Fe-Mn-Cr-C steels after annealing treatments, resulting in a significant reduction in ductility and toughness. In the case of Fe-27.3Mn-0.45C-3.9Cr-0.52Cu-0.20Si steel [43], the presence of heavy segregation of Cr and C, along with numerous $(\text{Cr, Mn})_{23}\text{C}_6$ -type carbide precipitates along the grain boundaries, strongly suppresses the secondary twinning system, leading to a substantial decrease in cryogenic toughness. However, grain boundary precipitation and segregation have minimal impact on the tensile properties, which may be attributed to the low strain rate involved. Wang et al. [44] reported that the cryogenic toughness of the Ti, V, and Mo-alloyed Fe-24Mn-0.49C-3.4Cr steel can be improved by increasing the solid solution temperature. However, the yield strength remains nearly constant due to the slow increase in the austenite grain size with the increasing in solid solution temperature. This phenomenon can be attributed to the superior thermal stability and resistance to coarsening exhibited by (Ti, V, and Mo) C precipitates.

3. Effect of the Microstructure

The microstructure plays a crucial role in determining the mechanical properties of high-manganese steels, both at RT and LNT. Currently, high-manganese steels for cryogenic applications are typically manufactured through hot rolling or a combination of cold rolling and annealing treatments. Cold rolling induces a high density of dislocations, resulting in increased strength but reduced ductility and toughness. Subsequent annealing processes promote recovery and recrystallization, leading to improved plasticity and toughness. Therefore, the microstructure of high-manganese steels for cryogenic applications is primarily controlled by optimizing the rolling and annealing parameters. By carefully adjusting the processing parameters such as rolling reduction, rolling temperature, annealing temperature, and annealing time, high-manganese steels with different grain sizes or heterogeneous structures can be produced. This provides the ability to tailor the microstructure according to specific requirements. The following section will focus on the effects of grain size and heterostructure on the toughening mechanisms and mechanical properties of high-manganese steels for cryogenic applications.

3.1. Grain Size Effect

With the exception of SFE, the activation of deformation twinning and martensitic transformation is highly influenced by the grain size [45–47]. A decrease in grain size leads to an increase in the critical stress required for deformation twinning and martensitic transformation during plastic deformation [24,48,49]. Rahman et al. [49] conducted a study on Fe-15Mn-2Al-2Si-0.7C steel, with grain sizes ranging from 0.7 to 48 μm , and found that the critical twinning stress increased as the grain size decreased. Coarse-grained samples exhibited thicker deformation twins. They proposed that deformation twinning occurred at sub-yield stresses and quantified the twin nucleation stress through cyclic tensile testing at stresses just below the yield strength. Xie et al. [48] investigated the influence of grain size on the cryogenic toughness and impact deformation mechanisms of Fe-25Mn-3Al-3Si steel. As shown in Figure 3, they observed that a sample with a grain size diameter of 47.8 μm exhibited the pronounced TWIP and TRIP effects, leading to improved cryogenic toughness. In contrast, these effects were significantly suppressed in a sample with a grain size diameter of 2.7 μm , resulting in the limited cryogenic toughness.

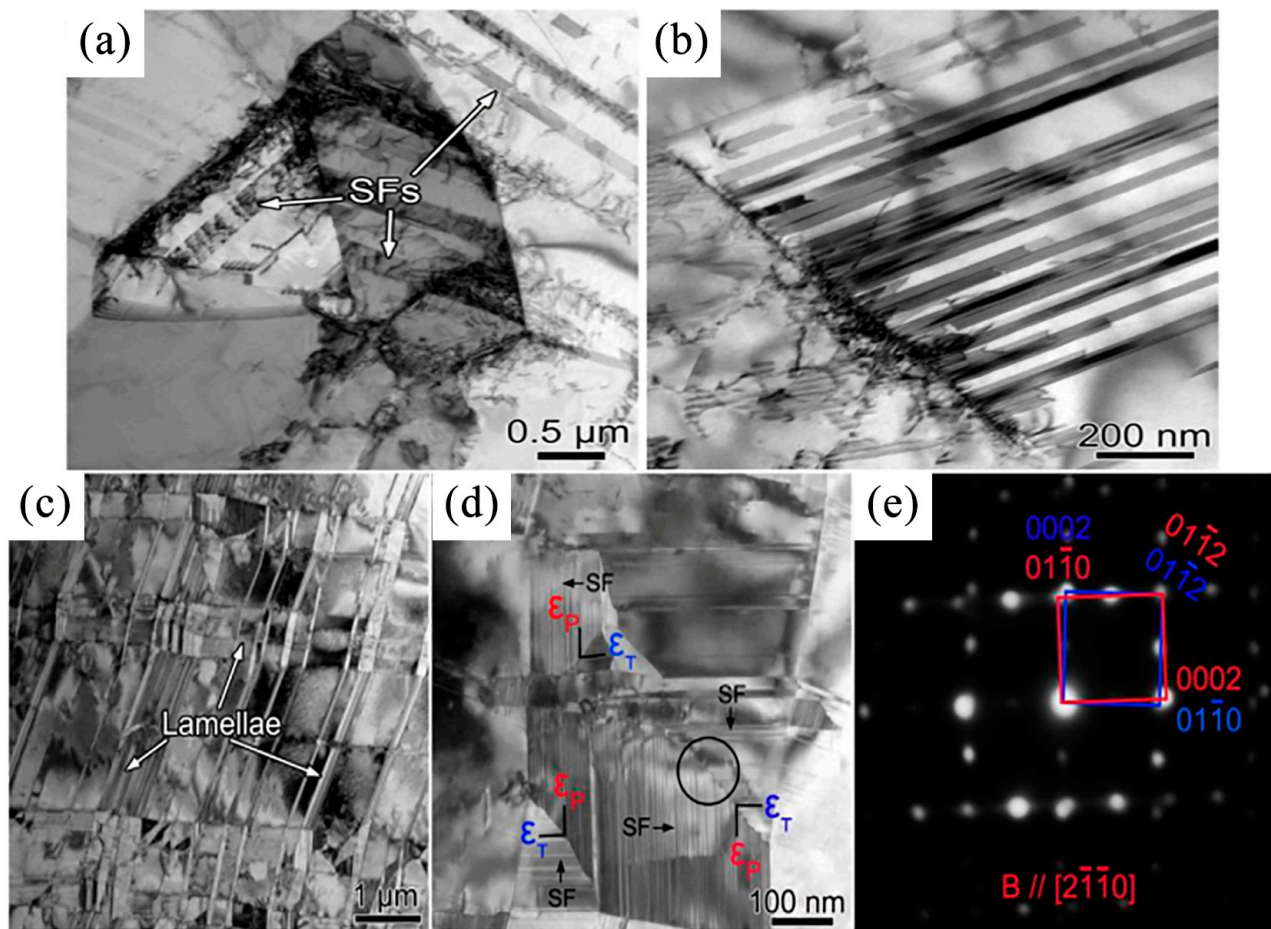


Figure 3. TEM characterization of the microstructure near the fracture of Fe-25Mn-3Al-3Si steel after impact test at LNT (a,b) 2.7 μm , (c–e) 47.8 μm [48]. Adapted from [48].

The deterioration in cryogenic impact toughness with the decreasing in grain size can be attributed to the reduced ability to store dislocations and hinder crack propagation [48,50]. According to the Hall–Petch relationship, the yield strength increases as the grain size decreases. However, the impact of grain size on the yield strength becomes less significant when the grain size exceeds 10 μm . Chen et al. [51] produced Fe-23.9Mn-4Cr-0.49Cu-0.48C-0.18Si-0.025V steel with average grain sizes of 8.5, 11.6 and 17.3 μm by controlling the final hot rolling temperature. They observed that the sample with a diameter of 17.3 μm exhibited the highest cryogenic toughness, which was attributed to the higher volume fraction of nano-twins formed in two or more twinning systems. Furthermore, Chen et al. [51] discovered that the cryogenic toughness increased from 130.5 to 177.6 J as the grain size increased from 11 to 47 μm , due to the activation of a higher volume fraction of deformation twins and the accumulation of high-density dislocations in the coarse-grained sample. However, when the grain size exceeds a certain range, cryogenic elongation and toughness decrease due to the formation of high-density primary twin bundles during the early stage of deformation, impeding the development of secondary twinning, as shown in Figure 4 [52]. Wang et al. [53] reported that the ductility and toughness increased with the increase in grain size from 14.9 to 92.4 μm for the Fe-22.28Mn-0.46C-0.34Mo-0.15Si steel at RT, but they seem to be unchanged at LNT conditions.

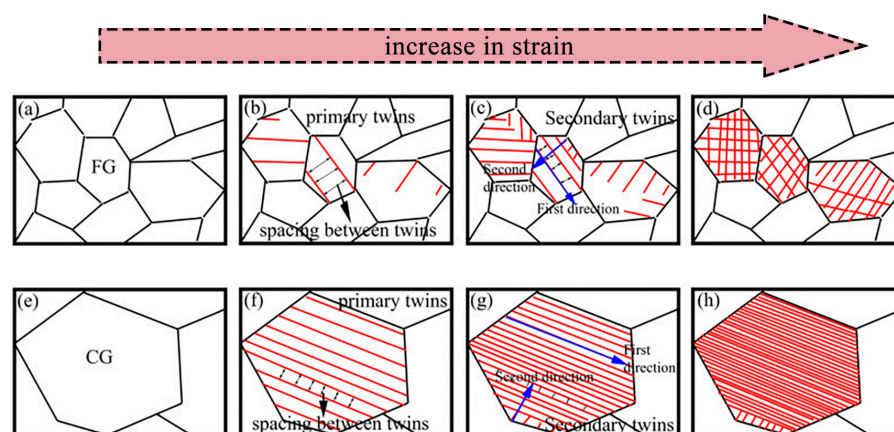


Figure 4. Schematic diagram of twinning behavior in fine grain (FG) and coarse grain (CG) [52]. (a) FG-No deformation; (b) FG- early deformation; (c) FG-medium-term deformation; (d) FGLate deformation; (e) CG-No deformation; (f) CG-early deformation; (g) CG-medium-term deformation; (h) CG-late deformation. Reproduced with permission from Wang, P.; Ren, J.; Chen, Q.; Chen, J.; Liu, Z., *Materials Characterization*; published by Elsevier, 2021.

Moreover, the cryogenic Hall–Petch strengthening coefficient for high-manganese steels was significantly higher than the value at RT, indicating that grain refinement has a more pronounced effect on enhancing cryogenic strength. Li et al. [54] obtained a heterogeneous grain size (ranging from 0.2 to 4 μm) in the Fe-24Mn-2Al-0.45C-0.1Nb-0.05Si steel through controlled thermo-mechanical treatment, where the precipitation of nano-scale k -carbides and Nb-rich carbides inhibited grain growth. The resulting yield strength reached 744 MPa. Tang et al. [55] suggested that the enhancement in cryogenic yield strength is attributed to an increase in lattice friction stress. With a decrease in the test temperature from 373 K to 77 K, the lattice friction of the Fe-24Mn-4Cr-0.5Cu-0.5C steel increased from 135 to 541 MPa.

3.2. Heterostructure Effect

In recent decades, various heterostructures, such as gradient structures, multimodal structures, heterogeneous lamellar structures, layer structures, and multiphase structures, have been developed to mitigate the trade-off between strength and ductility/toughness of metallic materials [56–59]. Generally, heterostructured materials consist of a combination of soft and hard regions. The preserved ductility or toughness is mainly attributed to the strain partitioning during plastic deformation and the substantial stress hardening [60].

High-manganese steels with heterostructures are commonly produced through severe plastic deformation and subsequent annealing treatments [54,61]. Wang et al. [62,63] successfully produced a laminated composite structure consisting of 10% recovered hard lamellae and 90% soft recrystallized lamellae in the single-phase Fe-34.5Mn-0.04C steel, through 90% cold rolling followed by annealing at 600 $^{\circ}\text{C}$ for 1 h, as shown in Figure 5. The formation of the laminated composite structure can be attributed to the distinct stored energy levels in different layers after severe deformation rolling. Consequently, the rates of recovery and recrystallization during annealing of these layers differentiate. It was demonstrated that the sample with the composite structure exhibited an exceptional combination of high strength and good ductility compared to fully recrystallized samples. Chen et al. [64] obtained a heterogeneous structure composed of 24% hardened structure and 76% softened structure in the Fe-23.7Mn-0.57C-1.92Al-0.55Si-0.31V steel through hot rolling followed by annealing at 900 $^{\circ}\text{C}$ for 600 s. The RT yield strength was enhanced by 86 MPa, while the cryogenic impact energy only decreased by 17 J compared to the fully softened structure.

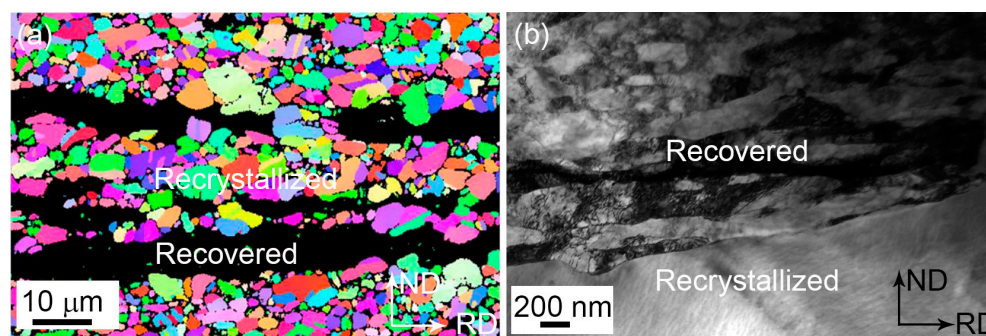


Figure 5. The laminated composite structure of Fe-34.5Mn-0.04C steel (a) EBSD map, (b) TEM image [62]. Reproduced with permission from Wang, Y.; Kang, J.; Peng, Y.; Wang, T.; Hansen, N.; Huang, X., *Scripta Materialia*; published by Elsevier, 2018.

Li et al. [54] developed the Fe-0.45C-24Mn-0.05Si-2Al-0.1Nb steel with a heterogeneous grain size ranging from 0.2 to 4 μm and a heterogeneous distribution of k-carbides through controlled thermo-mechanical treatment. They found that the bimodal grain size was attributed to the pinning effect of heterogeneous precipitates, which led to varying degrees of recrystallization during the annealing treatment. When the deformation temperature decreased from RT to LNT, the bimodal-grained sample exhibited increased strength and elongation. This was due to a transition in the dominant deformation mechanism from dislocation strengthening to a combination of nano-twins and forest hardening resulting from a higher density of dislocations. The key to obtain such heterogeneous structures lies in optimizing the alloy composition and precisely controlling the thermal processing parameters. Compared to the as-received states, the yield strength is significantly improved with minimal loss in cryogenic plasticity and toughness.

More recently, Zhong et al. [65] proposed a novel strategy to obtain a heterostructured Fe-0.44C-23.6Mn-0.047Si-1.8Al steel with varying grain size hierarchies through asymmetrical rolling (AR) followed by annealing. The formation of different grain size hierarchies, including ultra-fine grains (≤ 500 nm), sub-fine grains (500 nm–1 μm), and fine grains (≥ 1 μm), was attributed to different levels of deformation introduced by asymmetrical cold rolling and different driving forces for recrystallization during annealing. Their results demonstrated that the yield strength, ultimate tensile strength, and elongation of the AR-630 sample with the heterogeneous structure simultaneously increased, while the impact energy decreased as the temperature decreased from RT to LNT. The RT yield strength and cryogenic impact energy are 552 MPa and 183 J·cm⁻², respectively. The enhancement in ductility was mainly attributed to strain partitioning between heterogeneous domains and the sustainable high back stress. The combined effects of TWIP and heterogeneous strain partitioning resulted in the excellent cryogenic toughness.

3.3. Martensitic Transformation

Deformation twinning is widely acknowledged as the primary mechanism responsible for the significant improvement in cryogenic mechanical properties observed in high-manganese steels [66–69]. Nevertheless, as the temperature decreases from RT to LNT, the dominant deformation mechanism tends to shift from dislocation sliding to deformation twinning or martensitic transformation due to a typical decrease in the SFE by approximately 30–50% [33]. Consequently, in high-manganese steels with low or medium SFE, both martensitic transformation and deformation twinning can occur simultaneously during cryogenic plastic deformation. The sequence of martensitic transformation typically involves γ -austenite transforming to ϵ -martensite and then to α' -martensite. And ϵ -martensite commonly nucleates at twin intersections, while α' -martensite tends to nucleate at ϵ -martensite intersections [70]. It is worth noting that the effect of martensitic transformation on the cryogenic elongation and toughness of high-manganese steels is not yet well-understood and remains a subject of ongoing debate.

Numerous studies have demonstrated that deformation-induced ϵ/α' -martensite can serve as crack initiation sites, resulting in a significant reduction in cryogenic elongation and toughness. For instance, Sohn et al. [32] and Wang et al. [24] observed a substantial decrease in cryogenic Charpy impact energy following the martensitic transformation in high-manganese steel. Sohn et al. [32] found an increased volume fraction of martensite near the fracture surface as the Charpy impact energy decreased, and the fracture mode transitioned from ductile-dimpled fracture to quasi-cleavage fracture. Zhang et al. [71,72] suggested that enhancing the stability of the FCC structure is beneficial for improving the plastic work performance in the field of metallic materials. A crucial factor in maintaining FCC stability lies in preventing a decrease in plastic work due to phase transformation and, instead, suppressing the occurrence of phase transformation.

In contrast, some reports have indicated an improvement in the cryogenic elongation and toughness of high-manganese steels through martensitic transformation during plastic deformation [48]. It is well-known that martensitic transformation (TRIP effect) contributes to the plasticity and work hardening of medium-manganese steel at RT [73]. Recently, Zhang et al. [74] reported a cryogenic toughness of 140 J for a dual-phase maraging steel, attributed to the TRIP toughening effect during the impact testing at LNT. Xie et al. [48] showed that the impact energy of coarse-grained Fe-25Mn-3Al-3Si steel only slightly decreases as the test temperature decreases to LNT, as a result of simultaneous TRIP and TWIP effects. Kim et al. [75] found that a significant amount of ϵ -martensite and deformation twins formed in the Fe-22Mn-0.4C steel after dynamic compressive loading at LNT, leading to higher cryogenic toughness compared to other steels where only the TWIP mechanism is at work. It is noteworthy that high-manganese steels exhibiting TRIP and TWIP effects generally exhibit lower cryogenic toughness than those where deformation is primarily dominated by dislocation gliding and deformation twinning.

4. Mechanical Properties

The mechanical properties of typical ultra-low temperature high-manganese steels are summarized in Table 1. Figure 6 shows the relationship between RT yield strength and cryogenic Charpy impact energy of high-manganese steels. Most samples exhibit a relatively low RT yield strength (200–500 MPa) and good cryogenic Charpy impact energy (100–200 J). However, when compared to 9% Ni steel [76], high-manganese steels generally exhibit lower RT yield strength, which hinders their extensive utilization in cryogenic industrial applications. Consequently, the main challenge lies in introducing different strengthening mechanisms to enhance RT yield strength without significant deterioration of cryogenic plasticity and toughness.

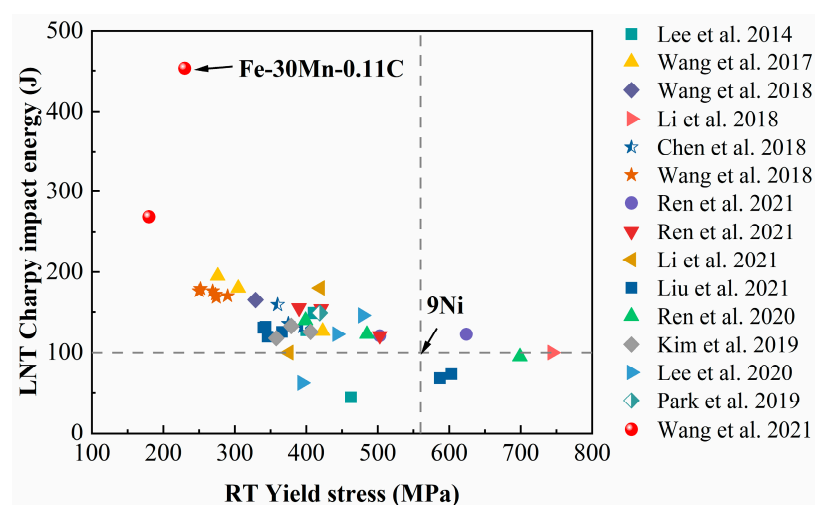


Figure 6. Relationship between RT yield strength and LNT Charpy impact energy of high manganese steels for cryogenic application. Data from [17,18,24,33,35,39,40,42,44,51,53,54,64,77,78].

Currently, only a limited number of high-manganese steels exhibit an RT yield strength of 600 MPa or higher and a cryogenic Charpy impact energy of approximately 100 J. For instance, in a previous study [54], it was reported that the RT yield strength was approximately 744 MPa, while the cryogenic toughness was around 100 J. The high yield strength of these steels can be attributed to a combination of solid-solution strengthening, grain refinement, nanoprecipitation and dislocation strengthening mechanisms, with grain refinement playing a dominant role. However, it is noteworthy that the composition and processing of these steels are relatively complex, and the prepared steel sheets have a limited thickness of only 5.4 mm, which poses certain limitations for industrial applications. In another study by ref. [40], the RT yield strength improved to 624 MPa while maintaining the cryogenic Charpy impact energy of 123 J by increasing the interstitial atomic C content and controlling the size of precipitates and dislocation density. In ref. [77] and ref. [64], high-density dislocations were introduced through hot rolling to enhance the RT yield strength. Although the process is relatively simple, the cryogenic impact toughness is less than 100 J. Notably, Fe-30Mn-0.11C steel exhibits an exceptionally high cryogenic Charpy impact energy of approximately 450 J compared to other steels, primarily due to the presence of a very stable austenitic phase [24]. The three-dimensional (3D) fracture surface morphology of Fe-30Mn-0.11C steel after the Charpy impact testing at LNT was characterized using 3D microcomputed tomography (micro-CT), as shown in Figure 7 [24]. The high toughness in this steel is attributed to the presence of manganese and carbon as austenite stabilizing elements, coupled with a reduction in grain size to the near-micrometer scale. Under these conditions, dislocation slip and deformation twinning serve as the main deformation mechanisms, while embrittlement caused by α' - and ϵ -martensite transformations is inhibited. This reduction in local stress and strain concentration retards crack nucleation and promotes work hardening.

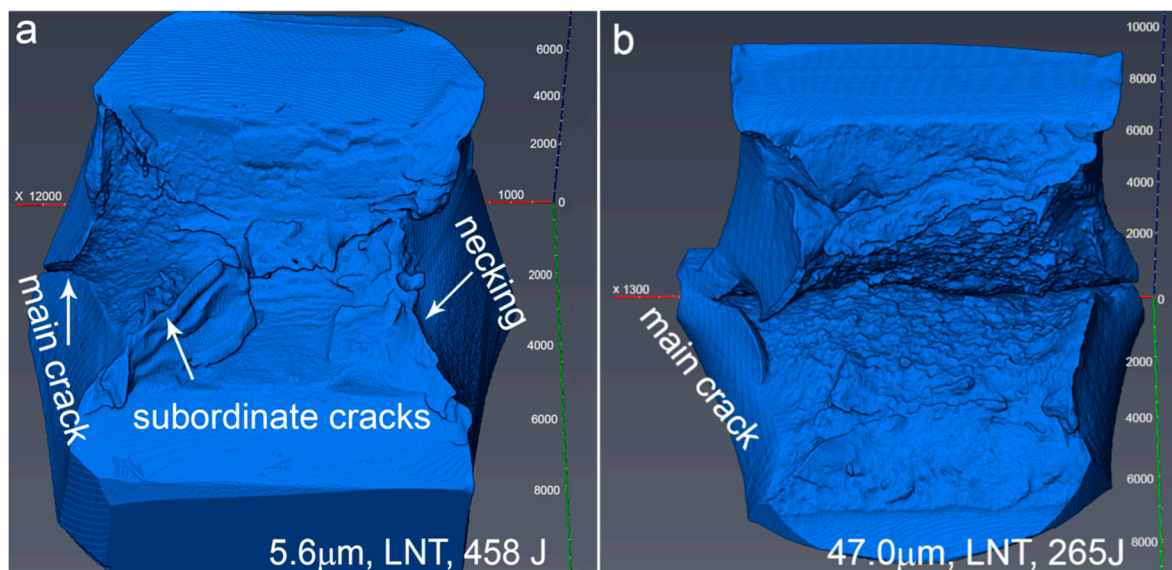


Figure 7. A 3D fracture surface morphology using micro-computed tomography of fine- and coarse-grained samples after Charpy impact testing at LNT [24]. T (a) fine-grained sample. (b) coarse-grained sample. Reproduced with permission from Wang, Y.; Zhang, Y.; Godfrey, A.; Kang, J.; Peng, Y.; Wang, T.; Hansen, N.; Huang, X., *Communications Materials*; published by Nature Publishing Group, 2021.

Table 1. Mechanical properties of high-manganese steels for cryogenic application.

Steels	RT				LNT				Ref.
	YS/MPa	UTS/MPa	TE/%	Cev/J	YS/MPa	UTS/MPa	TE/%	Cev/J	
Fe-17Mn-2Al-0.45C	462.5	861.6	68.2	226 (0 °C)	782.5	1082.8	16.6	44	[33]
Fe-19Mn-2Al-0.45C	400	816.2	77.6	255 (0 °C)	749.0	1227.5	36.2	128	
Fe-22Mn-2Al-0.45C	410.4	795.4	75.0	253 (0 °C)	755.7	1340.4	67.6	149	
Fe-22Mn-0.46C-0.15Si-0.34Mo-0.028Al	276	842	71.5	—	—	—	—	195	[42]
Fe-24Mn-0.46C-0.15Si-0.33Mo-0.027Al	305	830	71	—	—	—	—	180	
Fe-24Mn-0.48C-0.21Si-0.32Mo-0.024Al	423	906	70	—	—	—	—	127	
Fe-24Mn-0.49C-3.4Cr-0.29Mo-0.02Ti-0.02V-0.05Al	329	885	78	—	—	—	—	165	[44]
Fe-0.45C-24Mn-0.05Si-2Al-0.1Nb	744	980	~43	198 (half size)	945	1091	~62	100 (half size)	[54]
Fe-0.48C-0.18Si-23.9Mn-0.49Cu-4.0Cr-0.025V	395	—	—	—	—	—	—	132	[51]
	375	—	—	—	—	—	—	136	
	360	—	—	—	—	—	—	159	
Fe-22Mn-0.46C-0.34Mo-0.15Si	290	889	68	212	665	1300	35.5	170	[53]
	274	864	71	226	655	1280	37.5	168	
	273	852	73	237	630	1250	36.5	172	
	269	821	74	252	615	1140	34	176	
	252	782	76.5	252	605	1130	36	179	
	250	766	80	264	595	1100	35.5	176	
Fe-24Mn-2Al-0.6V-0.5Si-0.6C	503	867	57.8	—	—	—	—	121	[40]
Fe-24Mn-2Al-0.6V-0.5Si-0.8C	624	1035	53.9	—	—	—	—	123	
Fe-24Mn-2Al-0.5Si-0.6C	390	804	62.2	—	802	1409	75.2	155	[39]
Fe-24Mn-2Al-0.5Si-0.6C-0.3V	421	852	62.0	—	841	1430	71.4	154	
Fe-24Mn-2Al-0.5Si-0.6C-0.6V	503	867	57.8	—	983	1527	60.2	121	
Fe-20Mn-4Al-0.3C	375.7	660	58	~170	698.6	1196.5	77.4	~100	[35]
Fe-27Mn-4Al-0.3C	419.4	678	49	~310	729.8	1173	68.3	~180	

Table 1. Cont.

Steels	RT				LNT				Ref.
	YS/MPa	UTS/MPa	TE/%	Cev/J	YS/MPa	UTS/MPa	TE/%	Cev/J	
Fe-24Mn-3.8CrMo-0.3Si-0.4C-0.035NbTi	587	982	49.6	—	—	—	—	68	[77]
	346	879	66	—	—	—	—	120	
	343	858	62.5	—	—	—	—	132	
	340	854	62.4	—	—	—	—	131	
	603	951	54.3	—	—	—	—	73	
	366	895	62.8	—	—	—	—	126	
Fe-23.7Mn-0.57C-1.92Al-0.5Si-0.31V	699	952	41	—	—	—	—	95	[64]
	485	877	52	—	—	—	—	123	
	399	821	66	—	—	—	—	140	
Fe-22Mn-1Al-0.45C	358	793	84.5	175	697	1375	79.7	118	[17]
Fe-22Mn-1Al-0.45C-1Ni	379	799	80.2	211	713	1353	82.1	133	
Fe-22Mn-1Al-0.45C-1Cu	406	785	77.6	202	723	1322	87.4	126	
Fe-24Mn-0.45C	394	877	87.5	259	710	1431	83	62	[18]
Fe-24Mn-0.45C-3Cr	443	880	79.3	249	863	1459	78.9	123	
Fe-24Mn-0.45C-6Cr	479	883	73.9	234	924	1471	74.5	146	
Fe-25Mn	419	899	—	291	818	1453	—	149	[78]
Fe-30Mn-0.11C	180	495	66	372	280	777	87	269	[24]
	230	531	65	334	360	860	84	453	

5. Summary and Prospect

To fulfill an increasing demand for cryogenic alloys, it is of great significance to develop low-cost, high-strength, high-toughness ultra-low-temperature steels. The cryogenic mechanical properties of high-manganese steels significantly depend on the deformation mechanisms, which can be carefully tuned by adjusting the compositions and tailoring the microstructure. The excellent cryogenic mechanical properties of high-manganese steels can be attributed to the formation of deformation twins during plastic deformation. However, the occurrence of martensitic transformation and deformation twinning diminishes as the grain size decreases. While the ultra-fine-grained high-manganese steel with significantly improved yield strength has been achieved through cold rolling and annealing, the cryogenic toughness is generally limited by the decreased work-hardening ability. Moreover, the design of heterogeneous structures can improve the mechanical properties of high-manganese steels for cryogenic applications, but it has limitations in terms of industrial applications.

Currently, most cryogenic high-manganese steels exhibit an RT yield strength ranging from 250 to 500 MPa, along with a cryogenic Charpy impact energy ranging from 100 to 200 J. High-manganese steels possess relatively low strength compared to 9% Ni steel, commonly used in cryogenic applications. Enhancing the RT yield strength of high-manganese steels without compromising cryogenic toughness remains a significant challenge, necessitating composition design and microstructure tuning. A practical approach involves incorporating multiple strengthening mechanisms such as solid-solution strengthening, dislocation strengthening, precipitation strengthening, and grain-refinement strengthening.

Fe-Mn-C steels with a Mn content of 30–40 wt.% demonstrate excellent cryogenic toughness at a low cost. For instance, the Fe-30Mn-0.11C steel with a grain size of 5.6 μm exhibits a cryogenic Charpy impact energy of 450 J. However, limited research has focused on these steels. It is possible to achieve low-cost, high-strength, and high-toughness cryogenic high manganese steel by introducing additional strengthening contributions.

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