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Enhancement of yield strength by chromium/nitrogen alloying in highmanganese cryogenic steel

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ABSTRACT

Chromium (Cr)/nitrogen (N) alloying can enhance the yield strength of high-manganese (Mn) steels. This work investigated the mechanical properties of a high-Mn twin-induced plastic (TWIP) steel with 6.3% Cr and 0.2% N by tensile testing in an ambient atmosphere and impact testing at –196 °C. The yield strength of the high-Mn steel was improved significantly with Cr/N alloying and an excellent low-temperature toughness was maintained. Solid–solution strengthening resulting from dissolved nitrogen was the most effective strength mechanism to increase the yield strength of the steel compared with grain-boundary and precipitation strengthening, which result from the precipitation of aluminum nitride. Grain-boundary and precipitation strengthening result from the precipitation of aluminum nitride. Because of its excellent mechanical properties, high-Mn steel that is produced by Cr/N alloying can be used to manufacture storage tanks for liquefied natural gas.

1. Introduction

Urbanization has led to a rapid increase in the demand for liquefied natural gas (LNG), which is termed green energy. Traditionally, Nibased invar alloys, 9% Ni alloys, aluminum alloys and austenitic stainless steels are used in the storage and transportation of LNG. However, these materials have disadvantages, such as costly plates or welding consumables. Much attention has focused on replacing expensive Ni-based alloys with inexpensive high-manganese (Mn) steels [1–[4\]](#page--1-0). High-Mn steels are generally used in storage and transportation of LNG for their sufficient ductility and toughness [\[5,6\].](#page--1-1) But the development of high-Mn steels is limited by their relatively low yield strength, even with a high Mn or chromium (Cr) content [\[7](#page--1-2)–9].

In terms of the effects of alloying elements on the mechanical properties of austenitic steels, new types of N-alloyed austenitic steels are preferred because of their excellent mechanical properties [\[10,11\]](#page--1-3). N-alloyed austenitic steels possess a high yield strength, an excellent corrosion resistance and a strong austenite stability, which has drawn attention from steel plants [12–[15\].](#page--1-4) The effect of interstitial elemental N on yield strength is more effective than elemental carbon (C) [\[16\]](#page--1-5). Frehser and Kubisch were the first to discover that yield strength can be increased by elemental N incorporation in austenitic steels without an apparent decrease in toughness [\[17\].](#page--1-6)

However, a problem with N-alloyed austenitic steels is that the N

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has a low solubility during smelting. Fortunately, elemental Cr and Mn, especially elemental Cr, can increase the N solubility [\[18,19\].](#page--1-7) A higher elemental Cr content allows for an increase in the amount of N that can be dissolved. Elemental Cr addition to austenitic steels will increase the yield strength and improve the corrosion resistance [\[20\]](#page--1-8).

Research on Cr/N alloying in high-Mn cryogenic steels has rarely been reported. The main focus of this work was on the mechanical properties and microstructure of the new high-Mn steel with Cr/N alloying. The effect of Cr/N alloying on the yield strength of the high-Mn steel were discussed.

2. Experimental procedures

Three kinds of high Mn austenitic steels were prepared to study the effect of Cr/N alloying. Each composed specimens were made by casting in a 100 kg induction melting furnace within Ar atmosphere, and the steel ingots were hot forged to $120 \times 110 \times 60$ mm³ blocks. Inductively Coupled Plasma-Atomic Emission Spectrometer (ICP-AES) was employed to measure chemical compositions (wt%), which were shown in [Table 1](#page-1-0).

After soaking at 1200 °C for 1 h, the billets were hot rolled to a plate with thickness of 12 mm and total reduction ratio of 80%, and then quenched with water to room temperature.

To gain favorable low-temperature toughness, an appropriate

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Table 1

Chemical compositions of materials (wt%).

Alloys	C.	Si	Mn S		\mathbf{P}	Cr.	Mo	N	Al
22Mn 24Mn-3.3Cr 24Mn-6.3Cr- 0.2N				0.46 0.15 22.28 0.0019 0.0051 - 0.46 0.15 23.65 0.0073 0.0051 3.28 0.33 - 0.48 0.21 24.28 0.0091 0.0059 6.29 0.32 0.19			$0.34 -$		0.028 0.027 0.024

solid–solution treatment temperature should be selected to avoid Cr carbonitride formation. Therefore, equilibrium phase diagrams were required for 22Mn, 24Mn-3.3Cr and 24Mn-6.3Cr-0.2 N steels. The phase-equilibrium diagrams were calculated using Thermocalc software, as shown in [Fig. 1.](#page-1-1) The precipitation temperature of Cr carbonitride differs in different steels. The M_7C_3 precipitation temperature was \sim 700 °C in 22Mn steel (see [Fig. 1a](#page-1-1)), whereas it was 850 °C in 24Mn-3.3Cr steel (see [Fig. 1](#page-1-1)b). $M_{23}C_6$ precipitates may form in 24Mn-6.3Cr-0.2N steel when the temperature decreases to 900 °C or below, as shown in [Fig. 1](#page-1-1)(c). The strain-induced precipitation of Cr carbonitride could occur during hot rolling. Therefore, the solid–solution-treatment temperature should be higher than 900 °C to avoid Cr carbonitride precipitation. To prevent abnormal grain coarsening, the temperature should not be too high. Thus, in this investigation, the temperature was set to 1050 °C. The specific rolling and solid–solution treatment processes are shown in [Fig. 1](#page-1-1)(d).

The tensile tests were performed using a WE–300 tensile test machine in ambient atmosphere. The tensile specimens with Φ8 mm and 25 mm gauge length were machined from rolled plate after solution

treatment. Charpy impact tests were performed using a JBN-300N on standard Charpy V-notch specimens (size: $10 \times 10 \times 55$ mm) under –196 °C.

The metallographic observation was performed using OLYMPUS GX51 optical microscope and HITACHI S-4300. Phases present in the steels were identified by PANALYTICAL-MPD X-ray diffraction (Cobalt radiation, scan rate was 2° min⁻¹, and scan step size was 0.02 $^{\circ}$). Carbon extraction replicas were prepared for precipitate analysis including precipitate types and size distribution. The specimens were polished, and then etched in 4% nital for 2 min. A carbon coating about 20 nm in thickness was deposited on surface using an evaporator operated at a high vacuum. The carbon film coated surfaces of specimens were scribed using a blade to produce squares about 2×2 mm² in size. The replicas were released in 4% nital etched solution, and then analyzed in a transmission electron microscopy (TEM-Tecnai G^2F20). The particle size of precipitates was measured by a quantitative image analyzer. In addition, chemical analysis for precipitates was conducted using nanobeam EDS analysis.

3. Results

The mechanical properties of the steels are listed in [Table 2.](#page--1-9) All steels had an excellent tensile strength, ductility and low-temperature toughness. Compared with the 22Mn steel, the yield strength of the 24Mn-3.3Cr and 24Mn-6.3Cr-0.2N steels increased significantly with the addition of Cr and with Cr/N alloying. The yield strength of the 24Mn-3.3Cr steel was ~33 MPa higher than that of the 22Mn steel, while the tensile strength was lower than 22Mn steel. When the Cr content increased to 6.3% and 0.19% N was added, the yield strength of

Fig. 1. Phase equilibrium diagrams of (a) 22Mn, (b) 24Mn-3.3Cr and (c) 24Mn-6.3Cr-0.2N steels; (d) rolling and solid–solution treatment processes.

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