Casting and Constitutive Hot Flow Behavior of Medium-Mn Automotive Steel with Nb as Microalloying

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Abstract: A novel medium-Mn steel microstructure with 0.1 wt.% Nb was designed using Thermo-Calc and JMatPro thermodynamic simulation software. The pseudo-binary equilibrium phase diagram and time–temperature transformation (TTT) and continuous cooling transformation (CCT) diagrams were simulated in order to analyze the evolution of equilibrium phases during solidification and homogenization heat treatment. Subsequently, the steel was cast in a vacuum induction furnace with the composition selected from simulations. The specimens were heat-treated at 1200 °C and water-quenched. The results of the simulations were compared to the experimental results. The microstructure was characterized using optical microscopy (OM) and scanning electron microscopy (SEM). We found that the as-cast microstructure consisted mainly of a mixture of martensite, ferrite, and a low amount of austenite, while the microstructure in the homogenization condition corresponded to martensite and retained austenite, which was verified by X-ray diffraction tests. In order to design further production stages of the steel, the homogenized samples were subjected to hot compression testing to determine their plastic flow behavior, employing deformation rates of 0.083 and 0.83 s⁻¹, and temperatures of 800 and 950 °C.

Keywords: advanced high-strength steels (AHSS); medium-Mn steel; phase equilibrium

1. Introduction

The use of advanced high-strength steels (AHSS) in automotive parts has increased in recent years as they have been designed to meet the requirements of greater resistance while retaining their performance and conformability [1]. The AHSS are classified into three generations, according to their mechanical properties, mainly considering their ultimate tensile strength (UTS) and elongation...
The first generation of AHSS reaches a UTS of more than 600 MPa, but with a ductility below 20%, limiting its formability. The second generation of AHSS reaches excellent formability combined with resistance above 700 MPa and a ductility higher than 50%, but its high alloying elements content (>17 wt.%) increases the cost and hinders its automotive application [3]. The requirements to increase both resistance (UTS > 1200 MPa) and ductility (>30%) and reduce the alloying elements content and the associated cost have aroused interest in the development of the third generation of AHSS.

One type of steel that covers the combination of properties attributable to the third generation is the so-called “medium-Mn steel” [4]. This steel has a concentration of Mn in the range of 4–12 wt.% [5]. This steel is processed by intercritical annealing between the $A_{c1}$ and $A_{c3}$ intercritical temperatures, which is also named austenite-reverted-transformation (ART) annealing. As a consequence of ART annealing, the microstructure consists mainly of a large fraction of retained austenite ($\gamma_R$), ultrafine ferrite, and a small amount of martensite, which are responsible for the excellent mechanical properties that are attributed to medium-Mn steel. ART annealing is critical to obtain the retained austenite because the temperature and time strongly affect its volume fraction and mechanical stability [6–8], which triggers the phenomenon of twinning-induced plasticity (TWIP) and/or deformation transformation-induced plasticity (TRIP) during tensile deformation, improving the formability of AHSS [9,10]. Recently, Dong-Woo and Sung-Joon summarized some representative mechanical properties and austenite volume fractions of medium-Mn steels reported in the literature [11]. The ultimate tensile strength (UTS), total elongation (T. El), and austenite volume fraction ($\gamma_R$) are in the range of 808-1409 MPa, 15–58%, and 8–78%, respectively.

Although tensile properties such as tensile strength (UTS) and percentage of elongation (El.%) of the medium-Mn steels are extraordinary, an enhancement in the mechanical properties of these steels is still sought. In this sense, the use of micro-alloying elements such as Nb, V, Mo, and Ti has been recently used for this purpose [12–14]. However, the number of published studies on the effect of micro-alloying elements in medium-Mn steels is currently limited.

In addition, the deformation behavior of this new steel grade at high temperature has not been extensively studied. On an industrial scale, hot deformation processes such as rolling are carried out in austenitic and austenitic–ferritic phase regions in the interval between 800 and 1100 °C. For this reason, it is important to understand the microstructure evolution and plastic flow behavior around these temperatures. This will aid the design and optimize hot rolling process parameters such as the rolling temperature range, load requirements, strain rate, and pass reduction schedule. Nevertheless, previous studies have been mainly focused on the hot flow behavior of medium-Mn steel without micro-alloying elements [15–17].

Moreover, computer simulations have become indispensable for efficiently designing and developing these steels with specific properties for automotive applications. In this sense, it is essential to use simulated diagrams that allow for the study of the thermodynamic stability of the phases and their transformations, thus selecting the optimal route for heat treatment to achieve a given set of properties. Consequently, the simulated diagrams obtained through software such as Thermo-Calc® and JMatPro® have been widely used for this purpose [18,19].

Therefore, the objective of this investigation is to analyze the stable phases at room temperature in as-cast and homogenized states by thermodynamic simulation software in conjunction with microstructural characterization and the influence of deformation temperatures (850 and 900 °C) and strain rates (0.08 and 0.8 s$^{-1}$) on the hot flow behavior of medium-Mn steel micro-alloyed with Nb. For this purpose, Fe–C phase diagrams and property diagrams were calculated, and the predicted microstructure was qualitatively validated by experimental methods. Thereafter, hot compression tests were done to test whether Nb would exhibit a refining effect in the microstructure of this steel, as has been reported previously in high-strength low-alloy (HSLA) steels. This model will be used in the simulation of further stages of the hot working processing of this steel.
2. Materials and Methods

Thermodynamic calculation was performed to analyze the equilibrium phases and the corresponding property diagram of medium-Mn steel by using the TCFE9 database of the Thermo-Calc software v2018b (Thermo-Calc Software Inc., Solna, Sweden) [20,21] for the following nominal composition: Fe-0.14C-1.5Al-1.7Si-6.5Mn-0.1Nb (wt.%). Afterward, the medium-Mn steels were produced in a vacuum induction melting furnace. Rectangular bars of 100 mm × 100 mm and 250 mm in length were obtained after a casting and solidification process. Subsequently, square samples of cast steel of 30 mm × 30 mm with a thickness of 5 mm were homogenized in a tube furnace at 1200 °C for 2 h followed by water quenching. Thereafter, the Rockwell hardness of the as-cast and homogenized samples was measured. The average value was calculated from 10 indentations. The homogenized steel samples were machined into cylindrical pieces 10 mm high and 5 mm in diameter to carry out the hot compression tests. These tests were performed in the universal testing machine Instron model 1100 of 60 tons of capacity (Instron corporation, Norwood, MA, USA). Hot compression tests were performed with strain rates of 0.083 and 0.83 s⁻¹ and temperatures of 800 and 950 °C, using TiO₂ as a lubricant.

The metallographic analysis was used to characterize the as-cast and homogenized alloy. Optical microscopy (OM) and scanning electron microscopy (SEM) were used to observe the microstructures of the steel. The samples for optical and electron microscopy were color-etched as follows: Pre-etching for 1–2 s in Nital solution followed by etching for 20 s in sodium metabisulfite solution. The microstructural examinations were performed on an Olympus GX51-inverted reflected light microscope (Olympus Corporation, Tokyo, Japan) and a JEOL-6610LV scanning electron microscope at 30 kV (JEOL Ltd., Tokyo, Japan).

The phases present in the as-cast and homogenized conditions were determined by X-ray diffraction using the diffractometer Rigaku D/Max2200 (Rigaku Corporation, Tokyo, Japan) employing a Cu-Kα radiation source (λ = 1.5405 Å). The scanning range and step size were 30–100°, 1 s/step, and 0.02°, respectively. The MAUD software v2.92 (Luca Lutterotti, University of Trento, Italy).

Join institution (based on the Rietveld refinement method) was used for quantitative analysis by using the PDF-2/Release 2010 database. According to the powder diffraction file (PDF) database of the International Centre for Diffraction Data (ICDD), the PDF card number of austenite and ferrite phases was 00-052-0513 and 00-006-0696, respectively.

JMatPro software7.0.0 (Sente Software Ltd., Guildford, UK) was used to calculate the time–temperature transformation (TTT) and continuous cooling transformation (CCT) diagrams, to explain the evolution of the phases as a function of both time and temperature parameters during solidification and homogenization processes. It was necessary to evaluate the previous austenite grain size and the chemical composition in the as-cast state in order to build these diagrams. The CCT diagram was calculated at 1400 °C because, at that temperature, the steel had completely solidified while the TTT diagram was calculated at 1200 °C, because the homogenization heat treatment was performed at that temperature.

3. Results and Discussion

3.1. Thermodynamic Calculations

In order to predict the microstructure of the as-cast medium-Mn steel alloyed with Nb, its pseudo-binary phase diagram was simulated using Thermo-Calc software and is plotted in Figure 1a. The diagram predicts that the delta ferrite (δ) phase is formed from the liquid when the temperature decreases to around 1460 °C. As the cooling progresses, the solidification is completed at a temperature of 1400 °C, and below this temperature, the delta ferrite (δ) phase begins to transform into the austenite (γ) phase. Around 1300 °C, the transformation of the δ to γ phase is completed and the formation of the NbC phase begins. The formation of NbC ends when the temperature decreases to about 840 °C. Starting from this temperature and until it reaches about 620 °C, a part of the γ phase dissolves to form...
ferrite ($\alpha$), resulting in a phase-field where $\gamma + \alpha + \text{NbC}$ coexists. Below 620 °C, the transformation of $\gamma$ to cementite occurs. Around 460 °C, the cementite is transformed into $\text{M}_2\text{C}_6$ carbides and at 340 °C, the remaining $\gamma$ is transformed into the $\beta$-Mn phase. Then, in the range from 200 °C to room temperature, the stable phases are $\alpha + \text{M}_2\text{C}_6 + \text{NbC} + \beta$-Mn. In the range from 200 °C to room temperature, the $\beta$-Mn phase transforms to $\alpha$-Mn. Finally, the stable phases at room temperature are $\alpha + \text{M}_2\text{C}_6 + \text{NbC} + \alpha$-Mn.

![Simulated diagrams obtained by using Thermo-Calc software: (a) Pseudo-binary phase diagram, (b) amount of niobium in the phases as a function of temperature, and (c) amount of phases as a function of temperature.](image)

In Figure 1b, it is predicted that in the stable region of austenite, from 840 to 1380 °C, Nb is present as a solute or as an NbC phase. The presence of Nb in both states affects the high-temperature thermomechanical processing in the austenite region. Solute Nb retards austenite recrystallization and grain growth after deformation through the solute drag effect. In addition, solute Nb delays the transformation kinetics from $\gamma$ to $\alpha$. On the other hand, the NbC phase can serve as additional ferrite nucleation sites and increases the rate of transformation from $\gamma$ to $\alpha$.

Furthermore, the temperatures $\text{Ac}_1$ and $\text{Ac}_3$ (intercritical temperatures calculated by Thermo-Calc) are 620 and 840 °C, respectively, and the temperature at which the volume fraction of austenite and ferrite is equal is 714 °C, as shown in Figure 1c. Defining these temperatures will serve to optimize the further processing by the application of the intercritical annealing process as the annealing temperature and time determine the microstructure, specifically, the volume fraction of retained austenite ($\gamma_R$) and, in turn, the mechanical properties of the steel. However, it is important to note that some equilibrium phases at lower temperatures might not form in the as-cast microstructure due to a cooling
rate, unlike the thermodynamic equilibrium experiment during solidification. In order to deepen the understanding regarding the solidification and homogenization according to the cooling rate, JMatPro software was employed and the CCT and TTT transformation diagrams were built (Figure 2).

![CCT Diagram](image1)

![TTT Diagram](image2)

**Figure 2.** Diagrams simulated by using JMatPro software: (a) Transformation diagram in continuous cooling (CCT) and (b) time–temperature transformation diagram (TTT).

The cooling rate during solidification was close to 10 °C/min, which was measured using a thermocouple attached to the ingot mold. As shown in Figure 2a, this cooling rate crossed the start of ferrite formation and shows that neither perlite nor bainite could form in the sample. Therefore, according to the CCT diagram, it is expected that the microstructure in the as-cast state only consisted of martensite and ferrite. On the other hand, as shown in Figure 2b, at approximately 750 °C and 30 s, ferrite formation started, so the microstructure after the homogenization heat treatment is expected to be formed only by martensite and probably some retained austenite as the cross-section of steel samples was smaller than 5 mm and the quenching process was done in less than 15 s.

3.2. Microstructural Characterization of As-Cast and Homogenized Samples

X-ray diffractograms measured in the as-cast and homogenization condition are shown in Figure 3a,b. It can be noted that, in the first condition, there are several strong peaks from ferrite/martensite phases that formed during solidification. Weak diffraction signals are observed from the austenite phase in the corresponding diffractogram. On the other hand, it is evident that the austenite peak intensity increased after the steel was homogenized and quenched, while the intensity of the peaks from the ferrite/martensite phases decreased slightly. According to the thermodynamic calculation shown in Figure 2b, the microstructure was composed of martensite after homogenization and quenching. However, due to the segregation present in the microstructure, even after homogenization, there are regions in which the austenite phase was retained.

A quantitative analysis was performed using MAUD software, which is based on the Rietveld refining method [22]. It is shown that the austenite content in the as-cast condition was 2% (sigma = 1.49, Rwp (%) = 49.03), while this amount increased to 20% (sigma = 1.27, Rwp (%) = 39.03), after homogenization and quenching. Although austenite is a softer phase compared to martensite, the increment in the amount of the former phase after homogenization and water quenching was not reflected in the hardness of the steel, which was 5.03 GPa (50 HRc) in the as-cast condition and 5.83 GPa (55 HRc) after homogenization and quenching. This increment in hardening can be attributed to the dissolution and re-distribution of all alloying elements in the austenite matrix during the homogenization treatment, as it is shown in Figure 4, which was calculated by Thermo-Calc simulations. Consequently, solid solution strengthening had a higher effect in martensite formed from
the homogenization compared to the same phase in the as-cast state as Mn, Al, and Si were completely dissolved at 1200 °C.

![Figure 3](image3.png)

**Figure 3.** X-ray diffractograms of (a) as-cast and (b) homogenized samples.

![Figure 4](image4.png)

**Figure 4.** Distribution of alloying elements in the austenite matrix as a function of temperature.

The microstructure was characterized before and after homogenization heat treatment. Figure 5a,b and Figure 5c,d are optical and scanning electron microscope images showing the typical microstructure of the as-cast condition. Figure 5a,b show that the microstructure was composed of martensite with some off-white ferrite in the grain boundaries. Figure 5c shows that the morphology of this martensite was thin laths. Inside the laths, some carbide precipitates were observed (Figure 5d); presumably, these carbides can be of type Mn\(_{23}\)C\(_6\) or cementite according to Thermo-Calc predictions (Figure 1b). Recently, the former type was observed in 0.086%C–8.05%Mn–0.138%Si–0.0215%Al–Fe (wt.%) in the as-cast condition [19] and the latter has been reported to occur in GX12CrMoVNbN9-1 (GP91) cast steel [23]. When there is carbide precipitation in martensite laths, usually as small bars or plates morphologies, the phenomenon has been reported in the literature as auto-tempered martensite [24,25].
Figure 5. (a,b) Optical and (c,d) scanning electron microscope images showing the microstructure of as-cast condition.

At the same magnification, in Figure 6a,b and Figure 6c,d the microstructure of the steel is shown after homogenization and water quenching. Figure 6a,b show that the microstructure consisted of lath martensite in addition to retained austenite. On the other hand, there is no ferrite evidence in the microstructure. The absence of this phase is the result of the cooling rate (water quenching), considering that it was high enough to avoid the formation of this phase in agreement with the CCT diagram. The above results matched well with the diagrams simulated via JMatPro® and X-ray diffraction tests. Likewise, in Figure 6c, martensite laths are observed, but the presence of carbides inside the laths is not evident. As the homogenization was performed at 1200 °C, this temperature allowed M23C6 and/or cementite formed in the as-cast state to dissolve in the austenite, resulting in a greater amount of carbon available to incorporate in solid solution into this phase. On the other hand, in Figure 6d,e, the presence of NbC carbides in the austenite, previous grain boundaries, and their corresponding energy-dispersive X-ray (EDX) spectrum can be seen. The carbide evidence coincides with Thermo-Calc simulations, as according to Figure 1b, at 1200 °C, the Nb is both in the form of carbide and solid solution in the austenite matrix.
Figure 6. (a,b) Optical and (c,d) scanning electron microscope images showing the microstructure of the homogenized condition; (e) energy-dispersive X-ray (EDX) spectra of Nb carbides.

Figure 7 shows the results of the characterization of inclusions of the steel in the as-cast condition by means of the energy-dispersive X-ray (EDX) technique. The measurements confirmed the presence of coarse particles of aluminum nitrides (AlN) (Figure 7a) and small particles of manganese sulfides (MnS) (Figure 7b).
3.3. The High-Temperature Flow Stress Behavior

As mentioned earlier, hot deformation is carried out on an industrial scale in the temperature range from 800 to 1100 °C. For this reason, hot compressions were carried out considering both γ + NbC and γ + α + NbC phase regions to observe the effect of these phases on the hot plastic flow behavior. Therefore, Figure 8 shows the high-temperature flow curves of the medium-Mn steels with 0.1% Nb at two different deformation temperatures (800 °C and 950 °C) and two strain rates (0.083 and 0.83 s⁻¹). All the curves show a similar behavior where the flow stress increases with decreasing deformation temperature and increasing strain rate. In addition, the curves show a steady-state flow stress after they reach the highest stress. This behavior is characteristic of the softening process called dynamic recovery, which may occur during deformation at high temperatures. The main reason for this behavior is that a higher strain rate gives rise to a higher dislocation density, which will promote a higher stored energy and flow stress, while a higher deformation temperature weakens the resistance to dislocation motion, consequently reducing work hardening. These results are consistent with previous research about the effect of Nb on hot plastic flow behavior [26,27]. On the other hand, the results do not match at low strain rates [26,27], because, in contrast to the aforementioned investigations, we did not observe dynamic recrystallization evidence (DRX).

This disagreement may be associated with the presence of Nb, because, as predicted by Thermo-Calc calculations (Figures 1b and 4), in the stable region of austenite (840–1380 °C), this micro-alloying element is present both in the form of carbides and as Nb in solution in austenite. According to Thermo-Calc, the amount of Nb as solute and as NbC at 800 °C is close to 0.2 and 0.8 wt.%, respectively, whereas at 950 °C, it is approximately 0.4 and 0.6 wt.% respectively.

Xiao et al. [28] suggested that the Nb in solution has a greater inhibiting effect on austenite dynamic recrystallization than NbC during hot deformation. However, it should be mentioned that, at present, there are very few published studies regarding the effect of niobium in medium-manganese steels during its thermomechanical processing [29].
The modified Johnson–Cook model was selected to develop the hot constitutive equation of the analyzed steel [30]. This constitutive equation will aid further simulation by the finite element of the thermomechanical forming processes to which the material will be subjected. The modified Johnson–Cook model was proposed by Lin et al. [30]:

\[
\sigma = \left( A_1 + B_1 \varepsilon + B_2 \varepsilon^2 \right) \left[ 1 + C_1 \ln \dot{\varepsilon}^* \right] \exp \left[ \left( \lambda_1 + \lambda_2 \ln \dot{\varepsilon}^* \right) \left( T - T_{\text{ref}} \right) \right],
\]

(1)

where \( A_1, B_1, B_2, C_1, \lambda_1, \lambda_2 \) are material constants, \( \sigma \) is the equivalent stress, \( \varepsilon \) is the equivalent plastic strain, and \( \dot{\varepsilon}^* = \frac{\dot{\varepsilon}}{\varepsilon_{\text{ref}}} \) is the dimensionless strain rate. \( \varepsilon_{\text{ref}} \) and \( T_{\text{ref}} \) are the reference strain and reference deformation temperature, respectively. In this experiment, the reference strain and reference temperature were 0.83 s\(^{-1}\) and 800 °C, respectively, to determine the material constants in Equation (1).

To determine the \( A_1, B_1, B_2 \) constants, the reference temperature \( T_{\text{ref}} = 800 \) °C and reference deformation \( \varepsilon_{\text{ref}} = 0.83 \) s\(^{-1}\) were substituted into Equation (1), which transforms to

\[
\sigma = A_1 B_1 \varepsilon + B_2 \varepsilon^2.
\]

(2)

Substituting stress and strain data under the deformation conditions, a \( \sigma \sim \varepsilon \) curve was drawn, two-order polynomial fitting was conducted, and the values of \( A_1, B_1, \) and \( B_2 \) were determined to be 232.92, 131.87, and -551.35 MPa, respectively.

The constant \( C_1 \) was determined by substituting the reference temperature \( T_{\text{ref}} = 800 \) °C into Equation (1), which transforms to

\[
\sigma = \left( A_1 + B_1 \varepsilon + B_2 \varepsilon^2 \right) \left[ 1 + C_1 \ln \dot{\varepsilon}^* \right].
\]

(3)

Rearranging Equation (3):

\[
\frac{\sigma}{A_1 + B_1 \varepsilon + B_2 \varepsilon^2} = 1 + C_1 \ln \dot{\varepsilon}^*.
\]

(4)

At two different strain rates of 0.083 and 0.83 s\(^{-1}\), the stress values corresponding to eight strain values of 0.06, 0.07, 0.08, 0.09, 0.10, 0.15, 0.20, and 0.25 were selected. A total of 16 groups of data were gained. Substituting these data and \( A_1, B_1, \) and \( B_2 \) into Equation (4), a \( \frac{\sigma}{A_1 + B_1 \varepsilon + B_2 \varepsilon^2} \sim \ln \dot{\varepsilon}^* \) curve was drawn, and it was linearly fitted, obtaining \( C_1 = 0.1208 \).

Then, to determine \( \lambda_1 \) and \( \lambda_2 \) constants, the equation was rearranged in the following form:

\[
\frac{\sigma}{(A_1 + B_1 \varepsilon + B_2 \varepsilon^2) \left[ 1 + C_1 \ln \dot{\varepsilon}^* \right]} = \exp \left[ \left( \lambda_1 + \lambda_2 \ln \dot{\varepsilon}^* \right) \left( T - T_{\text{ref}} \right) \right].
\]

(5)
Natural logarithms were taken on both sides of Equation (5), obtaining

$$\ln\left(\frac{\sigma}{(A_1 + B_1 \varepsilon + B_2 \varepsilon^2)(1 + C_1 \ln \dot{\varepsilon}^*)}\right) = \left[(\lambda_1 + \lambda_2 \ln \dot{\varepsilon}^*)(T - T_{\text{ref}})\right].$$

(6)

At two different strain rates of 0.083 and 0.83 s\(^{-1}\) and two different deformation temperatures of 800 and 900 °C, stress values corresponding to the eight above-mentioned strains were taken. A total of 32 groups of data were obtained. Substituting these data and \(A_1\), \(B_1\), \(B_2\), and \(C_1\) into Equation (6), \(\ln\left(\frac{\sigma}{(A_1 + B_1 \varepsilon + B_2 \varepsilon^2)(1 + C_1 \ln \dot{\varepsilon}^*)}\right) \sim (T - T_{\text{ref}})\) curves were drawn under the two strain rates, and a linear fitting was done. The values of \(\lambda_1 + \lambda_2 \ln \dot{\varepsilon}^*\) under strain rates of 0.083 and 0.83 s\(^{-1}\) were determined to be \(-0.0022\) and \(-0.0010\), respectively.

Finally, a \(\lambda_1 + \lambda_2 \ln \dot{\varepsilon}^* \sim \ln \dot{\varepsilon}^*\) curve was drawn and fit to a line, obtaining \(\lambda_1 = -0.0022\) and \(\lambda_2 = -0.0005\) from this fitting procedure.

Therefore, the constitutive equation that relates the stress \(\sigma\), strain \(\varepsilon\), deformation rate \(\dot{\varepsilon}\), and deformation temperature \(T\) was established according to the modified Johnson–Cook model:

$$\sigma = \left(232.92 + 131.87 \varepsilon - 551.35 \varepsilon^2\right)\left(1 + 0.1208 \ln\frac{\dot{\varepsilon}}{\varepsilon_{\text{ref}}}\right)\exp\left[-0.0022 - 0.0005 \ln\frac{\dot{\varepsilon}}{\varepsilon_{\text{ref}}}\right](T - T_{\text{ref}}).$$

(7)

The comparison between experimental flow stress values and predicted values by the modified Johnson–Cook model is shown in Figure 9a,b. It can be observed that the predicted and experimental values displayed minor deviations; however, it has acceptable relative accuracy, which was demonstrated by the calculation of the correlation coefficient (R) and mean absolute relative error (MARE).

![Figure 9](image-url)

**Figure 9.** Comparison between experimental and predicted values by the modified Johnson–Cook model at two temperatures (800 and 950 °C); and constant strain rates of (a) 0.083 and (b) 0.83 s\(^{-1}\).

The correlation coefficient (R) and mean absolute relative error (MARE) were used to provide information on the accuracy and effectiveness of the linear relationship between experimental and predicted values and measuring the predictability of a numerical model, respectively, as it is shown on Figure 10. The correlation coefficient was 0.9962 and the corresponding mean absolute relative error was 1.43%. Finally, it is important to point out that this model can only be used effectively for the simulation of the mechanical behavior of medium-Mn steel with 0.1 wt.% Nb in the range of the strain rate and deformation temperature conditions under which it was established [30].
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![Figure 9. Comparison between experimental and predicted values by the modified Johnson–Cook model at two temperatures (800 and 950 °C); and constant strain rates of (a) 0.083 and (b) 0.83 s⁻¹.](image)

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![Figure 10. The proximity of experimental and predicted values by the modified Johnson–Cook model.](image)

4. Conclusions

1. We found that the microstructure of the medium-Mn steel with 0.1 wt.% Nb consisted of lath martensite, ferrite, and small retained austenite in the as-cast condition, whereas, in the homogenized condition, the microstructure was lath martensite and retained austenite. The volume fraction of retained austenite in the as-cast and homogenized conditions was 2 and 20%, respectively.

2. The thermodynamic simulation of the equilibrium diagram allowed the selection of homogenization parameters and the predicted precipitation of carbides of the type M_{23}C_6 and/or NbC. Experimental observations confirmed the existence of these carbides in the homogenized condition along the previous austenite grain boundaries.

3. We found that Nb delayed recrystallization during hot plastic deformation as the stress–strain curves did not show any peak stress and only showed a steady-state flow stress value after reaching the highest stress. These results were associated with the NbC precipitates, as well as Nb in solid solution.

4. The constitutive equation established by the modified Johnson–Cook model and its corresponding parameters were calculated by fitting the experimental data, and the accuracy of the constitutive equation obtained was verified by using the correlation coefficient (R) and mean absolute relative error (MARE), which were 0.9962 and 1.42%, respectively.

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References

1. Abey, A. Metallic Material Trends in the North American Light Vehicle. In Proceedings of the Great Designs in Steel Seminars, Livonia, MI, USA, 13 May 2015.
2. Singh, S.; Nanda, T. A Review: Production of Third Generation Advance High Strength Steels. IJSRD 2014, 2, 388–392.
3. Cai, M.; Di, H. Advanced High Strength Steels and Their Processes. In Rolling of Advanced High Strength Steels: Theory, Simulation and Practice, 1st ed.; Zhao, J., Jiang, Z., Eds.; CRC Press: Boca Raton, FL, USA, 2017; pp. 1–25.
4. Fonstein, N. Evolution of Strength of Automotive Steels to Meet Customer Challenges. In Advanced High Strength Sheet Steels; Springer: Berlin, Germany, 2015; pp. 1–14.
5. Fonstein, N. Candidates for the Third Generation: Medium Mn Steels. In Advanced High Strength Sheet Steels; Springer: Berlin, Germany, 2015; pp. 297–325.
6. Shao, C.; Hui, W.; Zhang, Y.; Zhao, X.; Weng, Y. Microstructure and mechanical properties of hot-rolled medium-Mn steel containing 3% aluminum. Mater. Sci. Eng. A 2017, 682, 45–53. [CrossRef]
7. Bansal, G.K.; Madhukar, D.A.; Chandan, A.K.; Ashok, K.; Mandal, G.K.; Sirvastava, V.C. On the intercritical annealing parameters and ensuing mechanical properties of low-carbon medium-Mn steel. Mater. Sci. Eng. A 2018, 733, 246–256. [CrossRef]
8. Li, Z.C.; Ding, H.; Misra, R.D.K.; Cai, Z.H. Deformation behavior in cold-rolled medium-manganese TRIP steel and effect of pre-strain on the Lüders bands. Mater. Sci. Eng. A 2017, 679, 230–239. [CrossRef]
9. Lee, S.; De Cooman, B.C. Tensile Behavior of Intercritically Annealed Ultra-Fine Grained 8% Mn Multi-Phase Steel. Steel Res. Int. 2015, 86, 1170–1178. [CrossRef]
10. Latypov, M.I.; Shin, S.; Cooman, B.C.D.; Kim, H.S. Micromechanical finite element analysis of strain partitioning in multiphase medium manganese TWIP + TRIP steel. Acta Mater. 2016, 108, 219–228. [CrossRef]
11. Suh, D.-W.; Kim, S.-J. Medium Mn transformation-induced plasticity steels: Recent progress and challenges. Scr. Mater. 2017, 126, 63–67. [CrossRef]
12. Haijun Pan, H.D.M.C. Microstructural evolution and precipitation behavior of the warm-rolled medium Mn steels containing Nb or Nb-Mo during intercritical annealing. Mater. Sci. Eng. A 2018, 736, 375–382.
13. Hu, J.; Du, L.-X.; Dong, Y.; Meng, Q.-W.; Misra, R.D.K. Effect of Ti variation on microstructure evolution and mechanical properties of low carbon medium Mn heavy plate steel. Mater. Charact. 2019, 152, 21–35. [CrossRef]
14. Lee, D.; Kim, J.-K.; Lee, S.; Lee, K.; Cooman, B.C.D. Microstructures and mechanical properties of Ti and Mo micro-alloyed medium Mn steel. Mater. Sci. Eng. A 2017, 706, 1–14. [CrossRef]
15. Yan, N.; Di, H.-S.; Huang, H.-Q.; Misra, R.D.K.; Deng, Y.-G. Hot Deformation Behavior and Processing Mapps of Medium Manganese TRIP Steel. Acta Metall. Sin. (Engl. Lett.) 2019, 32, 1021–1031. [CrossRef]
16. Klinkenberg, C.; Varghese, A.; Heering, C.; Lamukhina, O.; Grafe, U.; Tokmakov, K. 3rd Generation AHSS by Thin Slab Technology. Mater. Sci. Forum 2018, 941, 627–632. [CrossRef]
17. Steineder, K.; Dikovits, M.; Beal, C.; Sommitsch, C.; Krizan, D.; Schneider, R. Hot deformation behavior of a 3rd generation advanced high strength steel with a Medium-Mn content. Mater. Sci. Forum 2015, 651–653, 120–125.
18. Na, H.-S.; Kim, B.-S.; Lee, S.-S.; Kang, C.Y. Thermodynamic Alloy Design of High Strength and Toughness in 300 mm Thick Pressure Vessel Wall of 1.25Cr-0.5Mo Steel. Metals 2018, 8, 70. [CrossRef]
19. Magalhaes, A.; Moutinho, I.; Oliveira, I.; Ferreira, A.; Alves, D.; Santos, D.B. Ultrafinegrained Microstructure in a Medium Manganese Steel after Warm Rolling without Intercritical Annealing. ISIJ Int. 2017, 57, 1121–1128. [CrossRef]
20. Djurovic, D.; Hallstedt, B.; Appen, J.; Dronskowski, R. Thermodynamic assessment of the Fe–Mn–C system. Calphad 2011, 35, 479–491. [CrossRef]
21. Zheng, W.-S.; Lu, X.-G.; He, Y.-L.; Li, L. Thermodynamic modeling of Fe-C-Mn-Si alloys. J. Iron Steel Res. Int. 2017, 24, 190–197. [CrossRef]
22. Young, R.A. The Rietveld Method; Oxford University Press: Oxford, UK, 1993; p. 298.
23. Golański, G. Mechanical properties of GX12CrMoVNbN91 (GP91) cast steel after different heat treatments. Mater. Sci. 2012, 48, 384–391. [CrossRef]
24. Zajac, S.; Schwinn, V.; Tacke, K.-H. Characterisation and Quantification of Complex Bainitic Microstructures in High and Ultra-High Strength Linepipe Steels. *Mater. Sci. Forum* **2005**, *500–501*, 387–394. [CrossRef]

25. Bhadeshia, H.K.D.H.; Honeycombe, S.R. 9-The Tempering of Martensite. In *Steels*, 3rd ed.; Bhadeshia, H.K.D.H., Honeycombe, S.R., Eds.; Butterworth-Heinemann: Oxford, UK, 2006; pp. 183–208.

26. Wei, H.-L.; Liu, G.-Q. Effect of Nb and C on the hot flow behavior of Nb microalloyed steels. *Mater. Des.* **2014**, **56**, 437–444. [CrossRef]

27. Bao, S.; Zhao, G.; Yu, C.; Chang, Q.; Ye, C.; Mao, X. Recrystallization behavior of a Nb-microalloyed steel during hot compression. *Appl. Math. Model.* **2011**, **35**, 3268–3275. [CrossRef]

28. Xiao, F.-R.; Cao, Y.-B.; Qiao, G.-Y.; Zhang, X.-B.; Liao, B. Effect of Nb Solute and NbC Precipitates on Dynamic or Static Recrystallization in Nb Steels. *J. Iron Steel Res. Int.* **2012**, **19**, 52–56. [CrossRef]

29. Speer, J.G.; Araujo, A.L.; Matlock, D.K.; Moor, E. Nb-Microalloying in Next-Generation Flat-Rolled Steels: An Overview. *Mater. Sci. Forum* **2016**, **879**, 1834–1840. [CrossRef]

30. He, A.; Xie, G.; Zhang, H.; Wang, X. A Comparative Study on Johnson–Cook, Modified Johnson–Cook and Arrhenius-Type Constitutive Models to Predict the High Temperature Flow Stress in 20CrMo Alloy Steel. *Mater. Des.* **2013**, **52**, 677–685. [CrossRef]