Mechanical Properties and Phases Derived from TiO₂ Nanopowder Inoculation in Low Carbon Steel Matrix

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The effect of TiO₂ nanoparticle addition on mechanical properties of low carbon steel and the phases originated from this inoculation were investigated. Equilibrium phases were estimated by means of thermodynamic modeling and the results were compared with further microscopy characterization. Both techniques confirmed the dissolution of TiO₂ nanoparticles in the molten steel which derived in TiN and Ti₄C₂S₂ nanometric reaction products. The formation of these nanometric phases, were found to result in ferrite grain refinement and consequently in the enhancement of mechanical properties. In addition, the formation of these phases led to C and N depletion from the iron matrix and to a continuous yielding behavior in tensile stress-strain curves. [doi:10.2320/matertrans.M2013073]

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1. Introduction

Reinforcement by a fine and homogeneous dispersion of second-phase nanoscale particles is an effective way to achieve strengthening and stability in a metal matrix. Precipitation strengthening arises from looping of the dislocations between hard undeformable particles as described by Orowan.¹⁾ Non-metallic precipitates may also pin grain boundaries, thereby inhibiting austenitic grain growth.²⁾ In the latter case, their effectiveness as pinning sites is inversely proportional to their diameter and for this reason, finely dispersed particles should have a size below 100 nm to function optimally.³⁾

On the grounds of the aforementioned particle strengthening mechanisms, several steel grades have been historically developed. For instance, the well-known high strength low alloy steels are characterized by a small amount of alloying elements (Ti, Nb, V) which induce a fine grained microstructure, and the presence of very fine carbonitrides.⁴⁾ On the other hand, oxide dispersion strengthened steel grades (ODS) explore the addition of nano oxide particles in ferritic matrices through production routes, like powder metallurgy, which does not allow the production of large quantities exhibiting excellent quality, in terms of microstructural and mechanical properties homogeneity.⁵⁾ Alternatively, the manufacturing of ODS liquid steel by the metallurgy production route presents technical challenges that must still be addressed. In fact, classical and conventional casting methods have failed to produce uniformly dispersed oxides in casted steels due mostly to the difficulties in preventing the accumulation of oxide particles on the surface of the ingots.⁶⁾ However, recent research works have reported laboratory scale investigations based on the liquid metallurgy route with promising results aiming at the dispersion of nanophase particles in low alloy steel grades, but there is still very little research work found in the literature. K. Verhiest *et al.*⁷⁾ introduced a dispersion of nanosized yttrium oxides particles

into a steel matrix and concluded that the upper temperature limit in mechanical creep strength can be enhanced by at least 100 K. Furthermore, Hossein *et al.*⁸⁾ concluded in their work that when titanium oxide nanopowder is inoculated in plain carbon steel, fine intragranular ferrite is formed. Besides, particle incorporation into a liquid metal matrix is associated with mechanical and thermodynamic barriers in terms of wettability. This parameter was studied in a previous research work⁹⁾ which revealed that iron liquid drop presents high reactive wettability on sintered nano TiO₂ substrate, therefore it proves to be a good candidate to be added in a ferrous liquid matrix.

The motivation behind the work comes from the fact that the deliberate introduction of non-metallic inclusions are known to have a great efficacy in promoting desired microstructures. For instance, the efficacy of various non-metallic inclusions such as TiO₂, Ti₂O₃, TiN, VC, MnS, MnAl₂O₄ and Al₂O₃ has been examined already. It has been demonstrated that the nucleation potential of a given non-metallic inclusion is not exclusive and, in fact, depends on the nature of the nucleating phase, the chemical composition of the surrounding matrix and the transformation temperatures.^{10,11)}

The current work aims at contributing to the knowledge and understanding of the liquid metallurgy route for nanoparticle inoculation in a ferrous matrix. This production route seems to be a potentially and an innovative way of achieving the dispersion of second phase nanometric range particles compared with the powder metallurgical techniques used until now. The aim of the work is therefore to study the influence of titanium oxide nanopowder on the microstructure and the mechanical properties of a low carbon steel matrix when it is inoculated through liquid metallurgy. In this sense, thermodynamic stability and the reaction products derived from the dissolution of titanium oxide nanopowder in the steel matrix are also studied. This fact, which has proven to be an interesting route from which the remaining carbon and nitrogen in solution are stabilized through Ti-rich precipitates, and the results will be compared with the current titanium microalloyed or interstitial free steels (IF).

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Table 1 Chemical composition of low alloy carbon steel matrix and TiO₂ nanopowder inoculated low carbon steel matrix (mass%).

	Fe	C	Mn	Si	Ti	S	Ni	Cu	N	O (ppm)
Low alloy carbon steel	Bal.	0.09	0.03	0.15	0.001	0.007	0.02	0.01	0.002	27
TiO ₂ inoculated low carbon steel	Bal.	0.09	0.05	0.19	0.046	0.007	0.02	0.01	0.007	90

Fig. 1 TiO₂ P25 nanopowder X ray diffraction pattern.

2. Experimental Procedures

2.1 Materials and casting conditions

Table 1 shows the chemical analysis of the low carbon steel used within this study and the TiO₂ nanopowder inoculated low carbon steel. The TiO₂ nanopowder to be inoculated in the ferrous matrix is a commercially available Aeroxide®, P25, with an average particle size: $d_0 = 21$ nm. The X ray diffraction pattern shown in Fig. 1 shows two crystalline polymorphs present in the nanopowder, (a) anatase, with lattice parameters $a = 0.37852$, $b = 0.37852$ and $c = 0.95139$ (nm); and (b) rutile, with lattice parameters $a = 0.46083$, $b = 0.46083$ and $c = 0.29592$ (nm), being the anatase-rutile ratio 80:20.

The TiO₂ nanopowder addition into low carbon steel was performed by melting the alloy in a 5 kg high alumina crucible using an induction furnace in the 25–45 kHz frequency range. The inoculation of titanium dioxide nanopowder (0.8 mass%) was carried out through an original incorporation method, which comprised of inserting the powders into the melted iron stream during the sand mold pouring step. The melt temperature was measured through a B type thermocouple (maximum temperature: 1873 K). During the iron melting step, the melted surface was maintained using a pure argon gas flux (99.999%) to prevent oxidation of the melt. Another series with low carbon steel was melted and solidified under the same conditions in order to compare further mechanical and microstructural analyses. The 40 mm diameter specimens were hot-forged at 1473 K to 30 mm diameter, with a total reduction of 1.77 and were subjected to normalizing heat treatment (1193 K/1 h) followed by air cooling to room temperature for the tensile tests. Further microstructure and inclusion analysis was performed from mechanically tested specimens.

2.2 Analysis methods

Computational thermodynamic predictions were performed in order to know the phase equilibrium in the titanium oxide inoculated steel matrix through the Thermo-Calc software package. This software is a widely used and carefully verified thermochemical analysis software for multiphase equilibrium calculations in multicomponent systems. A combination of two software databases, TCS steels/Fe alloys database (TCFE) and SGTE substances database (SSUB), were applied in the present work to access appropriate thermodynamic data.

Transmission electron microscopy (TEM) was used to observe and analyze precipitates found in the inoculated matrix. The carbon extraction replicas method was followed for sample preparation. Several replicas were prepared by this method which allows separating the precipitates for study without any interference from the matrix. These were prepared by etching the polished surface in 2% nital and coating the surface with a thin carbon film using a Modular High Vacuum Coating System (Baltec, MED-004). The covered surface was then etched with 10% nital and finally the replicas were stripped in distilled water and supported in copper squared mesh. The TEM investigations were conducted with a PHILIPS CM200 microscope, supported with a supertwin lens, LaB₆ filament and equipped with EDS microanalysis. A field emission gun-scanning electron microscope (FEG-SEM) was used to analyze larger non-metallic inclusions.

The tensile tests were carried out according to the European standard UNE-EN ISO 6892-1:2010 at room temperature. Round tensile specimens were prepared in the longitudinal direction, having a gage diameter of 5 mm and gage length of 30 mm and were tested at room temperature at a crosshead speed of 0.05 mm/min in a MTS universal testing machine model 322.21 of 10 kN capacity. Four tensile tests were performed for each kind of specimen (titanium inoculated low carbon steel and non-inoculated low carbon steel).

The microstructure of the ferrous alloys (with and without TiO₂ nanopowder addition) were mounted, ground and polished using standardized metallographic preparation techniques. Following metallographic preparation, samples were etched in 2% nital and examined in a Leica DMI 5000M light optical microscope.

3. Results and Discussion

3.1 Thermodynamic modeling

The analysis aimed at assessing TiO₂ stability in the system considering the inoculated steel composition. Under ideal and equilibrium conditions phase equilibrium as a function of temperature was predicted using Thermo-Calc

Fig. 2 (a) Mass fraction of phases predicted in the TiO₂ nanopowder inoculated low carbon steel matrix as a function of temperature, (b) mass fraction of Ti, N and C present in the FCC crystal structure Ti(CN) precipitate as a function of temperature.

software with TCFE and SGTE substance databases. The TCFE is a steel/Fe alloys database which covers the critical assessments of many important systems within the 25 element framework. In turn, the SGTE database is a large database which contains over 5000 condensed compound or gaseous species.¹²⁾ The latter database has been used to append additional information to the TCFE database for other inorganic compounds as it is the case of the rutile phase (TiO₂), among other phases. The complementary use of both databases allows including the thermodynamic data for many non-metallic phases which may form in the ferrous alloy.

The chemical composition of the TiO₂ inoculated steel used for thermodynamic modelling calculations shows higher nitrogen and oxygen contents which are considered to influence on microstructures and mechanical properties. On the one hand, nitrogen is the main element which is known to be an interstitial element on the ferritic matrix because of small atom size and the electronic shell structure showing high diffusivity. Otherwise, it is known that nitrides are easily formed in the matrix affecting mechanical properties if nitrogen remains in solid solution or forming very fine and coherent nitrides, not to mention the fact that fine nitrides are known to be effective grain refiners. On the other hand, oxygen content is obvious to increase after TiO₂ nanoparticle inoculation in the melt. However, since the solubility of oxygen in liquid iron is known to be low, it combines to form non-metallic oxide inclusions during solidification. The total oxygen content and the oxides may affect negatively mechanical properties if they do not meet specific requirements, i.e., as inclusions can promote microvoid coalescence, the impact toughness is normally seen to increase with decreasing oxygen content.

Figure 2 shows the mass fraction of the phases in the equilibrium for the inoculated low carbon steel with regard to temperature. According to Fig. 2(a) the liquid steel solidifies at approximately 1765 K in conjunction with the formation of delta ferrite (BCC). The corundum crystal structure (Al₂O₃ with Ti in solid solution) is also formed in the liquid range, at around 1972 K and its mass fraction increases when decreasing temperature. Moreover, Ti₄C₂S₂ is readily formed

when the steel solidifies and as the temperature is decreased, MnS precipitate increases, while titanium carbo-sulfide decreases after passing through a maximum. This equilibrium approximation reveals there is a competing behavior between both precipitates for available sulfur. On the other hand, a Ti(CN) face-centered crystal cubic structure phase is found as a governing non-metallic phase in the present system which sharply increases during solidification. This phase contains the elements Ti, C and N in a stoichiometry which varies with temperature as shown in Fig. 2(b). This major phase does not show separate phases of TiN or TiC. It is a fact that binary carbides and nitrides precipitated in steels have a similar FCC lattice structure and their mutual solubility is likely, in this sense it should be clarified here that Thermo-Calc treats TiN and TiC as a single Ti(CN) phase since they do have the same FCC crystal structure.¹³⁾ The compound stoichiometry would be defined as Ti(C_yN_{1-y}) which is frequently simplified as Ti(CN), being y the mole fraction of C in the carbonitrides and $0 \leq y \leq 1$. Figure 2(b) suggests that at temperatures above 1300 K, the precipitate is TiN, while at lower temperatures the phase precipitates to a TiC stoichiometry like compound.

As shown in Fig. 2, Thermo-Calc does not predict the formation of TiS particles, while there is evidence of its formation in Ti-added steels. It is well known that in Ti-added ultra low carbon steels (IF-Steels) there exist various kinds of precipitates such as TiN, Ti₄C₂S₂, TiS and TiC and so on that significantly influence mechanical properties. The solubilities in austenite of the carbides, nitrides, carbonitrides and carbo-sulfides significantly affect the precipitation behavior of these compounds. Therefore, it is of interest to compare the solubility products of the compounds typically found in Ti-modified IF steels in austenite. Their equations are:

$$\text{Log}[\text{Ti}][\text{C}] = 5.33 - 10475/T^{14)} \quad (1a)$$

$$\text{Log}[\text{Mn}][\text{S}] = -9020/T + 2.929^{15)} \quad (1b)$$

$$\text{Log}[\text{Ti}][\text{S}] = -3252/T - 2.01^{16)} \quad (1c)$$

$$\text{Log}[\text{Ti}][\text{C}]^{0.5}[\text{S}]^{0.5} = -0.78 - 5208/T^{16)} \quad (1d)$$

$$\text{Log}[\text{Ti}][\text{N}] = -14400/T + 4.94^{17)} \quad (1e)$$

Fig. 3 TEM image and punctual EDS analysis of $\text{Ti}_4\text{C}_2\text{S}_2$ inclusion.

It is worth mentioning that the methodology used for the experimental determination of the constants A and B in the general equation $\log[M][I] = A + B/T$ is restricted to the relatively narrow compositions of the steels tested. However, the solubility of products increases in the order: $\text{TiN} < \text{TiC}_{0.5}\text{S}_{0.5}(\text{Ti}_4\text{C}_2\text{S}_2) < \text{TiS} < \text{MnS} < \text{TiC}$ in the typical hot working range (± 1100 – 1600 K). However, as the temperature is lowered, $\text{Ti}_4\text{C}_2\text{S}_2$ becomes increasingly more stable than TiS because the solubility product for TiS is significantly weaker than that for $\text{Ti}_4\text{C}_2\text{S}_2$.

The precipitation behavior of these non-metallic inclusions is hardly influenced by the chemical composition, especially the influence of S and Ti contents. Yoshinaga *et al.*¹⁶⁾ investigated the influence of S and Ti contents as well as slab reheating temperature on the precipitation behavior of sulfides in hot-rolled bands. According to the results, specimens with S content as high as 0.017% TiS were only found, whereas for lower contents (0.0095%) both $\text{Ti}_4\text{C}_2\text{S}_2$ and TiS were detected. On the other hand, in specimens with low Ti content (0.008%) the TiS was observed and $\text{Ti}_4\text{C}_2\text{S}_2$ was not, however, in specimens with Ti content of 0.028% $\text{Ti}_4\text{C}_2\text{S}_2$ was frequently found. Furthermore, only $\text{Ti}_4\text{C}_2\text{S}_2$ was observed in the specimen with the Ti content as high as 0.057%. In the current work, TiO_2 addition provides a Ti content of 0.046% (measured by optical emission spectroscopy), therefore Thermo-Calc predictions are in good agreement with previous findings.

Amongst steel, the microalloying elements, titanium is unique since it is able to form a sulfide or a carbosulfide. At low titanium levels (or high manganese levels), manganese sulfide is formed with titanium in solid solution while at high titanium levels, the more stable titanium sulfide is predicted, denoting that there is a competition between manganese and titanium for the sulfur. In the present study, both sulfide types have been predicted by Thermo-Calc analysis and its formation takes place in the austenite region. Gladman⁴⁾ suggests that the minimum titanium level necessary to form titanium sulfides should follow eq. (2):

$$\text{mass\% Ti} > \text{mass\% Mn}/10 + 4 (\text{mass\% N}) + (\text{mass\% S}) \quad (2)$$

The application of the equation for the TiO_2 inoculated low carbon steel matrix gives 0.041 mass% as a result. The titanium content in the nanopowder inoculated low carbon is

0.046 mass%, which is greater than the calculated minimum titanium level to form titanium sulfide or carbosulfide, thus titanium carbosulfides are expected to be found, as the experimental results confirm. Therefore, Thermo-Calc prediction and Gladman's approach are in good agreement when predicting the formation of titanium carbosulfide. Overall, thermodynamic simulations strongly suggest TiO_2 is not going to be thermodynamically favoured under system conditions. The formation of Ti-rich phases is attributed to the interaction of titanium oxide nanopowder at melting temperatures. It is suggested that TiO_2 dissolves within the matrix when added to the liquid steel matrix which produce metallic titanium and oxygen. Thus, Ti(s) is suggested to react with the surrounding elements like N, C and/or S so that they can play a role in the subsequent precipitation reactions as the material is cooled down. As a result, the thermodynamic calculations suggest that TiO_2 dissolution promotes the formation of $\text{Ti}_4\text{C}_2\text{S}_2$ and Ti(CN) taking into account the composition of the steel matrix as a function of temperature. Therefore, this equilibrium calculations may be of great guidance for a better understanding of microscopy results.

3.2 TEM, FEG-SEM and EDS studies

TEM was used to directly observe the nanometric precipitates in the carbon extraction replicas of the nanopowder inoculated low carbon steel matrix. The examination revealed a great number of nanometric particles distributed in the matrix.

Figure 3 shows a rounded inclusion image which according to the EDS and X-ray microanalysis, corresponds to $\text{Ti}_4\text{C}_2\text{S}_2$. EDS analysis detects a Cu signal because the iron based alloy replicas are collected in copper squared mesh.

The crystallographic parameters of this titanium carbosulfide are obtained from a Powder Diffraction File (PDF) database of the X-ray diffractometer. The structure information is confirmed through a comparison of the acquired diffraction pattern and the simulation database. According to the results, the rounded inclusion is confirmed to be $\text{Ti}_4\text{C}_2\text{S}_2$, which has an hexagonal structure with the zone axis of the incident beam along the directions $[1,1,0]$ and $[6,3,-1]$, as it is shown in Fig. 4.

In addition to the aforementioned titanium carbosulfides, MnS nanoparticles are also found throughout the inoculated low carbon steel matrix. Another type of nanometric

Fig. 4 Diffraction patterns corresponding to $\text{Ti}_4\text{C}_2\text{S}_2$ inclusion.

Fig. 5 TiN TEM micrograph and EDS analysis.

inclusion which contained titanium was found in the ferrous matrix. As shown in the bright field image from Fig. 5 the size of this type of inclusion is approximately 300 nm and presents a polygonal shape. The EDS analysis and the diffraction pattern confirm that the inclusion is TiN. These inclusions have a cubic structure with lattice parameters $a(\text{nm}) = b(\text{nm}) = c(\text{nm}) = 0.42401$ in the zone axis $[1,0,1]$, $[1,1,0]$ and $[1,1,2]$ as shown in Fig. 6.

Thermo-Calc based calculations, predict the formation of titanium carbonitride type precipitates which have not been localized in the specimen. The mutual solubility of TiN and TiC is likely to occur as they have the same FCC, but titanium nitride predominantly forms at higher temperatures than titanium carbides do. In addition, TiC particles have not either been identified. It is worth mentioning that smaller nanoparticles (≥ 15 nm) than the ones presented here were found dispersed along the matrix but due to their small size it was not possible to identify them accurately through EDS analysis. However, TiN precipitates are found, which is in good agreement with the elements distribution that turns up at high temperatures, richer in nitrogen than in carbon. These particles are detected as free-standing phases (as TEM images reveal), but some other observed TiN precipitates are associated with Al-oxide inclusions. These precipitates have

been found to be present as an envelope surrounding the Al_2O_3 particles, which are large enough to be seen through FEG-SEM as shown in Fig. 7. According to the results, experimental conditions have promoted the presence of phases which are likely to be found at higher temperatures, consequently, if lower temperature range phases exist, they are not found. In future work, statistical studies based on TEM micrographs are foreseen in order to obtain information on frequency and density precipitates.

In summary, according to the TEM and FEG-SEM microscopy analysis no TiO_2 inclusions are found. In fact, TiO_2 nanopowder leads to the formation of titanium nitride and titanium carbo-sulfide non-metallic phases. It is suggested that when TiO_2 nanopowder contacts the liquid carbon steel stream, it dissolves and system conditions promote the formation of the stable rounded shape $\text{Ti}_4\text{C}_2\text{S}_2$ and cuboid shape TiN nanometric inclusions. Overall, the microscopy analysis addressing titanium inclusion assessment corresponded well with the previous thermodynamic modeling for the calculation of the phase equilibrium of the system. Consequently, phase prediction through Thermo-Calc is revealed as a very helpful tool, when inclusion stability is studied in particular and when appending additional databases to the calculation, as in the present work.

Fig. 6 Diffraction pattern of TiN inclusion.

Fig. 7 FEG-SEM micrograph and EDS analysis of Al-O precipitate surrounded by TiN.

Fig. 8 Engineering stress–strain curves for TiO₂ inoculated low carbon steel and low carbon steel.

These results are in accordance with a previous investigation⁹⁾ related to the reactivity of TiO₂ nanopowder with a liquid iron matrix using sessile drop wettability measurements between an Armco iron (high purity iron alloy) ferrous matrix and sintered TiO₂ nanopowder. The work concluded that there is reactive wetting between the droplet, liquid iron and the ceramic substrate, sintered TiO₂ nanopowder, deriving in the formation of pseudobrookite (Fe₂TiO₅) and ilmenite (FeTiO₃) stable phases, thus TiO₂ nanopowder reacts with iron to form solid solution products. In this sense, comparing with the present work, TiO₂ nanopowder is found to derive into secondary Ti-phases under particular system conditions when it contacts with a liquid iron matrix.

3.3 Mechanical properties assessment

The TiO₂ nanopowder inoculated low carbon steel and the low carbon steel were assessed in terms of their mechanical properties through tensile tests and the results were compared.

In Fig. 8 the engineering stress–strain curves of titanium inoculated low carbon steel and non-inoculated low carbon steel are presented. The stress–strain diagrams of the tensile test specimens were further analyzed, in between the yield strength and ultimate tensile strength to evaluate the strain hardening behavior. The Hollomon model, the best known model to assess the work hardening behavior of metals, is defined by the following equation:²⁰⁾

$$\sigma = K\varepsilon^{n_H} \quad (3)$$

Where K is the strength coefficient, n_H work hardening exponent, σ and ε being the stress and strain. The true stress–strain curves were fitted by Hollomon–Jaffe model and were plotted on a logarithmic scale up to the point of the maximum load for work hardening exponent (n) determination. On the other hand, the Ramberg Osgood model is also a very used model to study elastoplasticity,²¹⁾ and it is described by the following equation:

$$\left(\frac{\varepsilon}{\varepsilon_0}\right) = \left(\frac{\sigma}{\sigma_0}\right) + \alpha \left(\frac{\sigma}{\sigma_0}\right)^n \quad (4)$$

where ε is the observed strain in the material at a given stress of σ at any instant, σ_0 is a reference taken as flow stress, ε_0 is

Table 2 Mechanical properties average values of the low carbon steel and the inoculated low carbon steel.

	YS (MPa)	UTS (MPa)	Elongation (%)	n
Low carbon steel	250	390	34	0.21
TiO ₂ inoculated low carbon steel	275	453	24	0.23

$\frac{\sigma_0}{E}$ and α is a dimensionless material constant determining n_{RO} , which represents the Ramberg-Osgood strain hardening exponent.

Table 2 shows the average mechanical properties of the specimens concerning yield strength, ultimate tensile strength and elongation values obtained from engineering stress and strain curves and n values which were obtained from the true stress and strain values. The slope of the line of Hollomon's equation in logarithmic coordinates yields the value of n and the strength coefficient (K) is a true stress at $\log \varepsilon = 0$ or $\varepsilon = 1$. The results show that titanium inoculated low carbon steel exhibits higher yield strength (YS, +10%) and ultimate tensile strength (UTS, +16%), while there is a ductility decrease. On the other hand, the results also show that the work hardening exponent value is higher for the TiO₂ nanopowder inoculated low carbon steel, which has second phase particles inoculated in the matrix and as it is reported in the following section, a finer grain size. However, the work hardening rate is well known to decrease with decreasing grain size due to an increase in yield strength. Morrison²²⁾ established an empirical relationship between n -value and grain size d (mm) thus the work hardening is expected to decrease with decreasing grain size due to the increase in the yield strength as it is shown in eq. (5):

$$n = \frac{5}{10 + d^{-1/2}} \quad (5)$$

The work hardening source is the storage of forest dislocation during plastic straining and the deformation microstructure is characterized by a single parameter, the forest dislocation density ρ_f . But when second-phase particles are present, additional effects must be considered.

Antoine *et al.*²³⁾ recognized that all the factors controlling yield strength will also affect n . In fact, they proposed an empirical model which predicts the n -value for a Ti-IF steel grade as a function of the different microstructural parameters controlled during thermomechanical processing, i.e., mainly dislocation density, grain size and volume fraction and size of precipitates. The work hardening is based on microstructural evolution during plastic straining, in particular dislocation density and arrangement of dislocations. When second phase non-deforming particles are contained in the metal matrix, particles do not deform plastically, they are shear-resistant. Consequently, the particles can only deform elastically when the matrix shears plastically and the interface between particle and matrix does not fracture, then secondary slip must occur locally round each particle when the crystal is deformed, even though the crystal may appear to deform by single slip.²⁴⁾ In this case, the shear-resistant particles are bypassed by Orowan loops around them and the contribution of the precipitates to the work hardening exponent is

established by Asbhy-Orowan which defines a work hardening increase when precipitates volume fraction increases.²⁵⁾ Consequently, the presence of second phase particles is suggested to be responsible for the extra work hardening rate found in the TiO₂ low carbon steel which increase the generation of strain gradients near them. When a dislocation moving in its slip plane encounters shear resistant particles, bypasses the particles and can punch through the area between the particles promoting the generation of Orowan loops. The contribution of these dislocation loops act as individual obstacles to slip via mobile dislocations and they also collectively create long-range back stresses which contribute to an overall work-hardening increment. In this sense, the presence of second phase particles is suggested to be stronger than that of finer grain size found in the inoculated low carbon steel matrix. Consequently this fact gives rise to a higher strain value and therefore to a higher work hardening rate in TiO₂ the inoculated steel. It seems that second particles size and distribution are presumably responsible for the matrix strengthening through precipitate strengthening mechanism.

A key finding from the tensile tests is that the yielding is completely different for each specimens. The TiO₂ nanoparticle inoculated specimen shows a gradual transition from elastic to plastic behavior, i.e., a continuous increased stress is required to produce further deformation of the specimen, there is no upper yield point, no yield plateau and no yield point elongation. On the other hand, further deformation of the non-inoculated low-carbon steel specimen occurs at a constant stress value when the elastic limit of the alloy is exceeded. The process of the aforementioned continuous yielding is known to be produced either by removing interstitial atoms (C and N) from the pre-existing dislocations, or by introducing fresh dislocation. In fact, the yield point in steel is associated with an absence of mobile or free dislocations. Any pre-existing dislocations appear to be tightly bound by the formation of “atmospheres” of carbon or nitrogen atoms or near the dislocation core.⁴⁾ Interstitial free steels meet previous requirements for no yield extension. These IF steels involve ultra-low carbon levels, with the carbon (and nitrogen)²⁶⁾ “stabilized” (by hyperstoichiometric additions of Ti and/or Nb), or removed from interstitial solid solution, by the addition of carbide forming alloying elements. The C stabilization is known to take place by the formation of TiC and sometimes Ti₄C₂S₂ in the austenitic range. Partial carbon stabilization by Ti₄C₂S₂ requires the presence of a minimum amount of S and the control of formation of specific sulfides, i.e., mainly TiS and to a lesser extent MnS and CuS. On the other hand, the IF steels are also characterized by Ti binding the N at high temperatures in the liquid phase as TiN. The solubility of TiN in Fe being very low, the full stabilization of N is always achieved in Ti IF steels.²⁷⁾ The formation of this type of titanium carbo-sulfide and the aforementioned TiN, has been extensively reported in Ti–Nb IF (interstitial free) steels.^{13,26,28,29,30)}

The present system follows the same trend as the one found in Ti IF steels and it is presented as an alternative route to stabilize interstitial elements. Owing to the formation of titanium nitride and titanium carbo-sulfide

precipitates, it makes sense to suggest that those second-phase particles have removed carbon and nitrogen interstitial free elements from dislocations and explains the continuous yielding found in the engineering stress–strain curves of the TiO₂ inoculated low carbon steel. It is interesting to point out another consequence derived from the removal of interstitial atoms which could be applied to the material investigated in the current work. In steels without interstitials, strain aging does not occur, that is, that the lightly deformed material will not show a return of the yield point. As a result, IF steels meet the formability requirements for extra deep drawable steel grades.³¹⁾ However, there is not a clear evidence whether the formation of TiN and Ti₄C₂S₂ results in the complete removal of C from solid solution. Previous studies by M. Hua *et al.*¹⁸⁾ reported precipitation behavior in ultra-low-carbon steels containing titanium which provided evidence that the stabilization of carbon can occur through the transformation of TiS to H–Ti₄C₂S₂, which provides a different view of achieving C stabilization. This is explained by *in situ transformation* where H–Ti₄C₂S₂ forms from the former TiS and not directly from austenite. TiS is converted to Ti₄C₂S₂ since C and Ti are diffuse out (during heating) or in (during cooling) according to the following expression:

This idea differs from the classic view of nucleation and growth of MC precipitates. One stabilization theory (for very low sulfur < 10 ppm or high Mn > 0.8 mass%) holds that the carbon removed from solid solution leaves through the direct precipitation of MC, not to mention the role played by sulfur.¹⁹⁾ Another view of stabilization suggests that a significant portion of the carbon is removed from solution through the direct or independent precipitation of Ti₄C₂S₂.²⁸⁾ According to the conclusions found by M. Hua *et al.*¹⁸⁾ sulfur, within a reasonable range (0.004 to 0.010 mass%) is believed to be beneficial to the stabilization of carbon in Ti-bearing ULC steels.

The predicted phases suggest that carbon solid solution may be stabilized through TiC and Ti₄C₂S₂ precipitates. At ferrite phase temperature ranges, Ti(CN) leads to a stoichiometric TiC compound. Despite the precipitation of carbon stabilizing phases, the formation of TiC nor Ti₄C₂S₂ is not expected to result in zero carbon solid solution. For instance, Thermo-Calc simulation data at different temperatures reveals that when Ti₄C₂S₂ first nuclei appear (1600 K), 0.087 C (mass%) remains in solid solution and as the system continues cooling down and other precipitates as Ti(CN) stabilize the C (572 K), the C solid solution mass percentage decreases up to 2.21×10^{-5} C mass%. The latter are C solid solution values in equilibrium, but the experimental values are difficult to predict.

3.4 Microstructure characterization

Further light optical analysis of the normalized microstructures revealed different ferrite grain sizes, as displayed in Fig. 9, where the inoculated ferrous matrix presents 14 μm equiaxed ferrite grain size and 20 μm low carbon steel grain size, which were determined using the comparison method procedure (ASTM E-112).

Fig. 9 Microstructures of: (a) low carbon steel, (b) TiO₂ nanopowder inoculated low carbon steel.

It is found that after TiO₂ nanoparticle inoculation, the ferrite grain size is refined. The refinement of ferrite microstructure in low carbon steel with TiO₂ nanopowder can be explained based on two different mechanisms: pinning of the previous austenite grain boundary by second phase particles and an increase of nucleation sites for ferrite transformation. On the one hand, austenite grain growth is suggested to be inhibited by the pinning effect of second phase particles arrayed randomly in the matrix. This arises from the fact that a small area of austenite grain boundary disappears when the grain boundary intersects a particle to give the Zener drag effect.³²⁾ When the boundary reacts to the driving forces of grain growth, it attempts to move away from the particle and it comes up the need to create a new boundary area which causes it to distort. Due to this fact, unpinning requires that additional energy is supplied by the driving force for grain boundary movement. In practice, Ti is the most effective austenite grain refiner. It forms TiN particles which present high stability at high temperatures and consequently prevent austenite grain growth in a high temperature range. Therefore, the TiN particles derived from the addition of TiO₂ nanopowder are suggested to have acted as moderate grain refiners in the titanium oxide inoculated low carbon steel.

On the other hand, complementary to the previous issue, γ to α nucleation site must be taken into account. S. Hossein Nedjad *et al.* have put forward that after TiO₂ addition to plain carbon steel⁸⁾ and C–Mn steel³³⁾ a thermodynamically favored chemical reaction of titanium oxide nanoparticles

with dissolved carbon occurs during melting and solidification. Then, the chemical reaction between solid carbon and solid titanium oxide is given by:

They showed that inoculation of steel with titanium augments the nucleation of intragranular ferrite by providing solute (C) depleted zones. Although detailed mechanisms and the potential of various oxides to govern ferrite nucleation exist, the extent of solute depleted zones around the nanoparticles might be different from that of conventional micrometer-sized inclusions. The introduced oxide particles could affect decomposition of austenite during subsequent cooling by either increasing the number of intragranular nucleation sites or retarding the growth velocity of the ferrite.⁸⁾ However, according to the thermodynamic simulations and transmission electron microscopy results found in this work, it appears that C is mainly stabilized by Ti-rich phases and if CO(g) is formed, it is a minor phase. Consequently, the reaction proposed by Hossein to stabilize C and originate solute depleted zones can not be considered here as the mechanism for refining ferrite grain size. However, TiO₂ nanopowder dissolution has brought to second phase particles which perhaps have promoted solute depleted zones as Hossein *et al.* concluded in their works, thus, this fact might have promoted ferrite nucleation. The nucleation mechanisms of ferrite on non-metallic inclusions can be compared with Ti-containing low carbon steels. In this case, non-metallic inclusions like TiO, MnS and TiN have been reported to be effective nucleation sites for acicular ferrite. In the current work, if the second phase particles have acted as nucleation sites, they meet different requirements to be suitable nucleation sites. The possible nucleating sites are MnS, Ti₄C₂S₂, TiN, TiC or Ti(CN) and not the intentionally inoculated TiO₂ nanoparticles because they dissolve in the metal matrix. However, it has not been further analyzed which non-metallic inclusions have promoted ferrite nucleation. Different phenomena must be considered to have an effect on acicular ferrite formation, i.e., the reduction in the interfacial energy at the surface of the inclusions, lattice mismatch strains between the inclusions and ferrite, thermal strains at the inclusions and the depletion of various elements such as B, C (as Hossein reported) or Mn, since it can happen around MnS particles. Due to the small size of the second phase particles present in the steel matrix, some of the phenomena described above could be negligible or may be altered, such as their capacity for solute absorption from the surrounding matrix. Owing to this fact, the mechanisms are often found to work together, but their individual importance for the nucleation in each different situation has not been determined.³⁵⁾ Nevertheless, further studies are needed to understand the mechanisms thoroughly.

The ferrite grain size refinement is found to have a direct influence on mechanical properties. The nanopowder inoculated low carbon steel has shown higher UTS and lower elongation values, which indicates the likely presence of different dislocation densities, manifested in the form of stored energy. Hence, a finer grain sized material is expected to have higher values of stored energy due to higher dislocation densities compared to a coarse grained material

subjected to the same strain level, as the experimental results have shown. Titanium nitrides which act as grain refiners, usually are too coarse to have an effect on precipitation hardening and its low solubility largely precludes its use as precipitation strengthening agent. In addition, it has been found that TiO₂ nanoparticles are dissolved, hence not contributing to precipitate strengthening.³⁴⁾ All things considered, it is proposed that the presence of nanometric precipitates has derived in a ferrite grain refinement and both facts have resulted in an enhancement of the mechanical properties.

4. Conclusions

The work focuses on the effects that the inoculation of an amount of nanoscale TiO₂ powder has on the mechanical properties of a low carbon steel and on the formation of Ti-based precipitates. Several issues are found from the results.

Thermo-Calc equilibrium prediction and microscopical analyses confirm the dissolution of TiO₂ nanopowder when it is inoculated into a liquid low carbon steel matrix. The system conditions promote the formation of TiN and Ti₄C₂S₂ nanometric phases, among other second phases. As a consequence, the formation of these newly created precipitates has been found to result in equiaxed ferrite grain refinement deriving in an increase of yield strength and ultimate tensile strength.

On the other hand, it is also found that those nanometric phases have led to interstitial elements depletion from the iron matrix. This phenomenon is compared with titanium stabilized interstitial free steels, where titanium combines with nitrogen and carbon as a precipitate instead of forming an interstitial solid solution. The binding of nitrogen and carbon interstitial elements have influenced the yielding point, avoiding the discontinuous yielding associated with Luders band propagation, as tensile curves have demonstrated. This methodology is found to be an alternative route to stabilize C and N at high temperatures through the formation of precipitates.

This experimental approach pursues contributing to a better understanding of nanopowder inoculation through liquid metallurgy research which seems to be a potential and innovative field which is still in its infancy. The fundamental knowledge gained at laboratory scale aims to be useful for conventional metallurgy at industrial scale.

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