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Phase Transformation in Micro-Alloyed Steels

Fahim Khan and Hossain M. M. A. Rashed

Abstract

Phase transformation in crystalline solid is an important factor that designs the microstructure and plays a great role in alloy development. Iron has an allotropic form, and this unique metallurgical property leads to phase transformation. Addition of micro-alloying elements enhances the phase transformation scenarios in steels. Phase transformation due to the addition of micro-alloying elements, together with exceptional precipitation hardening capabilities, substantially improves mechanical properties of steels of different grades. Ferrite transforming to other phases reduces the hardenability of steels. Micro-addition of elements forms precipitation in ferrite and austenite, which controls the microstructure and hence the mechanical properties of steels. Besides, interactions between different deformation sequences used in the production of steel and addition of elements as solute or precipitates regulate the microstructure. Ferrite grain refinement depends on the refinement of austenite grain size in one case, and austenite grain size growth can be varied by addition of various elements. Thus, a variety of elements influences phase transformation that leads to significantly modified properties.

Keywords: austenite grain size, mechanical properties, ferrite, microstructure, precipitation

1. Introduction

Micro-alloyed steel is a type of steel containing a minute amount of alloying elements (0.05–0.15%) including niobium, vanadium, titanium, molybdenum, zirconium, boron, and rare-earth metals [1]. They are mainly used to refine the grain microstructure or facilitate precipitation hardening. Micro-alloyed steel developed in the second half of twentieth century. A lot of advancements have taken place due to the development of micro-alloyed steels. Certainly, it improves the hardening, tensile strength, and other mechanical properties of steels. Micro-alloyed substituents like niobium, vanadium, titanium, etc. cause significant grain refinement by retarding recrystallization and forms precipitation of carbon-nitride by these micronutrients. Precipitation of Nb(C,N) that forms improve the microstructure and overall properties of final product. This precipitation further inhibits the recrystallization of austenite, as a result of which reduction of ferritic grains takes place after transformation of noncrystalline austenite. On the basis of this principle later, high-strength low-alloy (HSLA) was developed.

2. Effect of alloying element on ferrite

FCC has 8 and 4 octahedral and tetrahedral voids per unit cell, respectively, whereas BCC has 12 and 6, respectively. The octahedral void in FCC is bigger than the tetrahedral. Carbon occupies the octahedral void with less distortion. The octahedral void in BCC is smaller than the tetrahedral even in the case when carbon occupies octahedral void due to lesser distortion (only top atom and bottom need to be distorted) [2].

Alloying element	Group 1 Dissolved in ferrite	Group 2 Combined in carbide
Nickel	Ni	
Silicon	Si	
Aluminum	Al	
Copper	Cu	
Manganese	Mn	Mn
Chromium	Cr	Cr
Tungsten	W	W
Molybdenum	Mo	Mo
Vanadium	V	V
Titanium	Ti	
Adapted from Ref. [3].		

Table 1.
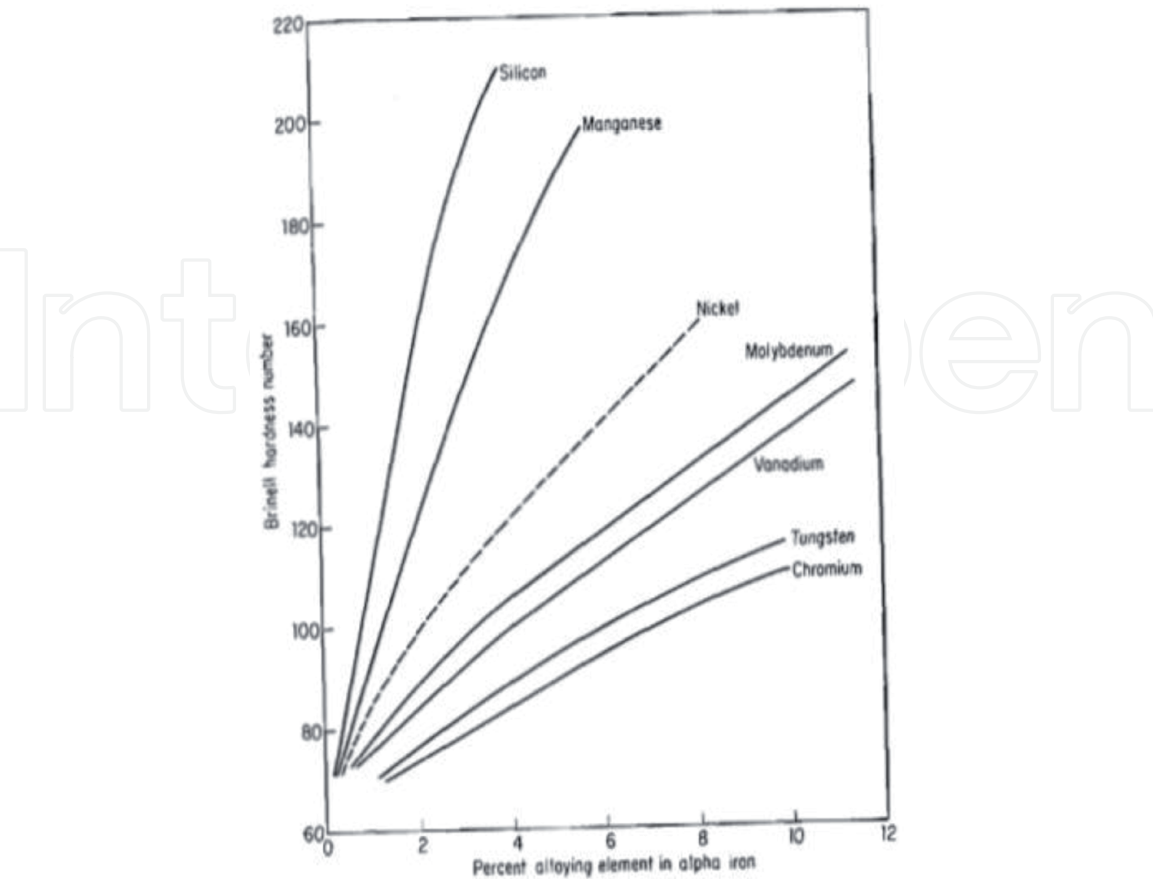*Behaviors of the individual elements in annealed steels.*

Figure 1.
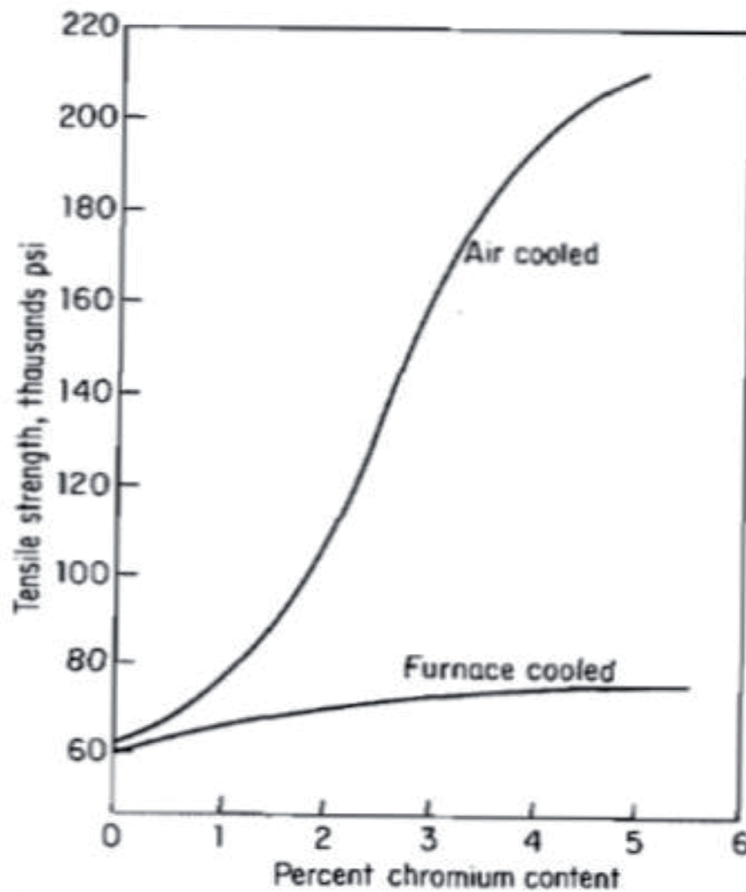*Probable hardening effect of the various elements as dissolved in alpha iron (reprinted from Ref. [3]).*

Figure 2.
The minor effect of chromium in annealed steels compared with the powerful effect as a strengthener through its influence on structure in air-cooled steels. Probable hardening effect of the various elements as dissolved in alpha iron (reprinted from Ref. [3]).

The number of voids in BCC is greater than that in FCC, whereas size of voids in BCC is significantly smaller than that in FCC. For this reason austenite have higher solubility of C than ferrite. But all the alloying elements have some sort of solubility in ferrite. It mainly depends on the amount of carbon present in the structure. Nickel, aluminum, silicon, copper, cobalt, etc. dissolve in ferrite in a large extent and play a significant role in increasing hardness and strength by solid solution hardening. Group 2 elements in **Table 1** dissolve in ferrite in the absence of carbon, otherwise it forms carbide.

In **Figure 1**, the probable hardening effect of various elements dissolved in alpha (α) iron is shown. When silicon dissolved in alpha (α) iron, then the hardening value lies in maximum among the addition of Mn, Ni, Mo, V, W, and Cr. Among the alloyed elements, the addition of chromium causes the least hardening effect.

The dissolved element has a little hardening effect in the contribution of ferrite to the overall strength of the steel. In the case of the low-carbon chromium steels, when the structural change occurs by any process, then hardening of such steels occur. The change of structure can be done in the case of annealed steels by cooling it from higher temperature by air. In **Figure 2** it is clearly understood. In **Figure 2** when the low-carbon chromium-annealed steels are air-cooled, then its tensile strength rises to a high value. On the other hand, when cooled in furnace, a little change in tensile property is seen.

3. Influence of alloying elements on iron-iron carbide diagram

The presence of alloying elements plays an important role in the change of critical range, position of eutectoid point, and location of the alpha and gamma

fields indicated by the binary iron-iron carbon diagram. Besides, the presence of nickel and manganese lowers the critical temperature on heating, which stabilizes austenite. If the critical temperature lowers than that of the standard region, then austenite becomes stable at room temperature. Thus nickel and molybdenum stabilize austenite at room temperature, and the addition of such alloying element is used in the preparation of austenitic stainless steel.

On the other hand, Mo, Cr, Si, and Ti raise the critical temperature range which contracts the austenite zone and enlarges the alpha and gamma regions as well.

Austenitic stainless steel plays a great role in industrial applications by giving corrosion resistance of steels and providing well mechanical strength. It is mainly used in pressure vessels, reactors, storage tanks which are used underground, and especially in aqueous environments containing chlorides. Austenitic stainless steels are used in manufacturing pump in the oil industry that injects saltwater to expel gas and oil. For the preparation of austenitic stainless steels, Ni and Mo play an important role.

From **Figure 3**, it is clearly shown that the addition of Ti, Mo, Si, W, and Cr raises the eutectoid temperature of steels. The rise of the eutectoid temperature of steels lowers the stability region of austenite, which ultimately stabilizes austenite at the elevated temperature. At this scenario, austenite becomes unstable at lower or room temperature. Besides, the addition of Mn and Ni lowers the eutectoid temperature which passively indicates that the stability of austenite at room temperature. As a result, Mn and Ni are the helpful alloying elements in the case of the austenitic stainless steels.

Chromium in particular lowers the eutectoid temperature. Thus with the addition of chromium, the austenite zone contracts as austenite is stable above the critical temperature. If the critical temperature rises up, then austenite gets stable at elevated temperature and unstable at room temperature. Thus with the addition of chromium
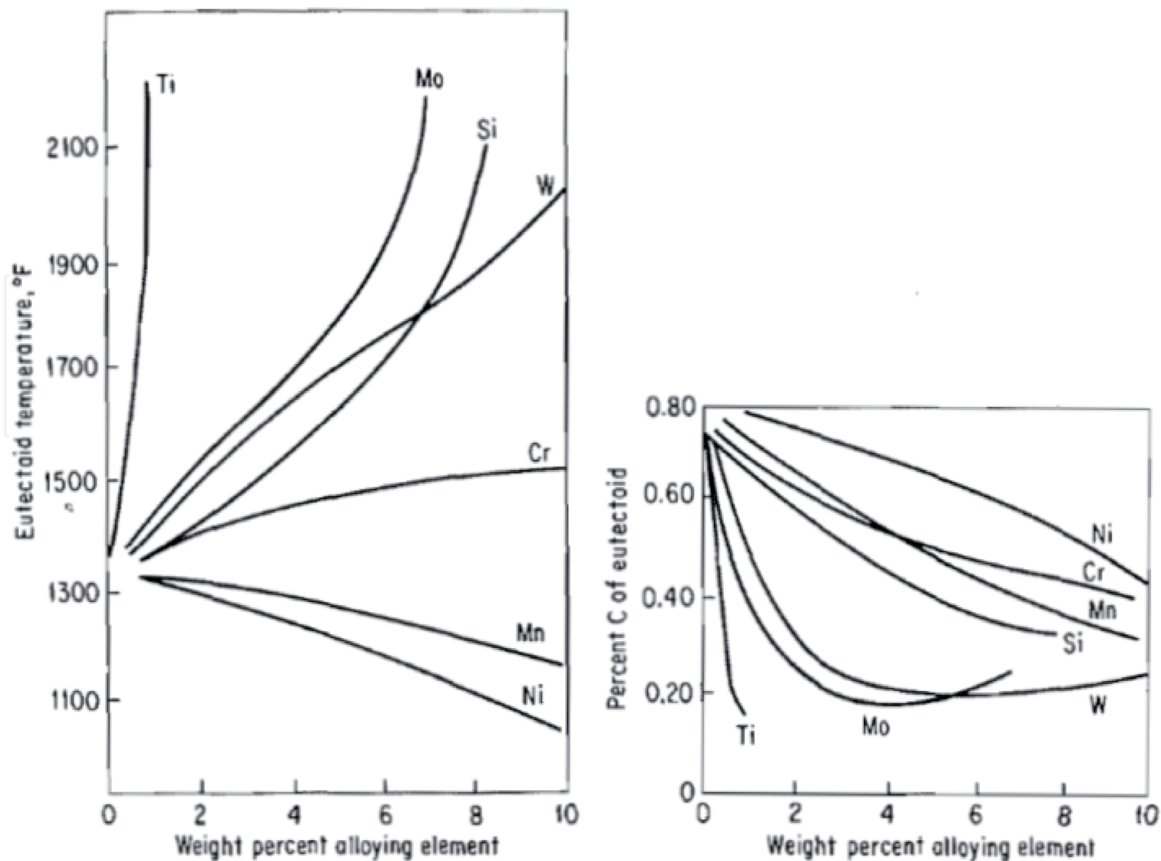

Figure 3.
Eutectoid composition and eutectoid temperature as influenced by several alloying elements. Probable hardening effect of the various elements as dissolved in alpha iron (reprinted from Ref. [3]).

the austenite zone contracts more and prone to the formation of austenitic stainless steel reduces. And austenitic stainless steels become unstable at room temperature.

4. Effect of alloying element on tempering

In the case of the tempering of the plain carbon steels, when the temperature is increased, then the hardness value is decreased; thus hardened steels are softened. At the same time, the hardness drops continuously. Some alloying elements play an important role in retarding the softening effect of the hardened steel at elevated temperature. When tempering is done at elevated temperature, then the steel may soften. Usually the elements that remain dissolved in ferrite, such as Ni, Si, and Mn, have very little effect in the retardation of the softening of steels at elevated temperature.

The complex carbide-forming elements such as Cr, W, Mo, and V retard the softening at elevated temperature while tempering. Besides, they do not only retard the softening effect but also improve the hardness of the plain carbon steels to some aspects.

5. Niobium-micro-alloyed steels

Niobium is a soft gray ductile and transition element. The main commercial source of niobium is mineral pyrochlore. Around 80% of the niobium produced is used in automotive industry, for oil and gas pipelines, and in construction. Adding niobium to steels causes the formation of niobium carbide and niobium nitride which improve grain refinement and retardation of recrystallization. Besides, it enhances precipitation hardening which increases toughness, strength, formability, and weldability of micro-alloyed steel [4].

Large-diameter pipes are used in transportation of oil and gas. It is manufactured by thermomechanical controlled processing (TMCP) [5]. Its performance can be enhanced by inducing its strength and toughness through grain refinements. Grain refinement can be done by controlling austenite parameters by the addition of niobium.

In austenitic-ferritic stainless steel, usually solidification starts at 1450°C with the formation of ferrite (α) which acts as an origin to start the formation of austenite near 1300°C. σ forms at the interphase of austenite and ferrite at 600–950°C, and the toughness of the steel gets reduced.

Figures 1–6 show the microstructural characteristics of the austenitic-ferritic stainless steel with or without niobium, after heat treatment.

Figure 5(a) shows the heat-treated steels without niobium with elongated austenitic grains in ferrite matrix. When the annealed sample is aged at 850°C/15 min then it is observed that the beginning of sigma phase forms.

When steel is modified with 0.2% niobium, then a little amount of sigma phase is observed than steel without niobium after being annealed and aged at 850°C/15 min. Besides no Laves phase is seen (**Figure 7**).

When steel is modified with 0.5% niobium after being annealed and aged at 850°C/min, then the Laves phase appears as needles associated with sigma phase.

In the aggressive environments, the preferential attack prone to the reduction of Cr and Mo near and alongside of the sigma phases. That is the reason for the reduction on pitting corrosion resistance in the steels.

The addition of niobium in supermartensitic stainless steel after tempering at 600°C for 2 h improves the mechanical resistance properties with lower degree of sensitization. Besides, given such properties, it never compromises its elongation and pitting corrosion resistance compared to the reference steels.
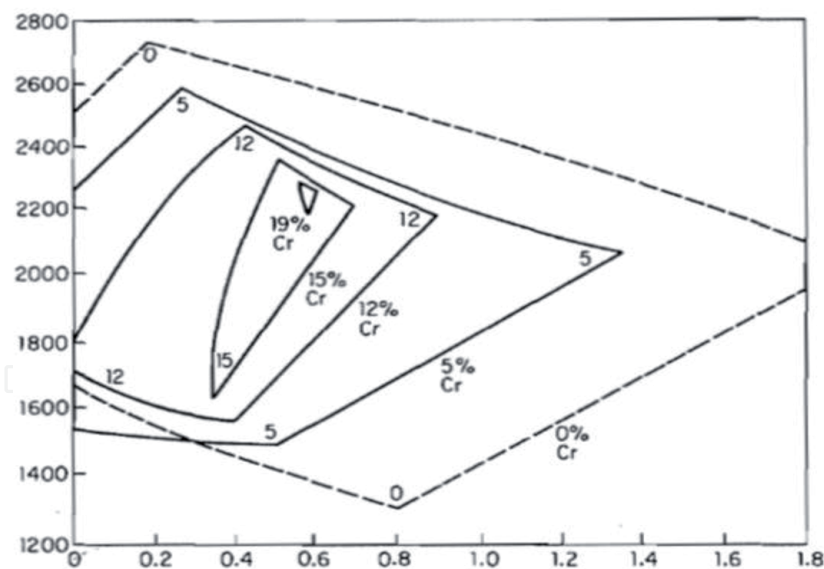
Figure 4.
Range of austenite in chromium steels (reprinted from Ref. [6] with permission).
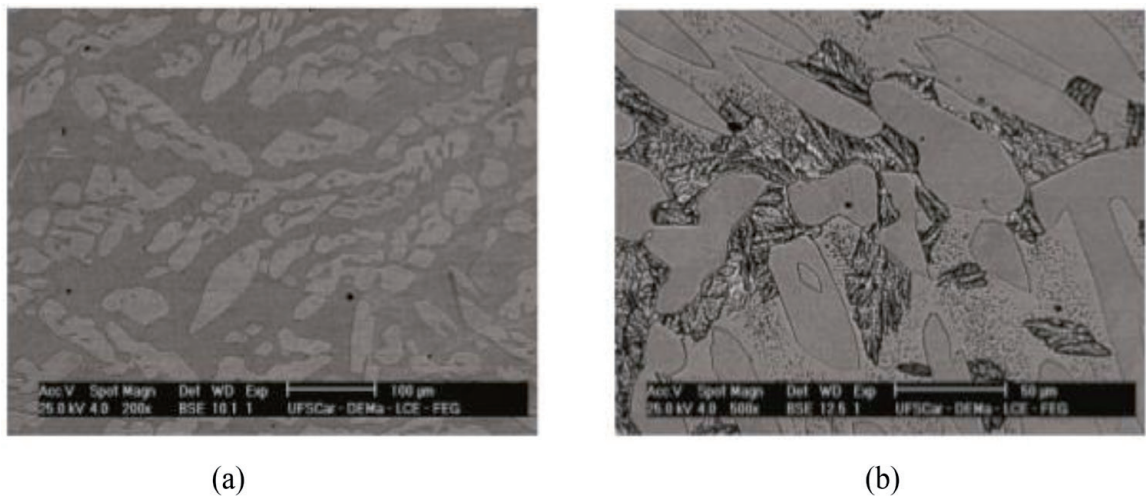

(a)

(b)

Figure 5.
Annealed steel without niobium (BSE after Behara etching) with (a) Austenite grains in ferrite matrix and (b) beginning of the sigma phase (adapted from Ref. [7], p. 802).
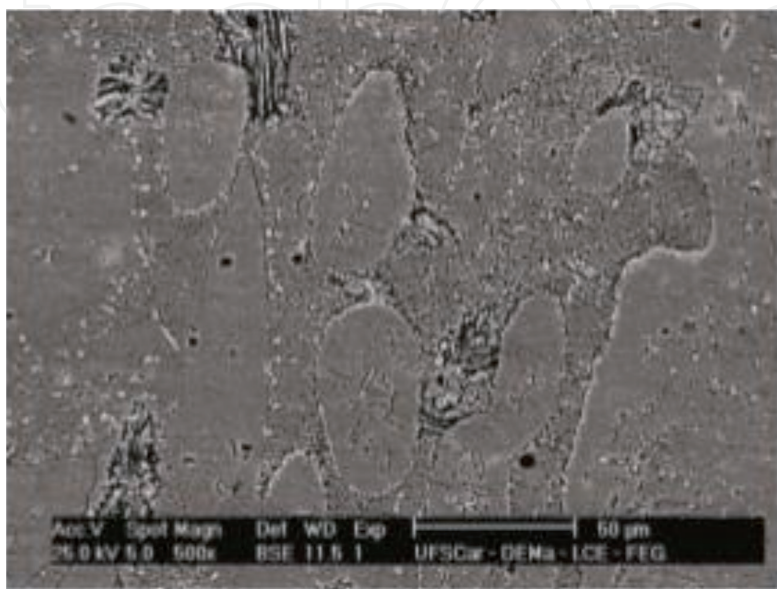

Figure 6.
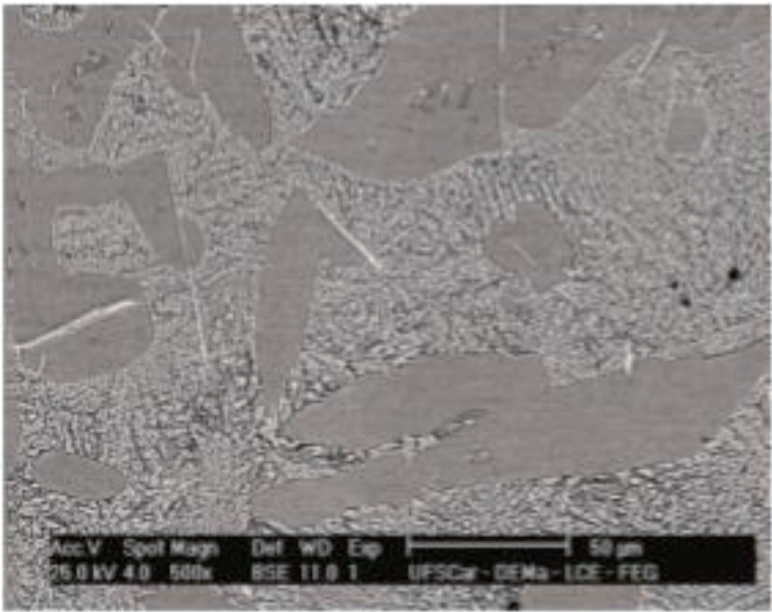*Steels modified with 0.2% niobium (adapted from Ref. [7], p. 803).*

Figure 7.
Steel modified with 0.5% niobium (adapted from Ref. [7], p. 803).

6. Titanium steels

Titanium alloys are mainly used in the structural materials in the aerospace and chemical industries due to lower density, high strength, and corrosion resistance. Tensile strength/density ratios of titanium alloys are considerably greater than that of steels and Al alloys at ordinary temperature. For these reasons Ti alloys are mostly used in the aerospace industries. And for this Ti is added to the steels to improve its properties to some extent (**Figure 8**).
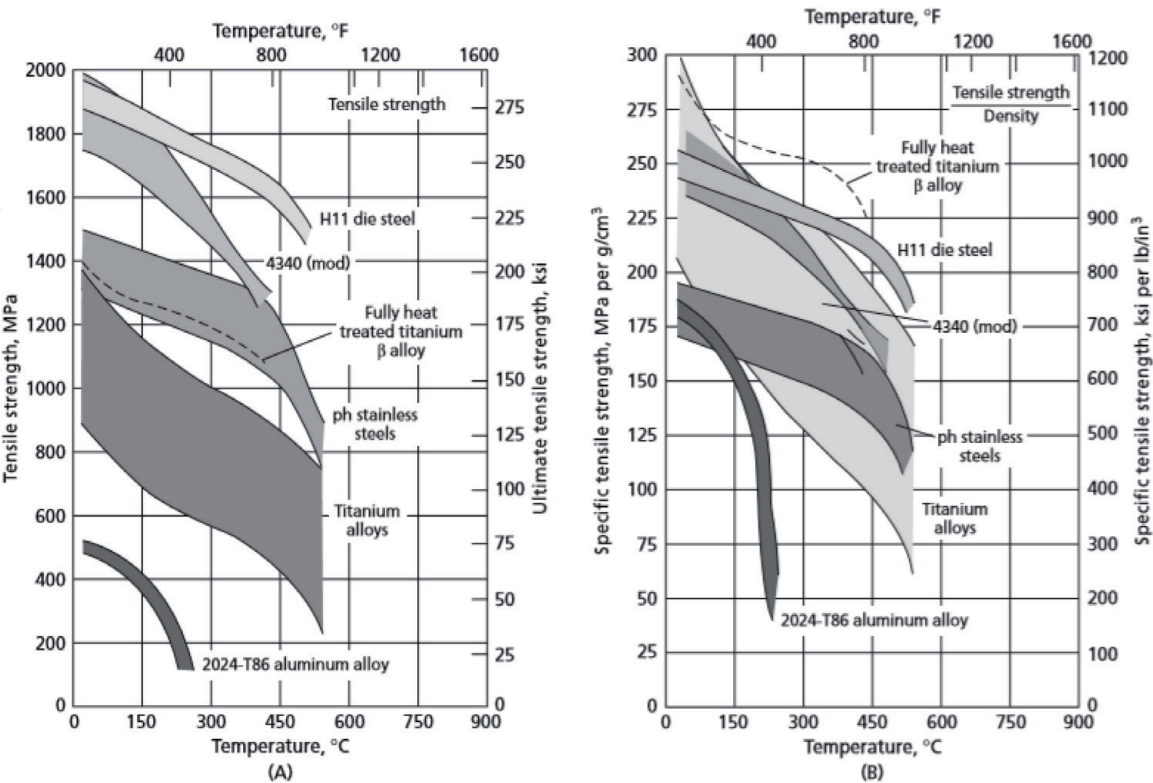

Figure 8.
Comparison of (a) short-time tensile strength and (b) tensile strength/density ratio for titanium alloys, three classes of steel, and 2024-T86 aluminum alloys included for annealed alloys with less than 10% elongation or heat-treated alloys with less than 5% elongation (reprinted from Ref. [8]).

When Ti is added to the steels, then it improves its high temperature properties as refractory metals [9]. The chemical behavior of Ti always limits its application at moderate to high temperature. At low temperature Ti passives to acids and minerals, but at elevated temperature, Ti oxidizes very fast. Besides, dissolution of hydrogen and nitrogen causes surface hardening.

Pure Ti undergoes allotropic transformations at about 1158 K. Thus if Ti remains in steels at around 1158 K, the properties may vary, because pure Ti at 1158 K transforms from a closely packed hexagonal structure to a body-centered cubic structure. The high temperature BCC of Ti is called alpha phase. On the other hand,
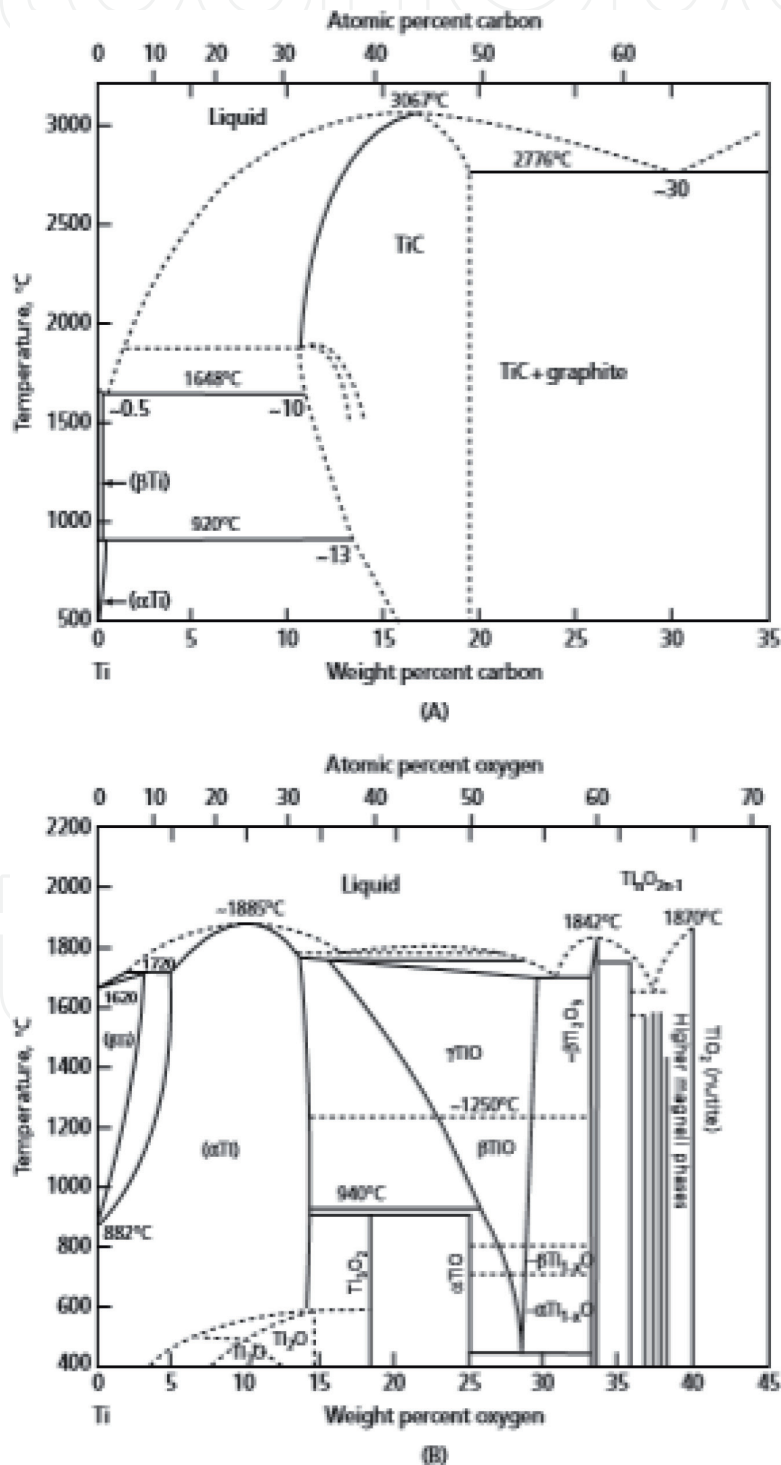

Figure 9.
Phase transformation of titanium with the weight percentage of (a) Cr and (b) Ni stabilizers (reprinted from Ref. [10]).

HCP at low temperature forms beta phase. Beta to alpha transformation happens by diffusionless martensitic transformation.

Allotropic transformation temperature depends on few alloying elements. Some alloying elements raise the transformation temperature called alpha stabilizers, whereas few lower the transformation temperatures called beta stabilizers.

Figure 9 shows that carbon, oxygen, and nitrogen are rapidly absorbed by Ti when the metal is hot. All these elements hardened and the solution hardened the alpha Ti. Al has significant solubility over alpha and beta phases. The reason to explain it is that Ti has many fold advantages on the steel acting as an alloying element.

Elements that lower the transformation temperature are of two classes. One is elements that undergo eutectoid transformations, for example, iron, Cu, N, Co,
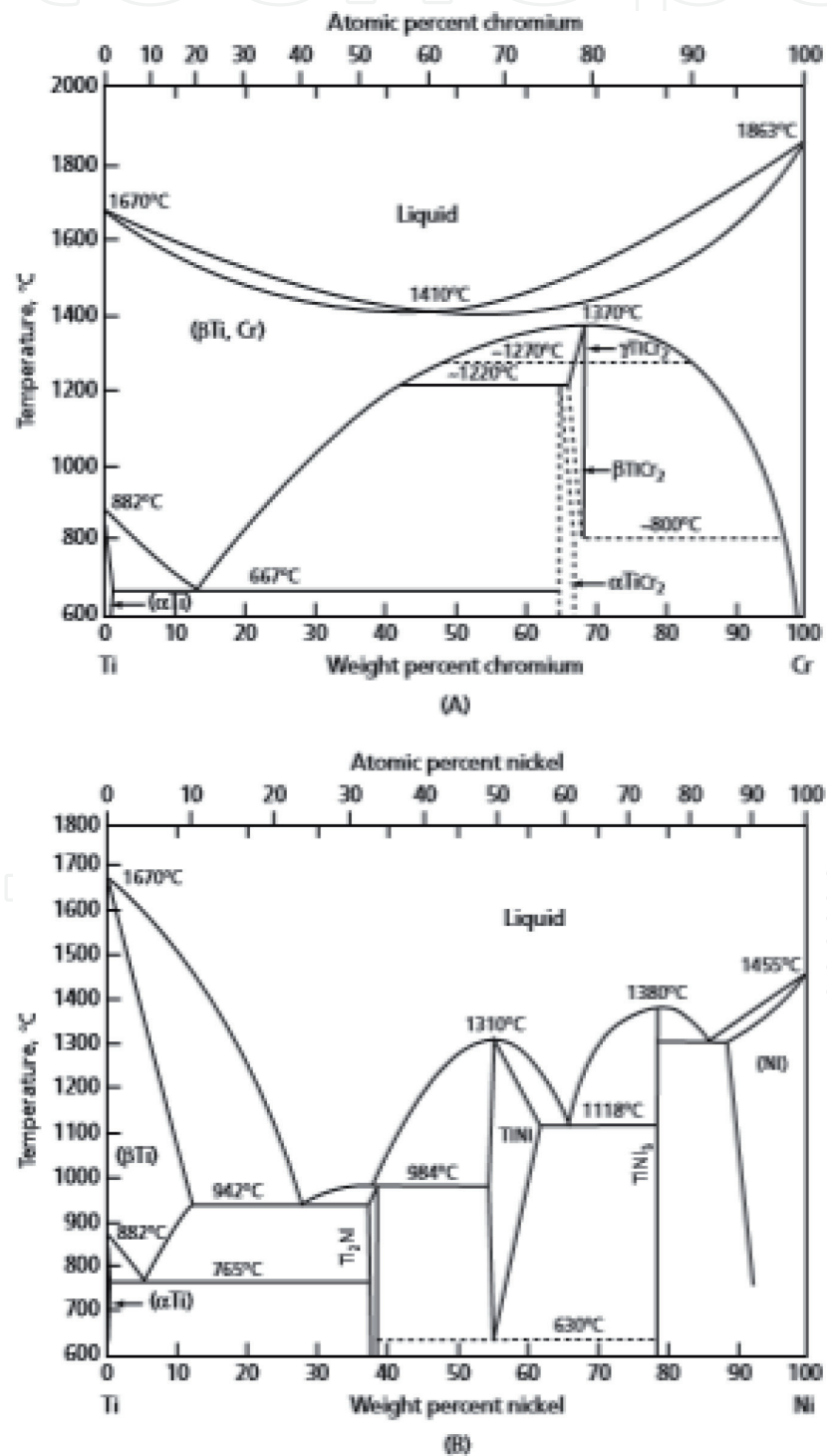

Figure 10.
Phase diagrams of titanium with selected stabilizers (reprinted from Ref. [10]).

Mn, etc. And the other one is those that are isomorphous with beta phase at high temperature and from alpha + beta equilibrium phase at ordinary temperature.

Figure 10 expresses that Mo, Ta, V, etc. have limited solubility in alpha phases.

The main role of Ti in steel is grain refinement strengthening and precipitation strengthening. The smelting of Ti-micro-alloyed steel should satisfy that most of the Ti dissolves in the molten steel and precipitates in the form of carbide or carbonitride after the subsequent solidification.

The affinity of Ti toward oxygen is less than that of the aluminum toward the oxygen. Besides, Ti has greater affinity than manganese toward oxygen. Thus if the molten steel during smelting is not deoxidized properly, then there is a large amount of titanium oxide.

The high content of nitrogen forms titanium nitride that forms inclusions in molten steels. On the other hand, titanium oxides and nitrides will obstruct the process of continuous casting. During the refining process by pyrometallurgy of Ti-micro-alloyed steel, it is required to remove sulfur, oxygen, and nitrogen. But emphasis should be given on the relationship between Ti, Al, and Ti, which are refractory elements. Compared with Nb or V, in the case of Ti, it is more difficult to control Ti-micro-alloyed steels which attributes to the more type of the secondary phase and wider temperature range of the precipitate.

During smelting Ti_2O_3 and TiN particles will precipitate in the liquid steel that improves as cast microstructure. During slab cooling process TiN and $Ti_4S_2C_2$ tens to hundreds of nanometers precipitate in the solid solution plays an important role in controlling the grain growth of austenite during soaking and recrystallization process (**Figure 11**).

During rolling TiC precipitation of TiC with the size below 10mm could result in the significantly precipitation hardening.

As a kind of micro-alloying element, Ti significantly improves the comprehensive properties of steel. However, when compared with niobium and vanadium micro-alloyed technology, Ti has not been used extensively in industry for a long time. Ti-micro-alloyed steel fluctuates largely and production process is not stable. Ti is very reactive and forms TiO and TiS that are very harmful. Formation of these phases consumes a portion of Ti that reduces the volume fraction of TiC precipitation at low temperature but also significantly changes the chemical free

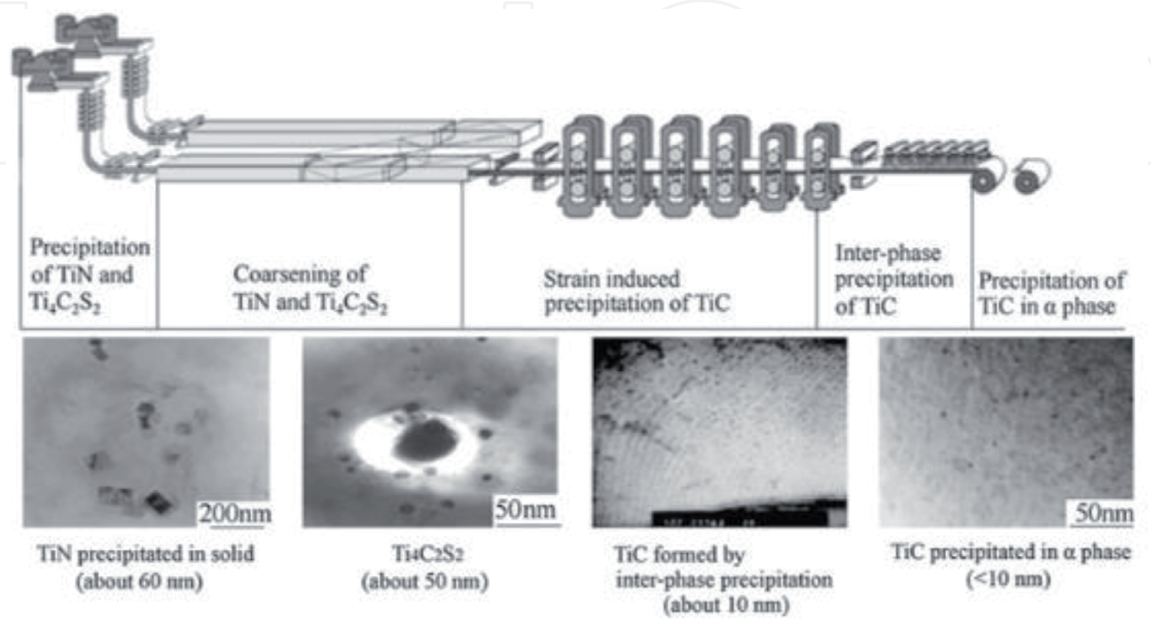| Precipitation of TiN and $Ti_4C_2S_2$	Coarsening of TiN and $Ti_4C_2S_2$	Strain induced precipitation of TiC	Inter-phase precipitation of TiC	Precipitation of TiC in α phase
TiN precipitated in solid (about 60 nm)	$Ti_4C_2S_2$ (about 50 nm)	TiC formed by inter-phase precipitation (about 10 nm)		TiC precipitated in α phase (<10 nm)

Figure 11.
Ti-bearing precipitation (adapted from Ref. [11]).

energy of TiC. Precipitation behavior of TiC changes and strengthening effect is greatly affected. Besides, TiC is sensitive to temperature and affects the properties of steel.

Besides, high-strength Ti-micro-alloyed steels are the precipitation-hardened ferritic steels. The ferrite grain refinement and TiC precipitation have a good combination in strengthening that plays an important role in obtaining both high strength and high toughness simultaneously for those steels. The ferrite grain refinement depends on the refinement of austenite grain size and on the control of transformation temperature. The refinement of austenite grain size mainly depends on the control of the austenite grain growth before hot rolling and recrystallized austenite grains during hot rolling.

7. Nickel steels

Nickel is the oldest and one of the fundamental alloying elements. It has unlimited solubility in gamma iron and is highly soluble in ferrite. As a result it gives high strength and toughness. Ni lowers the critical temperature of steels and retards the decomposition of austenite. As a result at low temperature or room temperature, austenite gets stable.

Ni does not form carbide. Besides, it reduces the carbon content of the eutectoid. As a result of which there is high percentage of pearlite forms compared to the equal composition plain carbon steels. Pearlite forms at the lower temperature thus become finer and tougher than the pearlite in unalloyed steels.

8. Chromium steels

Chromium is less expensive than Ni. Chromium is a carbide former and forms (Cr_7C_3, Cr_4C) or complex carbide [$(FeCr)_3C$]. This carbide has high hardness and wear resistance. It has 13% solubility in austenite and unlimited solubility in ferrite. In alloying steels, chromium containing more than 5% improves the corrosion resistance and high temperature properties.

9. Manganese steels

Manganese is less expensive and mostly acts as deoxidizers. The presence of manganese in alloy steel reduces the prone to the hot shortness. As a result of which, the alloy steel containing manganese can perform the hot work.

Besides, the absence of manganese in the steel may form FeS. FeS has low melting temperature. Ehen the steel sample is how rolled then due to the low melting temperature of the FeS it melted first. Thus the few places in steels containing FeS become slippery, and thus the hot-rolled samples may slip during rolling.

Mn and Ni both reduce the critical temperature and lowers the amount of carbon in eutectoid. Alloying steels containing more than 10% Mn become austenitic after slow cooling.

Hadfield Mn steel is a special type of steel (12% Mn) and has great abrasion resistance. If it is slow-cooled from 1750F, then a large brittle carbide forms surrounding the austenite grain. Ultimately forms the structure with low strength and ductility.

Nb micro-alloyed steels	Ti micro-alloyed steels	Ni micro-alloyed steels	Cr micro-alloyed steels	Mn micro-alloyed steels	Mo micro-alloyed steels	W micro-alloyed steels
Addition of Nb in steels causes formation of niobium carbide and niobium nitride which improves grain refinement, and retardation of recrystallization ultimately increases toughness, strength, formability, and weldability	Addition of Ti in steels passives to acids and minerals at low temperature and improves high temperature properties	Ni lowers the critical temperature of steels and retards the decomposition of austenite. As a result at low temperature or room temperature, austenite gets stable	In the alloying steels, chromium containing more than 5% improves the corrosion resistance and high temperature properties	The presence of manganese in the alloy steel reduces the prone to the hot shortness	Molybdenum is used in combination with Ni or Cr or both. Plain molybdenum steel is carburized to improve wear resistance	Tungsten is mainly popular for providing high temperature properties and hardenability of steels

Table 2.
Basic comparison of different types of micro-alloyed steels.

10. Molybdenum steels

Molybdenum is a little expensive alloying element. It has limited solubility in austenite and ferrite. As a result of which, it is a strong carbide former. Molybdenum is used in combination with Ni or Cr or both. Plain molybdenum steel is carburized to improve wear resistance.

A lot of research has been done in the case of interphase precipitation. In matter molybdenum plays significant roles. Four steels were manufactured with identical composition, and Ti, V, Mo, and N content is added to investigate the effect of composition on interphase precipitation. Alloys were rapidly cooled from the single austenite phase field and isothermally transformed at 630°C and 650°C for 90 min. When Mo is added, then there is a significant reduction in the austenite to ferrite transformation kinetics, particularly in the case of V steels. Interphase precipitation was observed in all alloys at both transformation temperatures. In the case of the Ti-bearing steel, two types of precipitate were observed, namely, TiC (finer) and Ti_2C (coarser), while for the V-bearing steels, VC (finer) and V_4C_3 (coarser) were observed. Where Mo was present in the alloy, it was found dissolved in all carbide types. The (Ti,Mo)C and (V,Mo)C were formed by classical planer interphase precipitation (PIP), while the $(Ti,Mo)_2C$ and $(V,Mo)_4C_3$, which had a much wider row spacing, were formed through curved interphase precipitation (CIP). Each adopted one variant of the Baker-Nutting orientation relationship. The Ti-micro-alloyed steels undergo the smallest precipitates of all the steels, which were approximately the same size irrespective of whether Mo was present in the alloy and irrespective of the transformation temperature. However, the addition of Mo to the V-bearing steels causes significant increase in precipitate volume fraction and a reduction in precipitate size.

11. Tungsten steels

Tungsten is mainly popular for providing high temperature properties and hardenability. It is mainly a carbide former. Approximately 2–3% W is equivalent to 1% Mo. Tungsten is mainly used in the tools industry (**Table 2**).

For achieving high strength and toughness, fine grain structure is essential in steels. To produce such microstructure, a carefully controlled high temperature processing of steels must be done. Hot working alone cannot refine the coarse or nonuniform grain. For example, grain coarsening behavior of laboratory heats of C-Si-Mn base steels varies with the concentration of Al, V, Ti, or Nb micro-alloy addition. Thus, steels containing the very insoluble TiN coarsen at much higher temperatures than steels containing the more soluble VCN.

The main strengthening mechanisms of micro-alloyed steels are grain refinement and precipitation [12]. It can be done by high temperature-controlled process and by adding proper alloying elements. Nowadays an economical alternative of the traditional quenched and tempered steels is micro-alloyed steels.

12. Conclusion

Strengthening mechanism can be done by precipitation forming and grain refining. Micro-alloy element hinders grain growth that causes grain refinement [13]. Precipitates forming on ferrite or austenite cause improvement of hardening or strengthening of steel. Phase transformation in some cases also causes strengthening of steels. In phase transformation, different micro-alloying elements appear to contribute considerably. Strengthening of steels can be done by different heat

treatment techniques as well in addition to alloying. Besides, the most economical alternative way of improving the mechanical properties of steel is adding smaller amounts of some special elements.

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References

[1] Abbaschian R, Abbaschian L, Reed-Hill RE. Physical Metallurgy Principles. 4th ed. Stamford: Cengage Learning; 1994

[2] Avner SH. Introduction to Physical Metallurgy. New York: MAcGraw-Hill Book Company; 1974

[3] Bain EC, Paxoton HW. Alloying Element in Steel. Metals Park, Ohio: American Society for Metals; 1961

[4] Oliveira M, Calderon–Harnandez J, Magnabosco R, Hincapie D, Alonso–Falleiros N. Effect of niobium on phase transformations, mechanical properties and corrosion of supermartensitic stainless steel. Journal of Materials Engineering and Performance. 2016;**26**. DOI: 10.1007/s11665-017-2610-1

[5] Javaheri V. Effect of Niobium and Phase Transformation Temperature on the Microstructure and Texture of a Novel 0.40% C Thermomechanically Processed Steel. Finland: Elsevier; 2018. pp. 295-308

[6] Davis Joseph R. Metals Handbook Desk. 2nd ed. ASM International. 1998. ISBN: 978-0-87170-654-6

[7] Filho AI, Silva RV, da Silva Cardoso W, Casteletti LC, et al. Effect of niobium in the phase transformation and corrosion resistance of one austenitic-ferritic stainless steel. Materials Research. 2013;**17**(4):801-806. DOI: 10.1590/1516-1439.190113

[8] ASM Handbook. Properties and Selection: Nonferrous Alloys and Special-Purpose Materials. Vol. 2. ASM International. 1990

[9] Mao X. Titanium Microalloyed Steel: Fundamentals, Technology, and Products. Beijing, China: Metallurgical Industry Press; 2019

[10] Massalski TB. Binary Alloy Phase Diagrams. 2nd ed. Vol. 3. Ohio, USA: ASM International Materials Park; December 1990

[11] Yong Q. Physical Metallurgical Principles of Titanium Microalloyed Steel—Dissolution and Precipitation of Titanium-Bearing Secondary Phases. China: Springer; pp. 71-139

[12] Leslie WC, Rickett RL, Dotson CL, Walton CS. Influence of Al content on the corrosion resistance of micro-alloyed hot rolled steel as a function of grain size. Transactions of the American Society of Metals. 1954;**46**:1470

[13] Joseph RD. Metals Handbook Desk Edition. 2nd ed. ASM International. 1998. ISBN: 978-0-87170-654-6