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Effects and Applications of Mo in Alloy Steels

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Abstract: Mo is one of the most important alloying elements in steels, and there are some Mo-containing steel grades in almost all the alloy steel categories. The paper will briefly describe effects of Mo in steels and demonstrates applications of Mo in alloy structural steel, tool and die steel, stainless steel and heat-resistant steel etc. Mo is a unique and irreplaceable alloying element in steels. On the basis of understanding effects of Mo, new high-performance alloy steels with Mo will be continuously emerging and the steel performance related with time, temperature and environment in steel will be improved.

1. Introduction

Most of Mo is consumed in alloy steel production [1]. As the economic development in our country, output of steel is continually increasing. The crude steel output in our country reached 567.84 million tons in 2009, accounting for 46.6% of that of the world. Most steel is consumed in common steel-based construction at present. As the development of China's manufacturing industry, especially the advance of localization of major equipment, demand of the amount and variety of alloy steel will increase. The development of alloy steel represents a country's industrialization level. However, there are still quite great differences between alloy steel output ratio in total steel, variety as well as quality in our country and that in industrialized countries. Hence, production and application level of alloy steel urgently need to be developed and improved. As a typical alloying element in production of alloy steel, Mo plays an important role in improving the quality of alloy steel in our country.

The development of molybdenum steel is a miniature of the development of alloy steel. The first application of Mo found in the late 18th century was armor plate with Mo produced by French Snyder (Schneider) in 1891. Mo had effectively replaced W in many steels for the density of Mo was merely half of W. Low-Mo alloy steels for the automotive industry were developed after World War I. The research on forging and heat treatment of Mo-based high-speed steel deepened the understanding of effects of Mo in steel in 1930s. Mo found

increasing application in steel as an alloying element. The application of Mo in steel, particularly tool steel with Mo, was further expanded after World War II. As the development of thermo-mechanical processing technology, Mo had found increasing application in high-strength low-alloy steel since 1960. High strength and high toughness steel plate was used in high grade oil and gas pipelines, high-rise buildings, large ships, pressure vessels, bridges and construction machinery. As the most effective alloying element promoting acicular ferrite phase transformation, Mo was widely used in high-strength low-alloy steel (HSLA) and results in the production of X70-X120 pipeline steel, 590-980MPa grade low yield ratio construction steel, fire-resistant construction steel, 780-1180MPa construction machinery steel and many other HSLA steels containing Mo.

As an important alloying element, Mo is used in all alloy steel categories. Currently, production of structural alloy steel, stainless steel, tool steel and heat-resistant steel continues to monopolize and influence the Mo consumption. The unique and irreplaceable effect of Mo in steel leads to a widely application in alloy steel. The paper will briefly describe effects of Mo as an alloying element and discuss current status and development trend of Mo-containing alloy steels.

2. Effects of Mo in steel

Adding Mo to steel produces interaction between heterogeneous atoms, such as interaction between Mo and Fe, C as well as alloying elements. This changes phase stability in steel and produces a lot of new stable phases, thus the microstructure is changed or new microstructure is formed. The origin of these changes is the difference in atomic structure, atomic size and crystal lattice between Mo and Fe, C as well as other alloying elements

Mo (at room temperature) has the same body-centered cubic crystal structure (a = 3.1468) as Fe, and it is a ferrite forming element. Mo has some solid solubility in steel (solid solubility can reach 4% for α-Fe, whereas it is 3% for γ-Fe at room temperature). Mo forms compounds with C, N, B and other elements and intermetallic compounds with other alloying elements [2].

Atomic radius ratio between C and Mo is rC / rMo = 0.56 (<0.59) and the formation of hcp type MC and M2C carbides leads to dispersion strengthening in steel. Complex M6C carbide (Fe3 (W, Mo) 3C) is formed in W-Mo steel. As atomic radius ratio between N and Mo rN / rMo = 0.52 (<0.59), face-centered cubic lattice Mo2N and hexagonal lattice MoN are formed in steel. In

combination with B complex interstitial compound whose crystal lattice structure shows CuAl2 type. Interaction with Fe and other alloying elements, various intermetallic compounds are formed, such as σ phase in Mo-Mn, Mo-Fe, Mo-Co and other systems. They lead to embrittlement in low-carbon high-Cr stainless steel, Cr-Ni austenitic stainless steel and heat-resistant steel. The complex hexagonal lattice AB2 Laves phase MoFe2 found in multi-alloying heat-resistant steel can strengthen the austenitic heat resistant steel, 12% Cr-type martensitic steel, Cr-Mo-Co system martensitic precipitation hardening stainless steel. In the multi-alloying heat resistant steel and alloy, Mo can replace Al in AB3 ordered phase Ni3Al and form Ni3Mo. Mo is a moderate various compound forming element. Therefore, adding Mo to different alloy steel can form the required compounds and lead to dispersion strengthening.

Mo in solid solution state can affect the Fe-C phase diagram and change the location of the critical point of steel, including the temperature and carbon content. Mo increases A3 point temperature, reduces A4 point temperature and narrows phase region. Mo has effect on austenite formation during heating, undercooled austenite transformation, martensite decomposition during tempering and other microstructure formation in steel. Mo strongly delays pearlite phase transformation, whereas delays bainite transformation less than the former. Meanwhile, Mo increases the temperature of maximum phase transformation speed of pearlite transformation and reduces that of bainite, thus two C-curves of pearlite and bainite obviously appear. Hence, Mo is the most important element in bainitic steel.

Mo is enriched to cementite when the tempering temperature is higher than 500 ℃ during tempering process of quenched martensite. Meanwhile, special carbide of Mo is precipitated, accompanied by the dissolution of cementite. In the steel with 4-6%Mo, precipitation sequence of special carbides is as the following: Fe3C s a2C → M6C. In the low-Mo steel, cementite and special carbides coexist. Precipitation of special carbide in steel leads to increasing hardness and strength and results in secondary hardening. Secondary hardening has been widely used in many alloy steels.

3. Applications of Mo in steel

Due to the above effects of Mo in steel, Mo can be used as an important steel alloying element to increase the strength and toughness of steel (especially high-temperature performance), improve corrosion resistance of

steel in acid solution and the marine environment, increase hardness and wear resistance, improve the hardenability and hardness of steel as well as clean grain boundaries to improve the resistance to delayed fracture. Mo and Cr, Ni, Mn, Si, W, V, Co, Nb, Ti as well as other elements can be added to create different types of alloy structural steel, stainless steel, tool and die steel, heat-resistant steel and other alloy steels.

3.1 Alloy structural steel

Alloy structural steel is a steel category that has large production and wide application. Such steels find extensive application in various industrial fields. Mo has the following effects in alloy structural steels:

●To increase hardenability. Hence, steel with large sections can be through quenched and hardened layer depth is increased.

●To prevent or reduce the tendency of steel to temper brittleness in steels containing elements leading to temper brittleness, such as steel alloyed with Mn, Cr, etc.

●To improve the tempering resistance or tempering stability of steel. Thus steel can be tempered at a higher temperature, so as to more effectively eliminate or reduce the residual stress in steel to enhance the service life of steel.

●In carburization structural steel, Mo leads to fine microstructure in carburized layer, reducing the tendency of carbides to form continuous network in grain boundary.

●In nitriding steel, Mo is an important alloying element in order to avoid the temper brittleness during nitriding process, such as the commonly used nitriding steel 38CrMoAl which has no tempering brittleness, ,good heat resistance (up to 500 ℃) and excellent abrasion resistance, keeping the temperature of heat preservation at the nitriding temperature for a long time and slowly cooling.

There are 23 grades of structural alloy steel with Mo within the 77 grades of structural alloy steels in the Chinese national standard GB / T 3077-1999. There are CrMo, CrMoV, CrMoAl, SiMnMoV, MnMoB, CrMnMo, CrNiMo, CrMnNiMo, CrNiMoV and other 9 types of steel containing Mo in accordance with alloy system. According to different type of steel, Mo content in steel varies and Mo content in alloy structural steels is in the range of 0.15% to 1.10%.

There are 6 Cr-Mo steel grades in the national standards, which are 12CrMo, 15CrMo, 20CrMo, 30CrMo, 35CrMo, and 42CrMo. Such steel grades containing 0.15%-0.55% Mo have high strength, good thermal stability and excellent stress corrosion cracking resistance. Hence, they are generally used for boiler steam pipes, mechanical parts with larger stress or large sections (such as shafts, bolts, gears, etc.). Steels 42CrMo and 35CrMo with high strength, toughness and hardenability as well as little quenching distortion have high temperature strength and creep rupture strength and can work for a long time at 500 ℃, which are used to produce important structural parts working under high load. Among these grades, 42CrMo is the steel grade which has bulk production and wide applications.

40CrMnMo and 20CrMnMo steel are the commonly used Cr-Mn-Mo type steels, which contain 0.20-0.30% Mo. Case-hardened steel 20CrMnMo with excellent cutting and welding performance has no temper brittleness and can be used in important carburizing parts required high surface hardness and wear-resistance, instead of case-hardened steel containing high nickel. 40CrMnMo steel has good hardenability and high tempering stability. The parts with diameter less than 100 mm, can be completely quenched after about 850 ℃ austenitizing, and they have high mechanical properties after tempering at 550-600 eel has good hardenability and high tempering stafts and gears.

There are five common Cr-Mo-V type steel grades including 12CrMoV, 35CrMoV and 25Cr2Mo1VA. Mo content in such steels is usually between 0.15-0.35%, however Mo content in 25Cr2Mo1VA steel is up to 1%. Adding V in Cr-Mo steel can refine grain, increase strength, particularly yield ratio, and inhibit diffusion of Mo in the carbide during long-term use at high temperature, thus enhance the microstructural stability and thermal strength. Such steel has good welding performance used after normalizing and annealing and is mainly used for structural parts of wheel turbine, blower and other machines.

3.2 Stainless steel

Stainless steel is an important application field of Mo. Mo finds application in austenitic stainless steel, martensitic stainless steel, ferritic stainless steel, duplex stainless steel and corrosion resistant alloys. In recent years, China's stainless steel production and consumption continued to grow year by year. China's production of stainless steel reached 5.95 million tons and consumption to 5.3 million tons in 2009, accounting for 1/4 of the world's

stainless steel output. A large amount of Mo was consumed in stainless steel production. Effects of Mo in stainless steel are as following: (1) Mo improves the corrosion resistance of steel, especially pitting resistance; (2) Mo increases the strength of martensitic stainless steel and the secondary hardening effect; (3) Mo improves the mechanical properties of steel at low temperature.

Mo and Cr are the elements which form and stabilize ferrite as well as enlarge ferrite phase region. As an important alloying element, Mo is added to further expand the scope of use. Main effect of Mo is to increase corrosion resistance of steel in reductive medium (such as H2SO4, H3PO4, and some organic acids as well as urea environment) and to improve pitting and crevice corrosion resistance and other properties. Commonly used austenitic stainless steel grades with Mo include 1Cr18Ni12Mo2Ti, 0Cr18Ni12Mo2Ti, 00Cr17Ni4Mo2, 0Cr17Ni12Mo2N, 00Cr18Ni14Mo2Cu2, 00Cr18Ni18Mo5N, and 00Cr17N17Mo7Cu2. Such steel grades are mainly used in strong corrosion environment. Generally Mo content changes in the range of 2-7%.

Besides improving corrosion resistance, Mo mainly increases strength and hardness as well as secondary hardening effect in martensitic chromium stainless steel. Especially in the case of low-temperature quenching, this effect is widely used in stainless steel tool. In the martensitic Cr-Ni stainless steel, the addition of Mo is to increase stability and strengthen the secondary hardening effect without reducing toughness. Mo content in such steel grades generally changes in the range of 0.5%-4%. In the precipitation hardening stainless steel, main effect of Mo is to improve the corrosion resistance, low temperature mechanical properties, high temperature strength, and tempering stability. Steel with 2% Mo can maintain high hardness after cryogenic treatment in different solution conditions. Martensitic stainless steel grades with Mo mainly include 1Cr13Mo, 9Cr18Mo, 00Cr13Ni5Mo, 0Cr15Ni7Mo2Al, 0Cr16Ni6MoCuAl, etc.

As a strong ferrite forming and narrowing γ area element, Mo has beneficial effect on the formation of α-phase in (α+γ) duplex stainless steel. Except for oxidation solution, Mo has prominent effect on reductive medium corrosion resistance, pitting and crevice corrosion resistance in (α+γ) duplex stainless steel. Therefore, All the (α+γ) duplex stainless steel contain 2-3% Mo. The common steel grades include 1Cr18Mn10Ni5Mo3N, 0Cr17Mn14Mo2N, 00Cr18Ni15Mo3Si2, 00Cr22Ni5Mo3N, etc.

3.3 Die steel

Mo is one of the chief elements in tool and die steels. Effects of Mo are as following: (1) The carbide is formed in large cross-section steel to improve the hardness and strength as well as to increase wear resistance; (2) Quenching deformation is reduced during quench hardening process; (3) Strength and toughness are increased; (4) The addition of Mo in hot working die steel improves hardenability and tempering stability.

Low-alloy hot working die steel belongs to low carbon steel. The commonly used steel grades include 5CrNiMo, 5CrMnMo, 5CrNiMoV, and 5Cr2NiMoV. Carbon content is generally 0.4-0.6%. The major alloying elements include Mn, Cr , Ni, Mo, etc. Mo content is usually in the range of around 0.15-0.55% (except, 5Cr2NiMoV which contains 1% Mo). Due to the appropriate ratio of various elements, undercooled austenite becomes stable leading to excellent hardenability and mechanical properties. Mo can effectively improve the thermal strength and inhibit the temper brittleness. The carbides formed by Mo and V improve strength as well as wear resistance. Such steel grade is mainly used for small forging module. In order to meet the needs of large modules, higher alloy content steel for module has been developed in recent years, such as 40CrNiMoV4, 30Cr2NiMoV, 2Cr3Mo2NiVSi, etc.

Medium alloy Cr hot workdie steel is medium-C medium alloy steel, commonly used steel grades including 4Cr5MoSiV, 4Cr5MoSiV1, 4Cr5MoWVSi, and 5Cr5MoWSiV. 4Cr5MoSiV1 is the representative steel (China's annual consumption reaches about 5 million tons). Such steel, which generally contains 5% Cr, 1% Mo and a certain content of V, has high hardenability and the supercooled austenite is stable. Large-section mould produced using such steel obtains high hardness when quenched in the air. The secondary hardening, good heat resistance, thermal fatigue resistance and corrosion resistance are obtained by 2-3 times tempering after quenching. Such steel finds wide applications in aluminum die casting, precision forging die, hot forging punch, hot extrusion mould, hot shear die, hot roll and hot die working in a variety of shocks and rapid cooling conditions.

W-Mo type hot work die steel was used to produce dies earlier in history. During World War II, W resource was constrained. Therefore, a series of Mo replacing W and W-Mo hot work die steel were developed. Such steel grades include 4Cr3Mo3VSi, 3Cr3Mo3W2V, 5Cr4W5Mo2V, 5Cr4Mo2W2SiV, and 5Cr4Mo3SiMnVAl. It generally contains 3% Mo and 8-18% W, in addition to some other elements such as V and Co. Due to high content of W, Mo, V and

other strong carbide forming elements, a large number of precipitation of alloy carbide leads to a strong secondary hardening phenomenon and high tempering hardness when tempering at about 500-550 ℃, which can be comparable with the quenched hardness,. Thus, it has higher temperature strength, hardness and temper resistance than Cr hot work die steel. W-Mo hot work die steel is applied to hot die with cavity temperatures in excess of 600 ℃, high static load bearing and low impact load, such as mechanical forging press die and hot extrusion die, especially materials with large deformation resistance during manufacturing and processing, such as stainless steel, high-temperature alloy, heat-resistant steel and so on.

High strength and toughness cold work die steel, which generally contains high carbon, 12% Cr and around 1% Mo, is one of ledeburite steel and is universal. Its representative steel grade is Cr12Mo1V1 (ASTM standard D2). A large number of carbide leads to high wear resistance and little distortion characteristics. Hence, it finds wide applications in blanking and cold forming dies and punches, including: blanking die, punch, press impression, drawing molds and other cold forming dies.

Air quenching low-distortion cold work die steel, which generally is one of the high-C and medium-Cr steel, contains around 1-3% Mo. Commonly used steel grades include Cr5Mo1V, and Cr4W2MoV. Such steel grades have good air-cooling hardenability and quench hardening penetration depth as well as excellent shape stability characteristics and combination of properties. It is widely used in blanking die, punch, pressure impression, drawing molds and other cold forming dies.

In matrix steel, C content is generally around 0.55-0.70%, Cr content is around 4% and Mo content is around 2-5%, besides adding W, V, Nb, Ti and other alloy elements. The representative steel grades include 6W6Mo5Cr4V, 6Cr4W3Mo2VNb, and so on. Its chemical composition is equivalent to that of matrix in high-speed steel after quenching. Therefore, a small number of eutectic carbide in matrix steel is fine and well-distributed and toughness is increased relatively. Such steel is mainly used for cold extrusion die, cold heading die, forming die, cutting die, cold-punched die, punch, etc.

In plastic mould steel, Mo is mainly used in pre-hardened plastic mould steel. Its representative steel grades include 3Cr2Mo (ASTM standard P20) and 3Cr2NiMnMo steel with 0.30-0.50% Mo. Such steel grades generally achieve hardening in plant with 28-34HRC hardness as well as excellent cutting and

polishing performance. Pre-hardened plastic mould steel is widely used in plastics, electrical appliances, rubber and other industries.

3.4 High speed steel

China's high-speed steel output ranked No. 1 in the world. W and Mo are the most important alloying elements in high speed steel, so high-speed steel production consumes a large amount of Mo. The main effects of Mo in high speed steel are as follows: (1) Mo forms a number of primary carbide that is difficult to dissolve, which makes it possible that the steel can be quenched in high temperature near the melting point and increases the wear resistance; (2) Mo also forms sufficient amount of secondary carbide, which are converted to Mo(W)-rich martensitic during high-temperature solid solution quenching. During tempering the precipitation of M2C and MC is key factor of producing secondary hardening and hot hardness; (3) Mo increases the strength and toughness of high-speed steel; (4) The addition of Mo improves the microstructure of primary carbide in pure W high-speed steel which increases its thermoplastic.

Universal high-speed steel, a basic steel grade in high-speed steel, is the most widely used in high speed steel cutting tools, accounting for the total amount of high speed steel more than 80%. Such steel grades mainly includes M2, T1, W9, M7, M10 steel, etc., in addition to T1 (W18Cr4V steel, are used very little, gradually replaced by M2), the rest being W-Mo high speed steel, Mo content generally changes in the range of 3 - 9%. Mo content in M2 steel has the maximum usage of 6%. Such steel is applied to the general steel cutting speed of 25-40m/min, when the tool tip temperature is 550-600 ℃, the hardness can be still maintained 55-60HRC. They are used to produce turning, milling, hob, planer knives, broaches, drills, etc., as well as high wear resistance of cold and hot die, roll, and high temperature bearings.

Super-hard high speed steel contains 1.10% C, about.3.25-10%Mo and a certain amount of W, V, Co (5-13%) and other alloying elements. Its representative steel grades include M41 and M42. The hardness reaches up to HRC68-69 after hot-quenching and 2-3 times tempering. Such steel can be used for common turning, milling and drilling tools. When workpiece is medium hard-quenched and tempered steel or common austenitic stainless steel with cutting difficulty, the cutting life of M42 steel cutting tool is 2 times higher than that of M2 steel cutting tool.

Low alloy high speed steel, a steel grade with less than 12% W equivalence, can save valuable alloying elements and reduce the cost of steel. The representative steel grades include M50, D950 (Sweden), W4Mo3Cr4VSi, W3Mo2Cr4VSi and so on. Such steel grades generally contain 2-5% Mo as well as Cr, W, V, Si and other alloying elements. The chemical composition is optimized to improve the performance of high speed steel. In recent years, low alloy high speed steel has been rapidly developed in our country, which is mainly used for rolling drill, hacksaw blades and wood planer as well as milling cutter and taps in part. China's annual output of low alloy high speed steel reaches nearly 10,000 tons, which is mainly used to produce twist drills and other tool products for export.

3.5 Heat-resistant steel

It was long since that people found Mo could increase high temperature strength of steel. Robin indicated that the addition of 0.5-2% Mo could improve high temperature hardness in 1909 [3]. In ferrite-pearlite heat-resistant steel, martensitic steel and austenitic heat-resistant steel, Mo in solid solution state strengthens the matrix, whereas, Mo has dispersion strengthening effect when it exists as compounds. In ferrite-pearlite heat-resistant steel, Mo may form M_2C and M_6C carbides in the poor stability, which reduces Mo content in the matrix phase and weakens strengthening effect of solid solution Mo in the matrix. Solid solution Mo is the most effective element to increase high temperature strength. All the typical ferrite-pearlite heat-resistant steels, such as 12Cr1MoV, 2.25Cr1Mo, 15CrMo and 12Cr2MoWVSiTiB contain Mo.

The main strengthening phases in Cr12-type martensitic steel are the MC, $M_{23}C_6$ and M_6C type carbides. Due to the existing of V and Nb, Mo and W partly form $M_{23}C_6$ and M_6C, whereas, most of them are soluble in the matrix and have solid solution strengthening effect. The proportion of Mo and W content will affect the creep strength and toughness of the steel. Studies show that the addition of Mo can increase the creep rupture strength [4]. Typical martensitic steel grades include 2Cr12MoV, 1Cr10Mo2VNb, 1Cr10Mo2VNb, 1Cr9W2MoVNbNB and so on.

The addition of Mo and W mainly plays solid solution strengthening effect in Cr18Ni9 type austenitic heat resistant steel. Generally, the addition of 2-3% Mo can improve the creep strength at 650 ℃, such as 1Cr18Ni12Mo2Ti. In carbide precipitation strengthening austenitic heat resistant steel GH36 and intermetallic compound precipitation hardening austenitic heat resistant steel

GH132 (A-286), most of Mo is soluble in the matrix, which leads to solid solution strengthening effect, and increases the creep strength of steel and decreases the notch sensitivity.

As a solid solution strengthening element, a large number of Mo (about 90% of species) is used in high temperature super alloys, such as GH4169 (nickel-based alloys, Mo content reaches 3.25%), GH4141 (Mo content reaches 10%), GH4049 (Mo content reaches 5 %) and so on. High temperature super alloys are widely used in aircraft engine blades, turbine disks and space rocket engine.

4. Concluding remarks

Due to special effects of Mo in steels, it becomes one of the most important elements, which is widely used in structural alloy steels, stainless steels, tool and die steels and heat resistant steels. China has the advantage of Mo resources and production, however the Mo consumption for unit steel in China lag behind that of industrialized countries. Thus, much more attention should be paid to the investigation of application technology of Mo in alloy steels so that we can produce high quality steel products to meet the increasing requirements of machinery industry. On the basis of understanding effects of Mo, new high-performance alloy steels with Mo will be continuously developed and the steel performance related with time, temperature and environment in steel will be improved.

Reference
1. K.Nakajima, K.Yokoyama, Y.Matsuno and T.Nagasaka, Substance flow analysis of molybdenum associated with iron and steel flow in Japanese economy, ISIJ International, 47(2007)3, 510-515.
2. Zhang S.H, Wu CJ. Materials Science in Iron and Steel. Beijing: Metallurgical Industry Press, 1992.
3. F.Robin, Rev.Met., 6(1909), 180.
4. Ota. Ferritic Heat Resistant Steel – Research and Development toward Cutting-edge. Beijing: Metallurgical Industry Press : 2003,157-158.

The brief biography of Prof. Han Dong

Prof. Han Dong is vice president of Central Iron and Steel Research Institute (CISRI), general director of Institute for Structural Materials of CISRI, and general secretary of Chinese Specialty Steel Society, Chinese Society for Metals. Prof. Dong has been undertaking plenty of research and development work in the field of steels, especially in special steels for automobiles and ordnance applications. As the chief scientist, Prof. Dong is currently in charge of a national key basic research program entitled "On the performance improvements of steels through structure control".

Heat-Treated Low-Alloy Carbon Steels: The Benefits of Molybdenum

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Introduction

Molybdenum (Mo) is an important alloying element in low-alloy carbon steels that can be heat treated to many excellent combinations of strength, toughness, fracture resistance, fatigue resistance, and wear resistance. Typical applications include automotive parts, machine parts, tools, and structures, for example gears, bearings, shafts, oil country tubulars, air craft landing gear, and fasteners. Properties depend on steel carbon content, alloy content, and heat treating parameters, and the following sections of this paper describe the important role that Mo plays in the alloy design for heat treatments that produce the wide variety of properties achievable in low-alloy carbon steels.

Mo-containing Low-Alloy, Carbon Steels

Steel parts quenched to martensitic microstructures have the highest hardness and strength possible in any steel, but this strength depends very much on carbon content, as shown in Fig. 1 [1,2]. The role of Mo is to make possible the formation of martensite as described in the section of hardenability. As-quenched martensite has low toughness, and therefore tempering is required. The highest strengths are preserved by low-temperature-tempering, as shown in the shaded region in Fig. 1. Mo has the greatest effect on microstructure and properties during high-temperature-tempering, as described below.

Three ranges of steel carbon content are shown in Fig. 1. The most widely used low alloy steels have medium-carbon content in view of the fact that they can be readily heat treated to a variety of combinations of strength and toughness. High-carbon steels are also heat treated but require special care because they tend to have lower toughness and potential embrittlement problems. Low-carbon steels are also widely heat treated and used, but are typically carburized to produce a high-carbon case microstructure. However

recently, low-carbon sheet steels for high strength automotive applications are being quenched to martensite after hot stamping [3].

Low-alloy steels are alloyed with relatively small amounts of the substitutional alloying elements Cr, Mo, and Ni. Stainless steels and tool steels are much more highly alloyed, including large amounts of Mo in some grades. Table 1 lists many low-alloy carbon steels [4]. The first two digits of the steel designation are based on the SAE/AISI system, but many countries have identical or similar grades of steels identified by their national
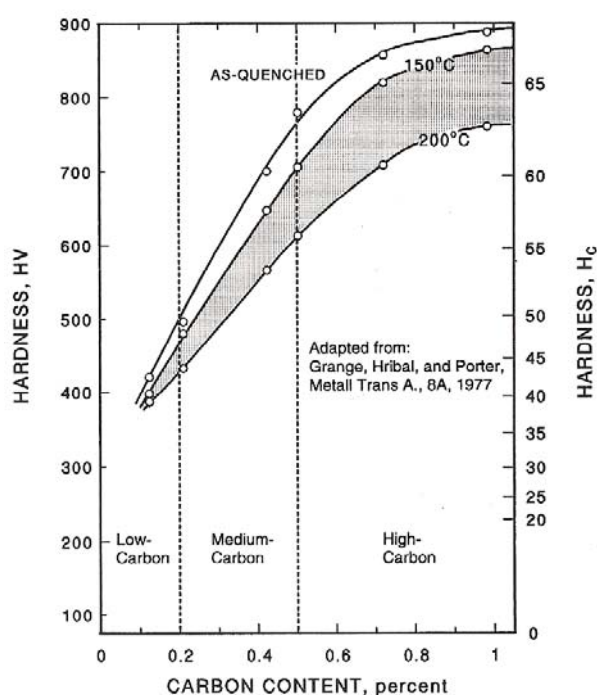
Fig. 1 Hardness as a function of steel carbon content in as-quenched and
low-temperature tempered conditions. Krauss [1, 2]

designation systems [5]. Table 1 shows that Mo is added in relatively small amounts to many of the steels, based on its ability to combine with the other elements to enhance hardenability and performance. The xx digits in the steel designations refer to the amount of carbon, an indication that the same alloying can be applied to grades of steel with different amounts of carbon.   A widely used low alloy steel is 4140, containing 0.38 to 0.43 pct C, 0.80 to 1.10 pct Cr, and 0.15 to 0.25 Mo.

As noted above, many low carbon steels are carburized. These steels need good hardenability in order to produce hardened core structures. Table 2 compares experimental (EX) grades of carburizing steels to standard SAE/AISI grades for various Groups of comparable hardenabilities, and shows

that small increases in Mo can significantly reduce the amount of Ni and still maintain the same hardenability [6].

Table 1 Nominal amounts of Cr, Mo, and Ni in Low-Alloy Carbon Steels, ASM [3]

Numerals and digits(a)	Type of steel and/or nominal alloy content	Numerals and digits(a)	Type of steel and/or nominal alloy content
Carbon steels		**Nickel-chromium-molybdenum steels**	
10xx	Plain carbon (Mn 1.00% max)	43xx	Ni 1.82; Cr 0.50 and 0.80; Mo 0.25
11xx	Resulfurized	43BVxx	Ni 1.82; Cr 0.50; Mo 0.12 and 0.25; V 0.03 min
12xx	Resulfurized and rephosphorized		
15xx	Plain carbon (max Mn range—1.00 to 1.65%)	47xx	Ni 1.05; Cr 0.45; Mo 0.20 and 0.35
		81xx	Ni 0.30; Cr 0.40; Mo 0.12
Manganese steels		86xx	Ni 0.55; Cr 0.50; Mo 0.20
13xx	Mn 1.75	87xx	Ni 0.55; Cr 0.50; Mo 0.25
		88xx	Ni 0.55; Cr 0.50; Mo 0.35
Nickel steels		93xx	Ni 3.25; Cr 1.20; Mo 0.12
23xx	Ni 3.50	94xx	Ni 0.45; Cr 0.40; Mo 0.12
25xx	Ni 5.00	97xx	Ni 0.55; Cr 0.20; Mo 0.20
		98xx	Ni 1.00; Cr 0.80; Mo 0.25
Nickel-chromium steels		**Nickel-molybdenum steels**	
31xx	Ni 1.25; Cr 0.65 and 0.80	46xx	Ni 0.85 and 1.82; Mo 0.20 and 0.25
32xx	Ni 1.75; Cr 1.07	48xx	Ni 3.50; Mo 0.25
33xx	Ni 3.50; Cr 1.50 and 1.57	**Chromium steels**	
34xx	Ni 3.00; Cr 0.77	50xx	Cr 0.27, 0.40, 0.50 and 0.65
Molybdenum steels		51xx	Cr 0.80, 0.87, 0.92, 0.95, 1.00 and 1.05
40xx	Mo 0.20 and 0.25		
44xx	Mo 0.40 and 0.52		
Chromium-molybdenum steels			
41xx	Cr 0.50, 0.80 and 0.95; Mo 0.12, 0.20, 0.25 and 0.30		

Table 2 Compositions, Grain sizes, and Hardenabilities of Various Carburizing Steels [6]

	Group I		Group II		Group III				Group IV
	EX24	SAE 8620	EX29	SAE 4320	20NiMoCr6	SAE 4817	SAE 4820	EX32	EX55
Composition, wt%									
Carbon	0.20	0.20	0.20	0.21	0.22	0.17	0.19	0.19	0.17
Manganese	0.88	0.89	0.87	0.58	0.58	0.54	0.60	0.82	0.87
Silicon	0.34	0.34	0.34	0.33	0.54	0.33	0.28	0.27	0.28
Phosphorus	0.015(a)	0.015(a)	0.015(a)	0.015(a)	0.021	0.015(a)	0.016	0.017	0.015(a)
Silicon	0.02(a)	0.02(a)	0.02(a)	0.02(a)	0.027	0.02(a)	0.02	0.02	0.02(a)
Chromium	0.51	0.47	0.48	0.52	0.64	NA(b)	NA(b)	0.53	0.49
Molybdenum	0.26	0.21	0.34	0.26	0.31	0.27	0.27	0.52	0.74
Nickel	NA(b)	0.53	0.54	1.76	1.56	3.56	3.48	0.80	1.84
Aluminum	0.08(a)	0.08(a)	0.08(a)	0.08(a)	0.043	0.08(a)	0.075	0.082	0.08(a)
ASTM grain size	9½	9½	9½	9½	7½	9½	9½	9	9½
D_I hardenability:									
Inches	1.6	1.7	2.0	1.9	3.0	2.5	2.7	3.3	4.7
Millimeters	41	43	51	48	76	63	69	84	120

(a) Amount added. (b) NA, none added. Source: Ref 21.23

The Hardening Process

Fig. 2 shows a schematic diagram of the processing steps required to produce hardened steel products. After primary processing, bars or long products may be forged at high temperatures to complex shapes and normalized to produce uniform fine microstructures for subsequent hardening or spheroidized for machinability. Some products are not forged, and are spheroidized to increase ductility for forming, as is the case for fasteners.

The heat treatment process for hardening consists of three steps: austenitizing, quenching, and tempering. Austenitizing converts low-temperature combinations of ferrite and cementite to the austenitic microstructures from which martensite will form on cooling; temperatures must be kept low to prevent the formation of coarse austenite grains. Quenching or rapid cooling is the step required to prevent the formation of low-strength microstructures other than martensite, and it is in this step where Mo plays an important role as discussed below. Finally, tempering is the step where the microstructure is adjusted to produce desired combinations of strength and toughness.
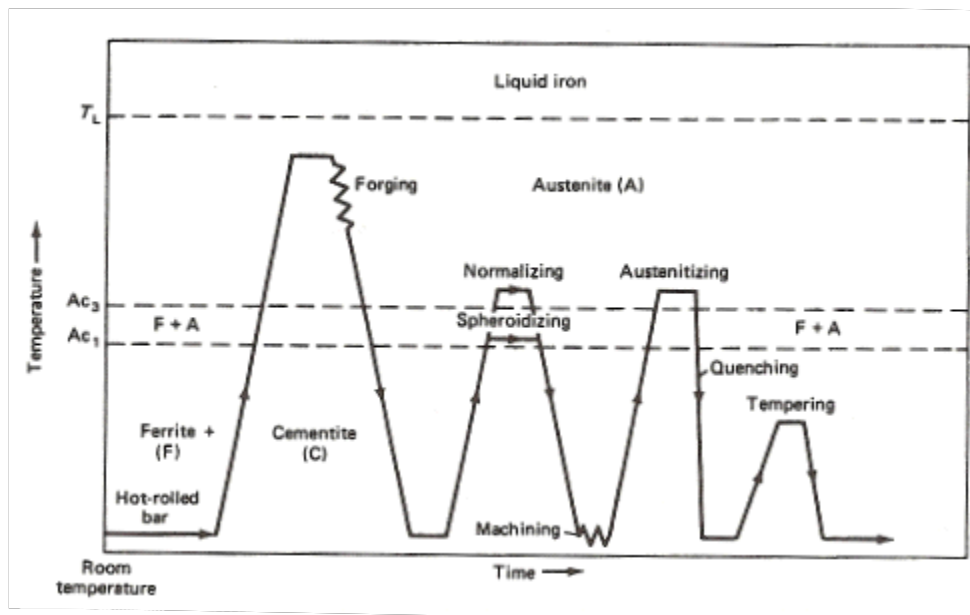
Fig. 2   Schematic diagram of the processing steps to produce hardened steel parts [1].

Hardenability

Hardenability describes the ability of a steel to be hardened and depends on the chemistry and microstructure of a steel, part size and geometry, and quenching conditions [1,7,8]. Fig. 3 shows, from early work that established the strong effect of Mo on hardenability, the significantly higher hardness at deeper depths in oil quenched bars of a steel containing Mo compared to that in a steel without Mo [9]. The steels each contained 0.45 pct C; the Cr steel contained 1.00 pct Cr and no Mo, the Cr-Mo steel contained 0.94 pct Cr and 0.17 pct Mo.
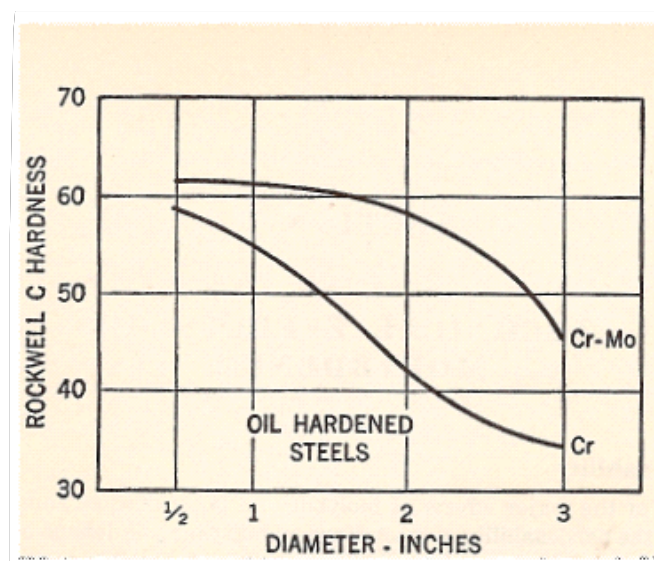
Fig. 3 Effect of Mo on the hardness distribution in 0.45 pct C steels with and without Mo [9].

One formal definition of hardenability, incorporating the various factors in hardening, is "the capacity of a steel to transform partially or completely from austenite to some percentage of martensite at a given depth when cooled under some given conditions". Because the depth of hardening is very much a function of quenching conditions, in order   to compare the hardenabilities of steels of different chemistries without variations in quenching, Grossman and Bain established the concept of an ideal diameter, DI, defined as the size of bar hardened to 50 pct martensite by a theoretically perfect quench [10]. The ideal diameter for a given steel is only a function of carbon content, austenitic grain size, and alloy content. Carbon content and austenitic grain size establish a base ideal diameter that is then multiplied by factors associated with the amounts of the various alloying elements in a steel.

Fig. 4 shows multiplying factors as a function of Mo content as determined by a number of early investigations. This work was reviewed and discussed by Doane [11]. Fig. 5 compares multiplying factors for the elements commonly added to carbon steels to increase hardenability, and shows the strong effect of Mo in relatively small amounts relative to other alloying elements [10].

Although in medium-carbon alloy steels hardenbility is effectively determined by steel C content, austenitic grain size, and alloying element content, another factor, undissolved carbide content, may also be important, especially in high carbon steels. If austenitizing temperatures are low, some carbides may not be dissolved and therefore the carbon and alloy content of the austenite may be less than given by the chemical analysis of the steel,

therefore resulting in lower hardenability than expected. Jatczak has demonstrated this effect of austenitizing, Fig. 6, and also shows the very strong effect of Mo in increasing hardenability in high carbon steels [12]. Although high-temperature austenitizing may produce higher hardenbility, such austenitizing in high carbon steels may not be advisable because of the tendency for quench embrittlement in microstructures quenched from high-carbon austenite [1].
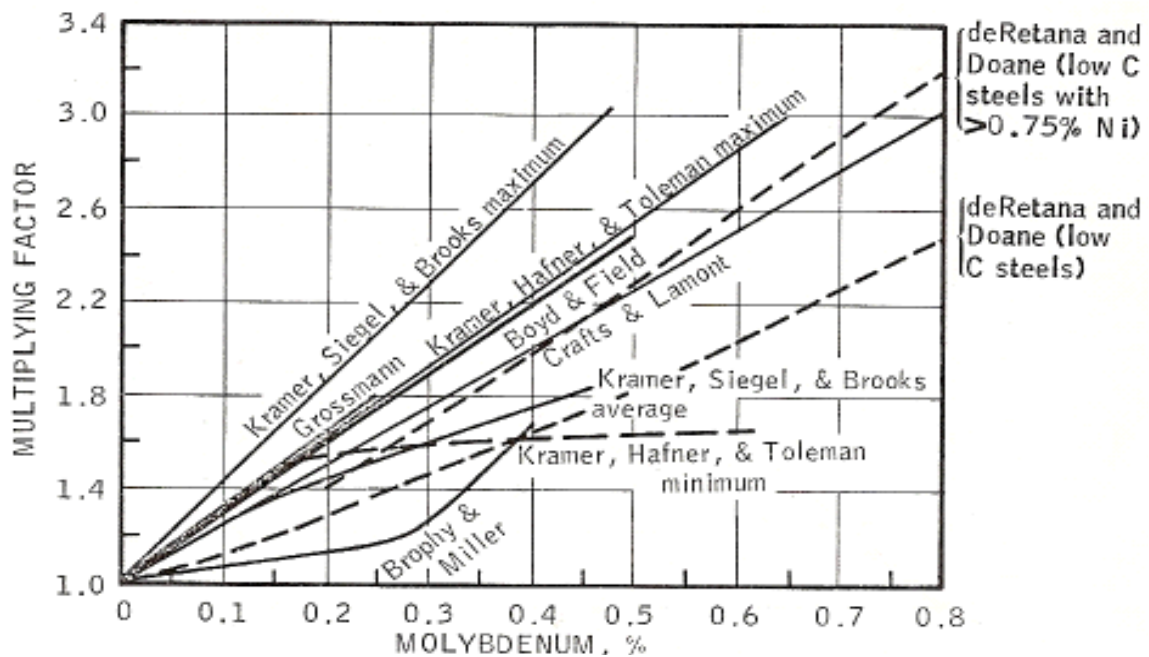

Fig. 4 Effect of Mo on multiplying factors for hardenability. Doane [11]
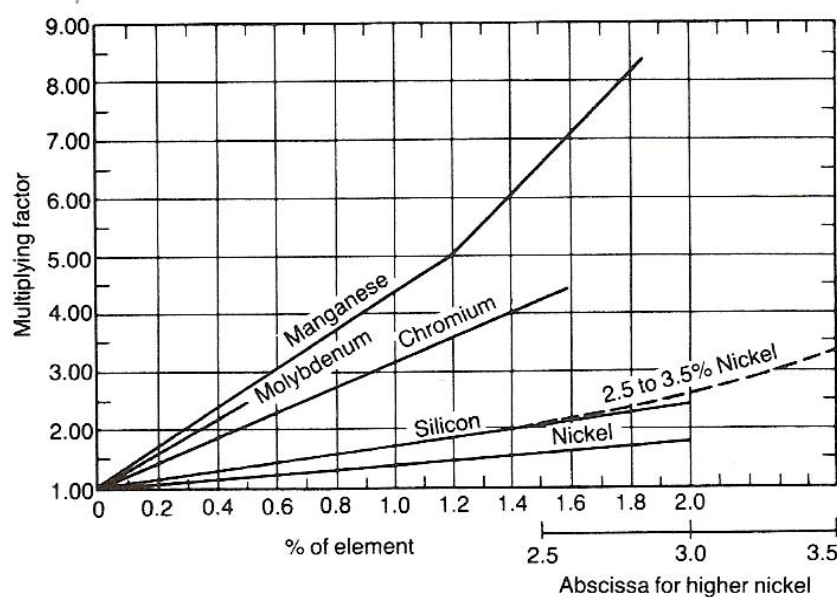
Fig. 5 Multiplying factors as a function of concentration for various common alloying elements in alloy steels. Grossman and Bain [10]
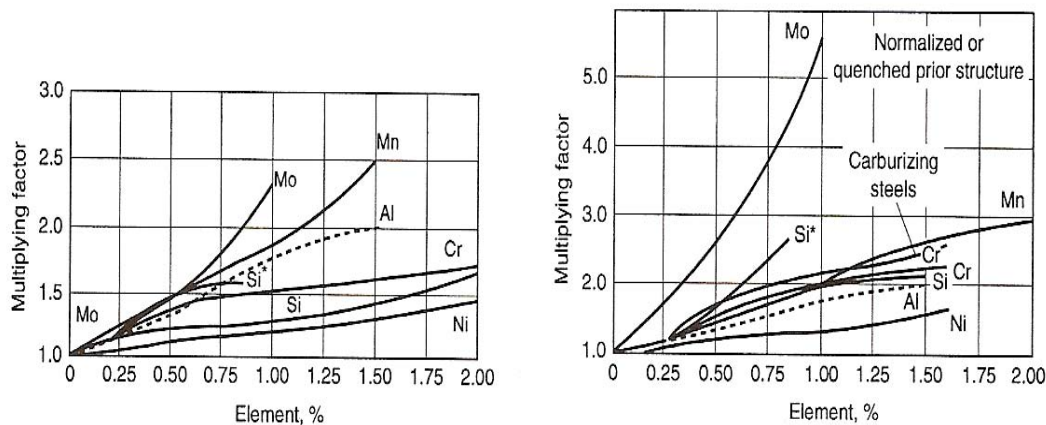
Fig. 6   Multiplying factors for various alloying elements in high-carbon steels austenitized at 830 C (left) and 927 C (right). Jatczak [12]

Mechanisms of Hardenability Increases Due to Mo

Hardenability, i. e. the transformation of austenite to martensite, is made possible by preventing the diffusion-controlled formation of microstructures with lower hardness than martensite during quenching. Mo is an element that tends to concentrate in ferrite and carbides, and therefore the formation of such phases requires the diffusion of Mo. The diffusion coefficient of Mo in austenite is low, and therefore additions of Mo retard the formation of ferrite and ferrite/carbide microstructures such as pearlite and bainite during cooling. Figures 7 and 8 show continuous cooling curves for medium-carbon steels without and with Mo. The steel with Mo, Fig. 8, has much more sluggish transformation to diffusion-controlled transformations than the steel without Mo, Fig. 7, and therefore has higher hardenability.
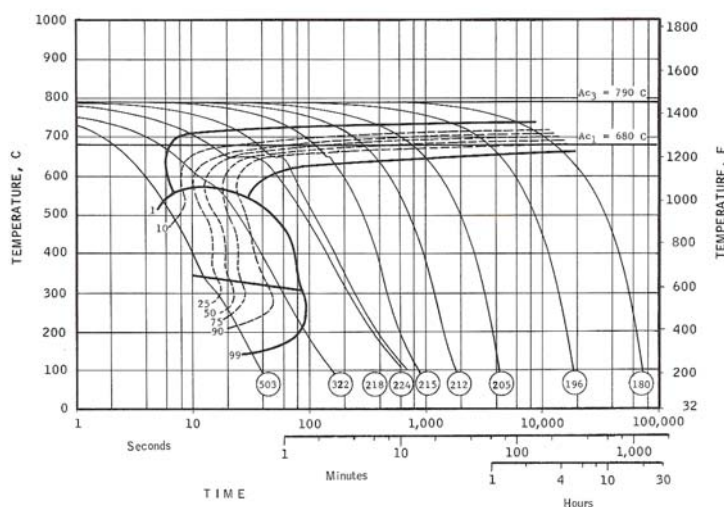
Fig. 7 Continuous Cooling Transformation Diagram for steel containing 0.37 pct C, 0.37 pct Si, 0.85 pct Mn, and 0.74 pct Cr. Cias [13]

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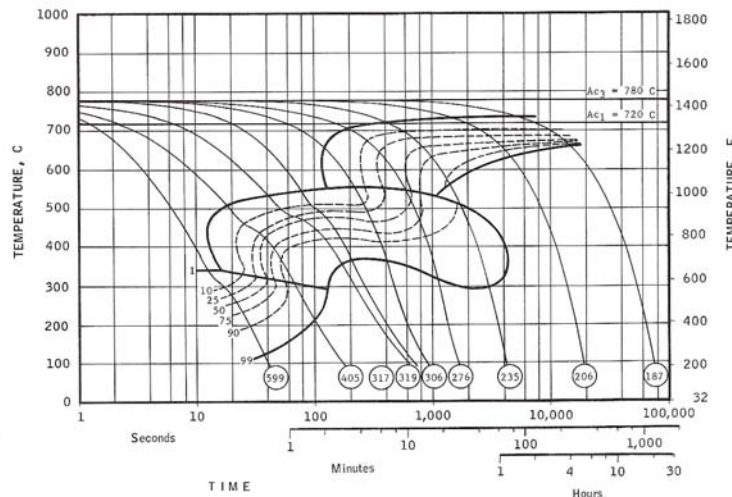
Fig. 8 Continuous Cooling Transformation Diagram for steel containing 0.37 pct C, 0.39 pct Si, 0.85 pct Mn, 0.73 pct Cr, and 0.26 pct Mo Cias [13]

Effect of Mo on Tempering

Almost all steels that are quenched to martensite are also subjected to the subcritical heat treatment step referred to as tempering, as shown schematically in Fig. 2. As-quenched martensite may have low toughness and low fracture resistance; tempering reduces residual stresses and causes the formation of microstructures with improved toughness and ductility. Any temperature up to the lower critical temperature, Ac1, may be used for tempering, but the higher the temperature the lower will be the resulting hardness and strength. Fig. 9 shows the changes in the engineering stress-strain curves of 4340 steel tempered at various temperatures.
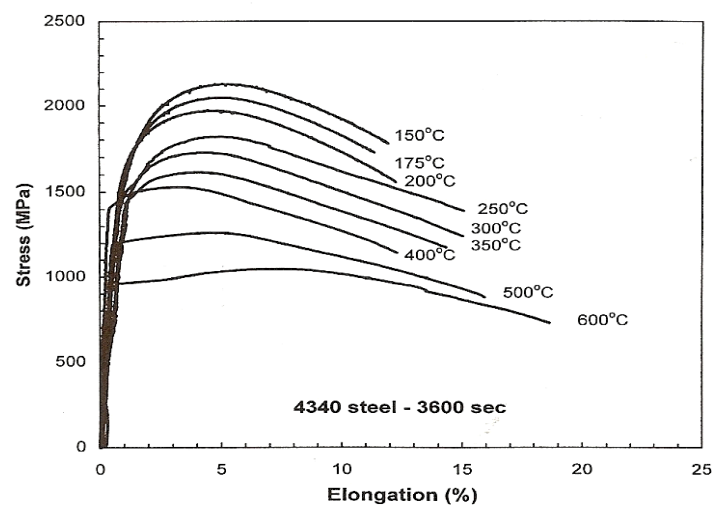
Fig. 9 Engineering stress-strain curves for 4340 steel quenched to martensite and tempered at marked temperatures for one hour. Young-Kook Lee [1]

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There are two major temperature ranges that are commonly used for tempering: the range between 150 and 200 C, shown in Fig. 1, and a range around 500 C. Tempering at the former retains very high strength and produces good toughness, while the range around 500 C and 600 C produces moderate strengths, high ductility, and excellent toughness and fracture resistance. Between those two temperature ranges, tempering may produce reduced toughness, termed tempered martensite embrittlement, the severity of which is a function of carbon and residual element content [1].

Tempering in the range 150 to 200 C causes dispersions of very fine nanometer-sized eta or epsilon transition carbides to form within crystals of martensite and retains high densities of dislocations formed by the martensitic transformation [1]. The precipitation requires only carbon atom diffusion and so Mo has little effect on the substructure formed during low-temperature tempering. Thus the major benefit of Mo in medium carbon steels tempered at low temperatures is increased hardenability that makes the formation of martensite possible in large sections at moderate cooling rates.
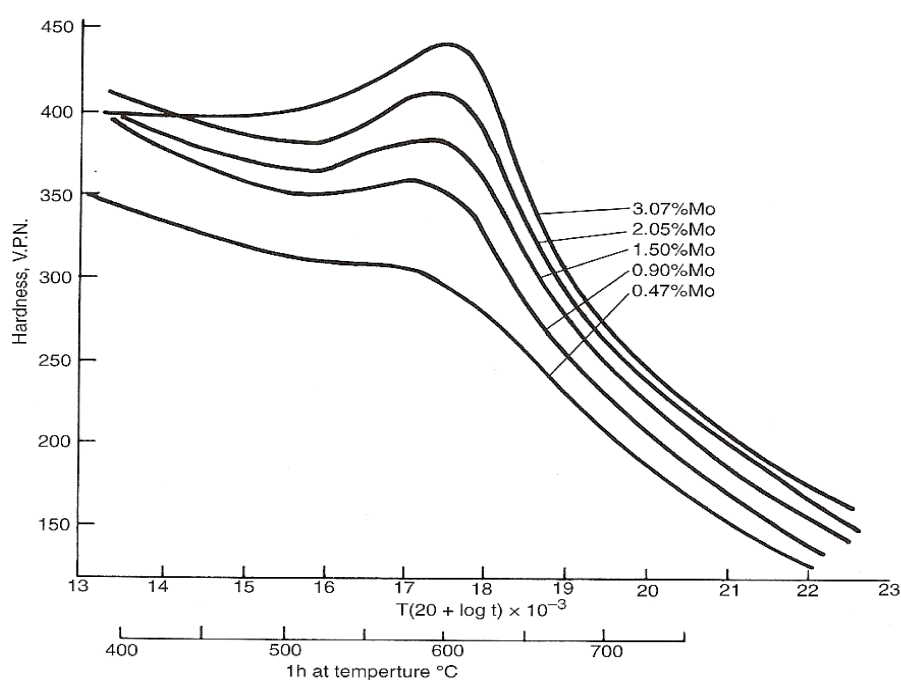
Fig. 10 Effect of various amounts of Mo on the hardness changes of during high-temperature tempering. Rollason [14]

Mo has a much stronger effect on microstructure and properties at high tempering temperatures. Fig. 10 shows the effect of various amounts of Mo on hardness changes of carbon steels tempered at high temperatures [14]. As shown in Fig. 10, steels containing large amounts of Mo actually increase

hardness, a phenomenon referred to as secondary hardening. Secondary hardening is an important mechanism of strengthening in tool steels and in Mo-containing steels is a result of the precipitation of very fine Mo2C and Mo6C carbide particles at high tempering temperatures [15].

At moderate levels, as represented by the curve in Fig. 10 for the steel containing 0.47 pct Mo, Mo slows down the effect of tempering on softening relative to steels without Mo. Fig. 11 shows the effects of various alloying elements on retarding hardness decreases during tempering at 540 C (1,000 F). The parameter ΔH represents the increment in hardness over plain C steels that is provided by the various elements when tempered at 540 C [16]. As shown, Mo, compared to other commonly used alloying elements such as Mn, Cr, and Ni, is the alloying element that most strongly causes martensitic steel to maintain high strength and hardness during tempering at high temperatures.
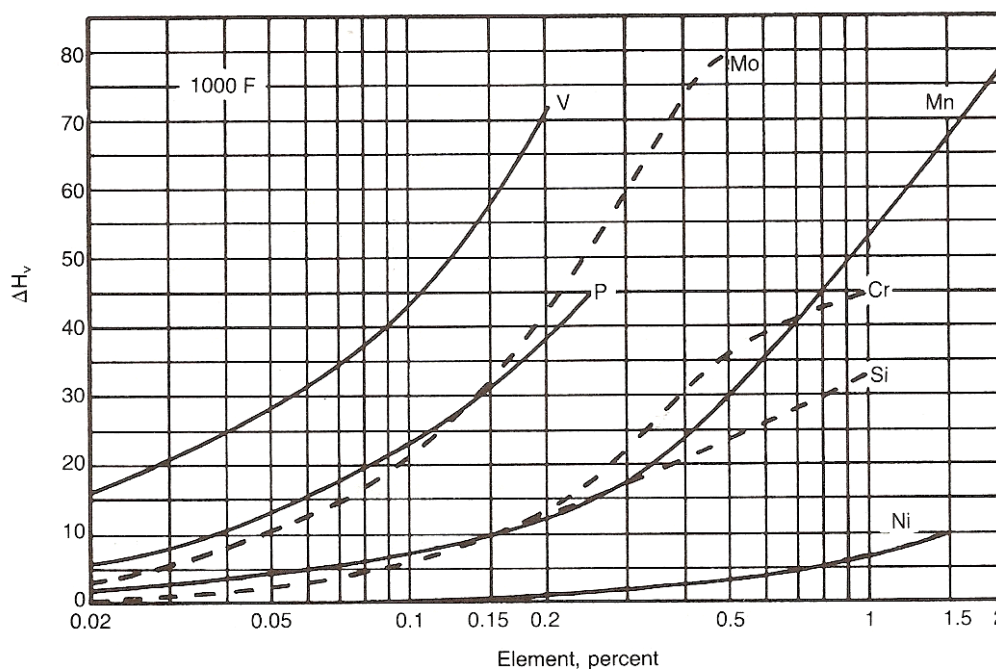
Fig. 11 Effect of alloying elements on the retardation of softening relative to plain C steel during tempering at 540 C (1,000 F). Grange et al [16]

As noted above, although any temperature below the lower critical temperature at which austenite forms can be used to temper a hardened steel, there are two widely used temperature ranges. The low temperature range, 150 to 200 C, is used where maximum strength, fatigue resistance, and hardness is required with good fracture resistance. The carbon content of such through-hardened quench and tempered steels should be kept at or below 0.5 pct C in order to minimize susceptibility to quench cracking and quench

embrittlement [1]. Carburized steels, which develop compressive residual surface stresses, and steels with higher carbon contents if intercritically austenitized, are also widely used in the low-temperature tempered condition for applications such as bearings, shafts and gears.

Steels quenched to martensite and tempered at high temperatures retain good strengths but also develop microstructures with excellent toughness. Good examples of applications that require the benefits of highly tempered microstructures are quenched and tempered tubular products for oil and gas extraction in hydrogen sulfide environments. Such products are often manufactured with Cr-Mo steels such as 4130, and it has been shown that amounts of Mo at the 0.9 pct level have excellent resistance to hydrogen embrittlement associated with sour oil and gas [17, 18].

Summary

This paper has reviewed only a small amount of the technical literature, information and experience that clearly demonstrates the benefits that Mo brings to quench and tempered steels. Low-alloy, carbon steels heat treated to excellent combinations of strength and toughness have been emphasized. Mo is often added together with other alloying elements, and there is no question that Mo brings significant benefits to hardenability and temper resistance over and above those that can be achieved in low-alloy, carbon steels without Mo.

References

1. G. Krauss: STEELS: Processing, Structure, and Performance, ASM International, 2005

2. G. Krauss: "Heat Treated Martensitic Steels: Microstructural Systems for Advanced Manufacture", ISIJ International, Vol 35, 1995, p 349-359

3. M. Säglitz, D. K. Matlock, and G. Krauss: "Tempering and Mechanical Properties of Low-Carbon Boron-Containing Martensitic Sheet Steels", Proceedings, International Conference on New Developments in Advanced High-Strength Sheet Steels, AIST, 2008, p 147-154

4. Metals Handbook, Desk Edition, American Society for Metals, 1985, p 4.6

5. Worldwide Guide to Equivalent Irons and Steels, 4th Edition, ASM International, 2000

6. D. E. Diesburg and G. T. Eldis: "Fracture Resistance of Various Carburized Steels", Metallurgical Transactions A, Vol 9A, 1978, p 1561-1570

7. C. A. Siebert, D. V. Doane, and D. H. Breen: The Hardenability of Steels, American Society for Metals, 1977

8. Hardnability Concepts with Applications to Steel, D. V. Doane and J.S Kirkaldy, Editors, The Metallurgical Society of AIME, 1978

9. R. S. Archer, J. Z. Briggs, C. M. Loeb, Jr.: Molybdenum Steels Irons Alloys, Climax Molybdenum Company, 1953

10. M. A. Grossmann and E. C. Bain: Principles of Heat Treatment, 5th Edition, American Society for Metals, 1964

11. D. V. Doane: "A Critical Review of Hardenability Preditctions", in Reference 8, p 351-396

12. C. F. Jatczak: "Assessment of Hardenability in High Carbon Steels", Metallurgical Transactions, Vol 4, 1973, p 2267-2277

13. W. W. Cias: Phase Transformation Kinetics and Hardenability of Medium-Carbon Steels, Climax Molybdenum Company, p 40 and 41

14. E. C. Rollason: Fundamental Aspects of Molybdenum on Transformation of Steel, Climax Molybdenum Company, p 30

15. G. Roberts, G. Krauss, and R. Kennedy: Tool Steels, Fifth Edition, ASM International, 1998

16. R. A. Grange, C. R. Hribal, and L. F. Porter: "Hardness of Tempered Martensite in Carbon and Low-Alloy Steels", Metallurgical Transactions A, Vol 8A, 1977, p 1775-1785

17. D. L. Sponseller, R. Garber, and T. B. Cox: Design of H2S -Resistant Steels for the Tubular Products Used in Oil and Gas Wells", in Current Solutions to Hydrogen Problems in Steels, C. G. Interante and G. M. Pressouyre, Editors, ASM, 1982, p 200-211

18. P. J. Grobner, D. L. Sponseller, and D. E. Diesburg: "Effect of Molybdenum Content on the Sulfide Stress Cracking Resistance of AISI 4130 Type Steel with 0.035 pct Cb", NACE, 1979

The brief biography of Dr. George Krauss

Dr. George Krauss is currently University Emeritus Professor at the Colorado School of Mines and a metallurgical consultant specializing in steel microstructural systems. He received the B. S. in Metallurgical Engineering from Lehigh University in 1955 and the M. S.   and Sc. D. degrees in Metallurgy from the Massachusetts Institute of Technology in 1958 and 1961, respectively, after working at the Superior Tube Company as a Development Engineer in 1956. In 1962-63, he was an NSF Postdoctoral Fellow at the Max Planck

Institut für Eisenforschung in Düsseldorf, Germany. He served at Lehigh University as Assistant Professor, Associate Professor, and Professor of Metallurgy and Materials Science from 1963 to 1975, and in 1975, joined the faculty of the Colorado School of Mines as the AMAX Foundation Professor in Physical Metallurgy. He was the John Henry Moore Professor of Metallurgical and Materials Engineering at the time of his retirement from the Colorado School of Mines in 1997.

In 1984, Dr. Krauss was a principal in the establishment of the Advanced Steel Processing and Products Research Center, an NSF Industry-University cooperative research center at the Colorado School of Mines, and served as its first Director until 1993.   He has authored the book **Steels: Processing, Structure, and Performance**, ASM International, 2005, coauthored the book, **Tool Steels, Fifth Edition**, ASM International, 1998, and edited or co-edited conference volumes on tempering of steel, carburizing, zinc-based coatings on steel, and microalloyed forging steels. He has published over 300 papers and lectured widely in technical conferences, universities, corporations and ASM International Chapters, presenting a number of keynote, invited and honorary lectures. He presented the Edward DeMille Campbell Memorial Lecture of ASM International in 2000 and the Howe Memorial Lecture of ISS in 2003.

Dr. Krauss has served as the President of the International Federation of Heat Treatment and Surface Engineering (IFHTSE), 1989-91, and as President of ASM International, 1996-97. He is Fellow of ASM International, TMS, and IFHTSE. He has been awarded the Adolf Martens Medal of the German Society for Heat Treatment and Materials, the Charles S. Barrett Silver Medal of the Rocky Mountain Chapter of ASM, the George Brown Gold Medal of the Colorado School of Mines, and several other professional and teaching awards, including the ASM Albert Easton White Distinguished Teacher Award in 1999. He is an Honorary Member of the Iron and Steel Institute of Japan, a Distinguished Member of the Iron and Steel Society, an Honorary Member of ASM International, and an Honorary Member of the Japan Institute of Metals.

The Benefit of Molybdenum in Stainless Steel

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Abstract: This paper discusses the beneficial effects of molybdenum in stainless steels. The main beneficial effect of Mo in austenitic or ferritic stainless steels is improvement in corrosion resistance, and the higher the molybdenum content, the stronger is the effect. Besides the improvement in corrosion resistance, molybdenum also has the effect on the strength in high-strength martensitic stainless steels. Molybdenum has powerful effects, which is more significant when molybdenum interacts with chromium, on corrosion resistance in austenitic stainless steels. Molybdenum promotes the development of super austenitic stainless steels with high performance. Due to the existence of molybdenum, the corrosion resistance of super austenitic stainless steels can be equivalent with that in nickel-based superalloy. A small amount of molybdenum can significantly improve the corrosion resistance of ferritic stainless steels for muffler. The corrosion resistance of 444 ferritic stainless steel with 1% Mo is better than SUS 304 stainless steel. The corrosion resistance of 444 ferritic stainless steel with 2% Mo is equivalent with that of SUS316 stainless steel. Adding 1% Mo to 444 ferritic stainless steel leads to that its low-temperature corrosion resistance is better than that of SUS316L stainless steel and its high-temperature corrosion resistance is equivalent with that of Mo-free 445 ferritic stainless steel. The corrosion resistance of 445 ferritic stainless steel with 2% Mo is fully better than that of SUS304 stainless steel. Molybdenum reinforces the tempering resistance and secondary hardening effects of high-strength martensitic stainless steel and it improves the strength and crack resistance. The strengthening mechanism is that Mo promotes the formation of dispersion of fine Fe2Mo laves phase.

Key words: molybdenum; austenitic stainless steel; ferritic stainless steel; high-strength martensitic stainless steel

Introduction

Stainless steels are divided into martensitic stainless steels, ferritic stainless steels, austenitic stainless steels and duplex stainless steels in accordance with microstructure. Molybdenum as a typical alloying element in stainless

steels has powerful effects. The influence of molybdenum on stainless steels mainly consists of three aspects: First, it is clear that Mo has effects with regard to the structure in stainless steel. Molybdenum is an important element for ferrite formation. The factor of molybdenum is 1.5 times of that of chromium [1], ensuring phase equilibrium inferritic and duplex stainless steels. Furthermore, molybdenum has powerful effects on formation of σ intermediate phase in austenitic, ferritic or duplex stainless steels, which should be avoided in consideration of corrosion resistance. Second, molybdenum has effects on mechanical properties of stainless steels, which is evident in high-strength stainless steels. Molybdenum promotes the formation of strengthening phase, leading to the enhancing of strength. Third, molybdenum is of great benefit to corrosion resistance in stainless steels. It is observed that above 80% of effects of Mo is related to corrosion resistance. For all the stainless steels, Mo is beneficial to pitting and crevice corrosion resistant properties. Effects of Mo is 2.3 times more than that of Cr in PREN formula [2].

Considering that the effects of Mo is different in different kinds of stainless steels, the paper will describe such effects separately and discuss the beneficial effects of Mo in austenitic, ferritic and high-strength martensitic stainless steels, respectively.

1. Austenitic stainless steel

As one of the most important branches of stainless steels, austenitic stainless steel consumption accounts for above 60% of all stainless steels. Mo is added to act as an element promoting the corrosion resistance in the austenitic stainless steels. The austenitic stainless steels alloyed with Mo show excellent corrosion resistance, especially the pitting and crevice corrosion resistance. Therefore, molybdenum-containing austenitic stainless steels are used mostly in harsh corrosion environments. Fig. 1 shows the linear relationship of critical temperature and equivalent of pitting corrosion in some austenitic stainless steels containing Mo [3]. In the same test conditions, the critical pitting temperature of 00Cr18Ni12Mo2（316L）is about 15℃; that of 00Cr18Ni18Mo5 and 00Cr20Ni25Mo4.5Cu（904L）is about 40℃; that of 00Cr18Ni18Mo7 and Sandvik254SMO is about 65 ℃ ; that of 00Cr18Ni18Mo7CuN is about 67.5℃; that of 00Cr25Ni25Mo4N is about 70℃; and that of 00Cr25Ni25Mo4.5N is about 87.5℃. Mo significantly promotes the pitting corrosion resistance in austenitic stainless steel. Many experiments indicate that the effects of Mo merely work in steel with high Cr content. Mo

mainly strengthens the effect of Cr that improves corrosion resistance. Meanwhile, the corrosion inhibition of Mo when molybdate formed has been confirmed by experiments.
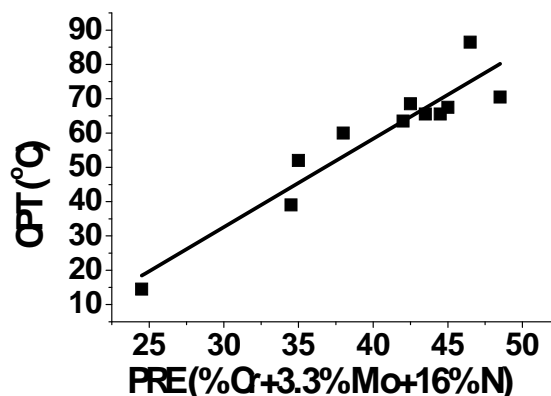

Figure 1 Relationship of critical temperature and equivalent of pitting corrosion

The beneficial effects of Mo in austenitic stainless steels have greatly promoted the development of austenitic stainless steels, especially super austenitic stainless steels. The concept of super austenitic stainless steel was put forward together with super ferritic stainless steel and super duplex stainless steel in the 1980s, similar to the Ni-based super alloys concept for highly alloyed Ni-based alloy [4]. Super austenitic stainless steels have higher mechanical properties and corrosion resistance compared with conventional austenitic stainless steels. A typical example is the so-called 6Mo stainless steel. Throughout the development of austenitic stainless steels, the development of super austenitic stainless steel can be divided into three stages: The first stage was in the 1930s. To solve the problem of corrosion in sulfuric acid media, Uranus B6 (20Cr-25Ni-4.5Mo-1.5Cu) was developed in France and number 20 alloy (20Cr-30Ni-2.5Mo-3.5Cu）in US. The second stage was in the early1950s. 6Mo steel（16Cr-30Ni-6Mo) was developed by Avesta Jernverk AB (Sweden) and AL-6X(20Cr-25Ni-6Mo) by Allegheny (US). The representative of this stage was 254SMO(20Cr-18Ni-6Mo-0.7Cu-0.2N) developed by Avesta in 1976 as well as AL-6XN(20Cr-24Ni-6Mo-0.22N) and Cronifer 1925hMo (20Cr-15Ni-4.5Mo-0.4N). The characteristic was further increasing Mo content and beginning to pay attention to and utilize the beneficial effects of N. The third stage characteristic of the super austenitic stainless steel development mainly lay in nitrogen alloying. In order to improve the solubility of N, alloying element Mn was introduced. The sharp increase of Cr, Mo, and N contents

was to enhance the synergy between alloying elements. The typical brand was 654SMO（24Cr-22Ni-7Mo-3Mn-0.5Cu-0.5N）(Avesta, Sweden). Table 1 shows chemical compositions of some super austenitic stainless steels.

Table 1 Chemical compositions of some super austenitic stainless steels

Alloy name	Cr	Ni	Mo	Cu	N	other	remark
20 alloy	20	30	2.5	3.5	—	—	US
UB6，904L	20	25	4.5	1.5	—	—	France、US
Sanicro28	27	31	3.5	1	—	—	Sweden Sandvik
AL-6X	20	25	6	—	—	—	Allegheny Ludlum
254SMO	20	18	6.1	0.7	0.2	—	Sweden Avesta
AL-6XN	20.5	24	6.3	—	0.22	—	Allegheny Ludlum
1925hMo	20	25	4.5	—	0.4	—	VDM
934LN	20	15	4.5	—	0.4	10Mn	Avesta-Sheffild
1.4565	24	28	4.5	—	0.4	6Mn	
654SMO	24	22	7.3	0.5	0.5	3Mn	Avesta-Sheffild
B66	24	22	5.6	0.45	0.5	3Mn2W	France CLI

Mo content in 654SMO steel is up to 7% and the corrosion resistant property of 654SMO steel is even better than Ni-based corrosion resistant alloys in many harsh corrosive environments. Table 2 indicates that pitting and crevice corrosion properties of 654SMO have been better than Ni-based corrosion resistant alloy Hastelloy C-276 [5]. Therefore, super austenitic stainless steels can replace expensive Ni-based corrosion resistant alloy in the flue gas desulfurization, paper and other industrial environments.

Table2 Comparison of 654SMO and C-276 performance in different corrosion environments

Point corrosion rate in boiling solution 11%H_2SO_4+3%HCl+1%$FeCl_3$ +1%$CuCl_2$（mg/dm^2.d）	Crevice corrosion rate in 70℃ 6%$FeCl_3$ solution（g/m^2.h）	
654SMO(0.46N)	13.392	0.0075
654SMO(0.40N)	15.048	0.0427
654SMO(0.35N)	17.952	0.2348
C-276	220.8	0.5602

2. Ferritic stainless steel

As an important type of economical stainless steels, ferritic stainless steels are being widely advocated and applied. Mo can greatly improve the corrosion

resistance resulting in a wide application in ferritic stainless steels, especially in medium/high chromium ferritic stainless steel. On the other hand, considering the economy of ferritic stainless steels, Mo content should be controlled to be relatively low in steel grade design. Therefore, in many high level ferritic stainless steels, Mo content is controlled within 2%, though it has important effects on the properties.

The 409 ferritic stainless steel is commonly used in automobile exhaust muffler system abroad. However, the same steel used in China has serious corrosion problem. The main reason is that corrosive environment of exhaust muffler becomes worse due to the application of high-sulphur crude oil in China. Therefore, it is necessary to develop a ferritic stainless steel that has better corrosion resistance than 409 steel with equivalent economy. As the common needs of economy and corrosion resistance, whether to add Mo or how much Mo to add becomes one of the research topics. Fig. 2 shows pitting potential scan curve of Cr17-18% ferritic stainless steel with 0-1.2% Mo. Fig. 3 indicates relationship between pitting potential and Mo content. Pitting potential goes up along with the increase of Mo content. The pitting potential is 214/216mV for 00Cr17TiNb stainless steel without Mo, whereas it is increased to 281/326mV for 00Cr17Mo1.2Ti with 1.14% Mo. Every increased 1 percent of Mo, the pitting potential is increased around 99mV [6].
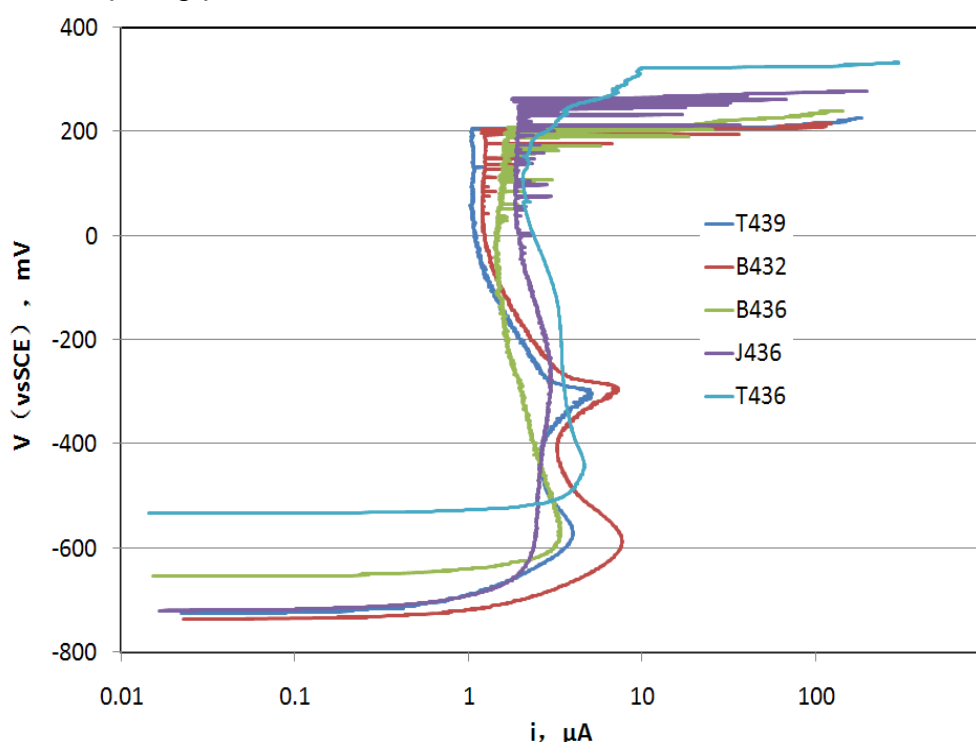
Figure 2: The pitting potential scan curve of Cr17-18% ferritic stainless steel with 0-1.2% Mo
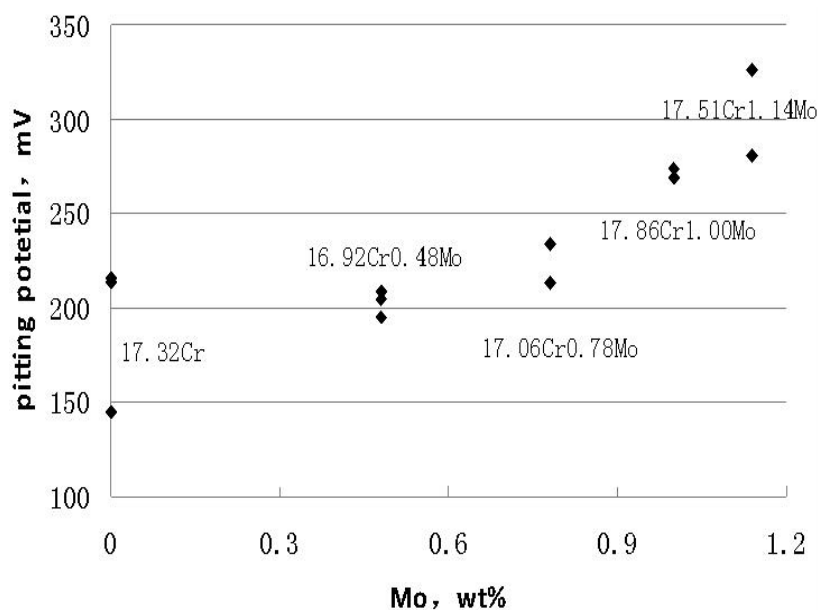
Figure.3 Relationship between pitting potential and Mo content

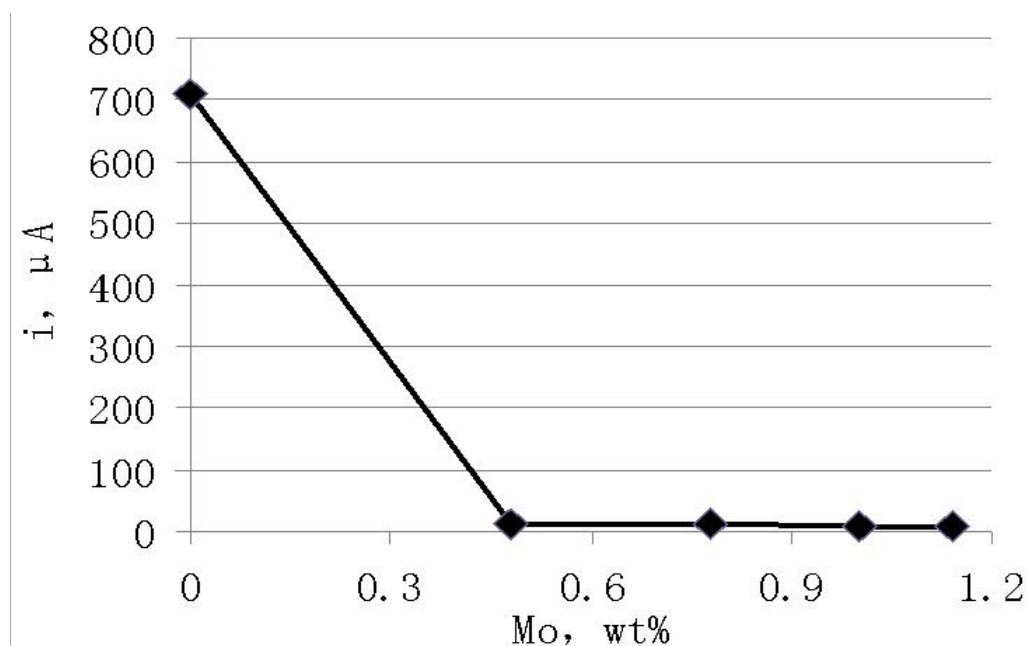Fig. 4 shows anode polarization curve of 17-18%Cr ferritic stainless steel with 17-18% Mo in solution, simulating internal environment of pitting corrosion pit. Fig. 5 demonstrates relationship between maximum current in active state and Mo content. It is clear that adding 0.5% Mo significantly reduces the maximum current in active state from 710μA down to 13.5μA. Then further increase Mo content, effects are not obvious. Maximum current in active state maintains in the range of 9.1-13.5μA with Mo content lower than 1.2%.
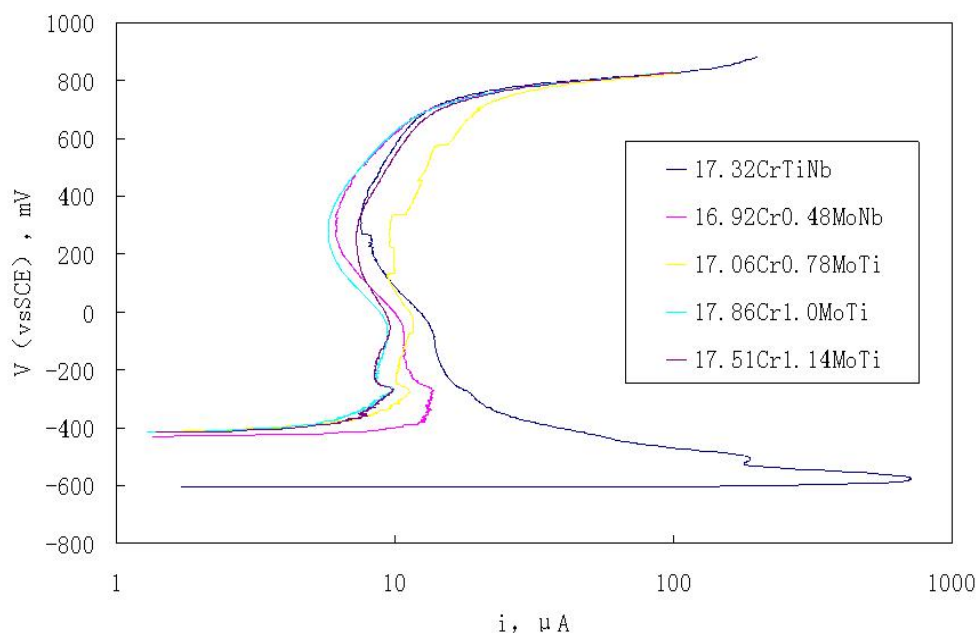
Figure.4 Anode polarization curve of 17-18%Cr ferritic stainless steel with 17-18% Mo in solution simulating internal environment of pitting corrosion pit

Figure 5 Relationship between Mo content and maximum current in active state of Cr17-18% ferritic stainless steel in solution simulating internal environment of pitting corrosion pit

Fig. 6 shows effects of Mo on corrosion weight loss in condensate simulating corrosion test. As Mo content increases, corrosion weight loss is reduced. Corrosion weight loss is 9.9/10.2mg for sample without Mo, whereas corrosion weight loss after 10 cycles is reduced to 4.5/3.6mg for sample with 0.78% Mo, only 2/5 of the former. As Mo content is further increased to 1.14%, corrosion weight loss is reduced to 4.1/4.0mg. The influence of Mo on corrosion weight loss is not obvious.
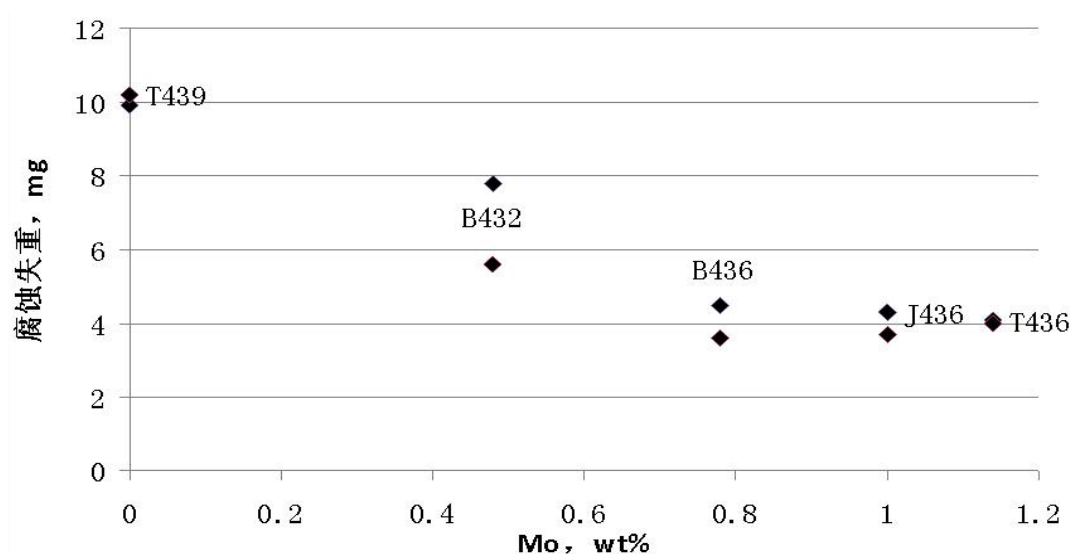
Figure 6: Relationship between corrosion weight loss and Mo content in ferritic stainless steel (condensate simulating corrosion test, 10 condensate cycles)

Fig. 7 shows effects of Mo on pitting corrosion depth in condensate simulating corrosion test. As Mo content increases, pitting corrosion depth is reduced. The maximum pitting corrosion depth is 0.11 mm for ferritic stainless steel without Mo, whereas it is reduced to 0.08 mm for ferritic stainless steel with 0.78% Mo, only 2/3 of the former. A further increase of Mo content to 1.2% does not change the maximum pitting corrosion depth, which is still 0.08 mm. Then it has no evident influence on maximum pitting corrosion.
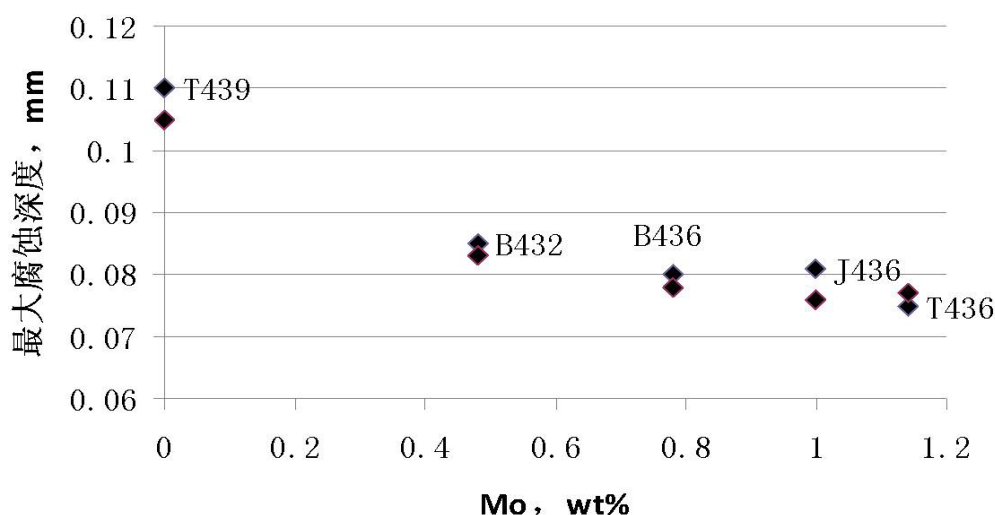
Figure 7: Relationship between maximum corrosion depth and Mo content in ferritic stainless steel (condensate simulating corrosion test, 10 condensate cycles)

Adding 0.5%Mo into Cr17 ferritic stainless steel, which is used in automobile exhaust muffler system, will significantly improve its corrosion resistance in service environment. This provides basis for designing muffler materials used in high-grade cars.

The 444 (00Cr18Mo1-2Ti) ferritic stainless steel has good resistance to stress corrosion cracking caused by chloride and thus has very wide applications. Stainless steel plates and decorative pipes find increasing applications in civic architecture design, such as urban landscapes, hotels, shopping centers, entertainment venues, office buildings, international hotels, etc. SUS304 stainless steel is mainly used for these applications in China currently. However, these decorative materials can be replaced completely by ultra-low C and N Cr18Mo1Ti ferritic stainless steel, which has low cost, excellent corrosion resistance and formability. Austenitic stainless steel is prone to stress corrosion cracking when used in hot water tank, hot water heater, service pipe, solar energy collection converter, electric water heaters, heat exchangers, thermal storage tanks and other equipment, as well as in harsh corrosive environments, such as coastal outdoor decoration or pools.

Thus, 00Cr18Mo2Ti and 00Cr18Mo2NbTi ferritic stainless steels have been widely used abroad. The standard for Mo content is less than 2% in 444 ferritic stainless steel. The effects of Mo on performance in 444 steel should be studied to make its price more competitive, especially compared with SUS304 and SUS316 stainless steels. Fig. 8 shows the pitting potential of Cr18Mo ferritic stainless steel with different Mo content measured in 3.5% NaCl solution (30 ℃). The breakdown potential of Cr18Mo stainless steel increases with the increase of Mo content. The pitting potential of 00Cr18Mo1Ti steel is equivalent to that of SUS304 stainless steel and the pitting potential of 00Cr18Mo2Ti steel is equivalent to that of SUS316 austenitic stainless steel in 3.5% NaCl solution. Fig.9 indicates the pitting potential of Cr18Mo ferritic stainless steel with different Mo content measured in 3.5% NaCl solution at different temperatures (30℃,40℃,50℃,60℃). All pitting potential of Cr18Mo ferritic stainless steel with different Mo content reduces with the increase of solution temperature. The pitting potential of Cr18Mo1 ferritic stainless steel is almost equivalent to that of SUS304 in 3.5% NaCl solution at different temperatures. The pitting potential of Cr18 ferrite stainless steel with1.5%, 2%, and 2.5%Mo are higher than that of SUS304 at different temperatures. The pitting potential of Cr18Mo2 ferritic stainless steel is equivalent to that of SUS316 in 3.5% NaCl solution at different temperatures.
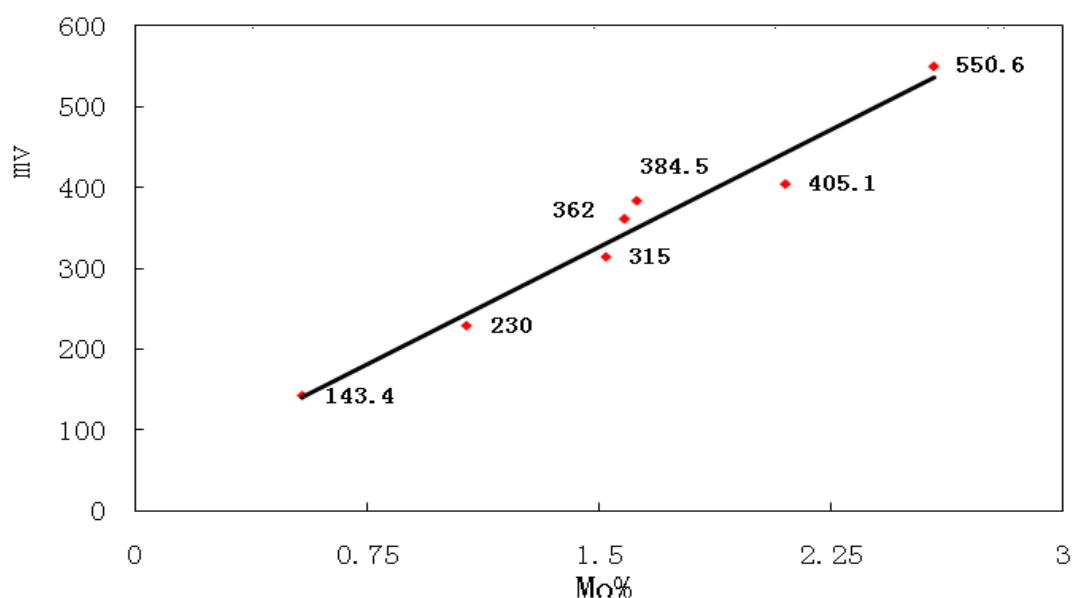
Figure 8: The pitting potential of Cr18Mo ferritic stainless steel with different Mo content in 3.5% NaCl solution (30 ℃)
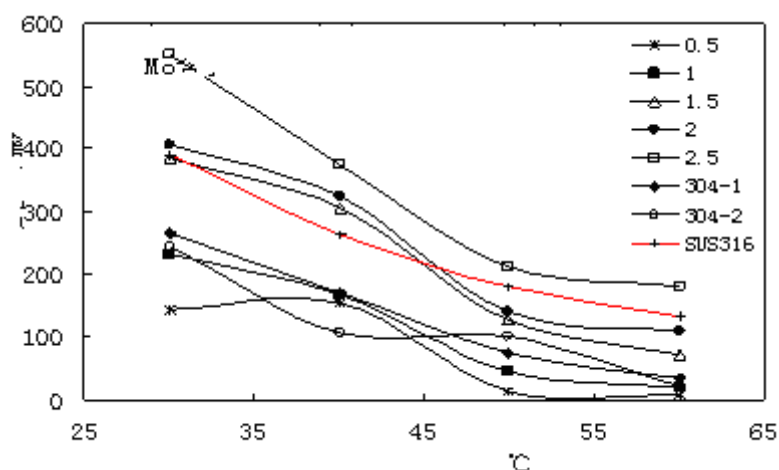
Figure 9 The pitting potential of Cr18Mo ferritic stainless steel with different Mo content in 3.5% NaCl solution at different temperatures

The breakdown potential of Cr18Mo1.5 and 0Cr18Ni9 stainless steels changes when sample immersion time is different in 3.5% NaCl solution (30 ℃) as shown in Fig. 10. The breakdown potential of Cr18Mo1.5 stainless steel increases with the increase of immersion time and tends to a constant at last. However, the breakdown potential of 0Cr18Ni9 stainless steel has no significant change in such case. This indicates that 0Cr18Mo1.5 ferritic stainless steel is more easily passivated than 0Cr18Ni9 austenitic stainless steel in chloride solution, thereby enhancing the breakdown potential. This also explains that the corrosion resistance of Cr-Mo ferritic stainless steel with high breakdown potential is better than that of Cr-Ni austenitic stainless steel in humid atmosphere containing chloride.
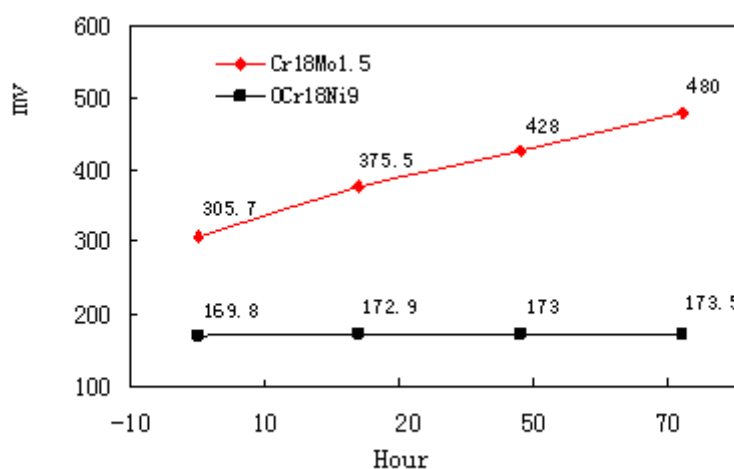
Figure 10: Influence of immersion time on breakdown potential of Cr18Mo1.5 and 0Cr18Ni9 stainless steel in 3.5% NaCl solution (30 ℃)

Fig. 11 shows the complete immersion test results of Cr18 ferrite stainless steels with different Mo content in 10%FeCl3·6H2O solution at different temperatures. It can be seen that the pitting resistance of 00Cr18Mo1 steel is better than that of 0Cr18Ni9 steel and equivalent to 0Cr18Ni9 austenitic stainless steel. However, the pitting resistance of 00Cr18Mo2 steel is comparable with that of SUS316, as shown in Fig.11.
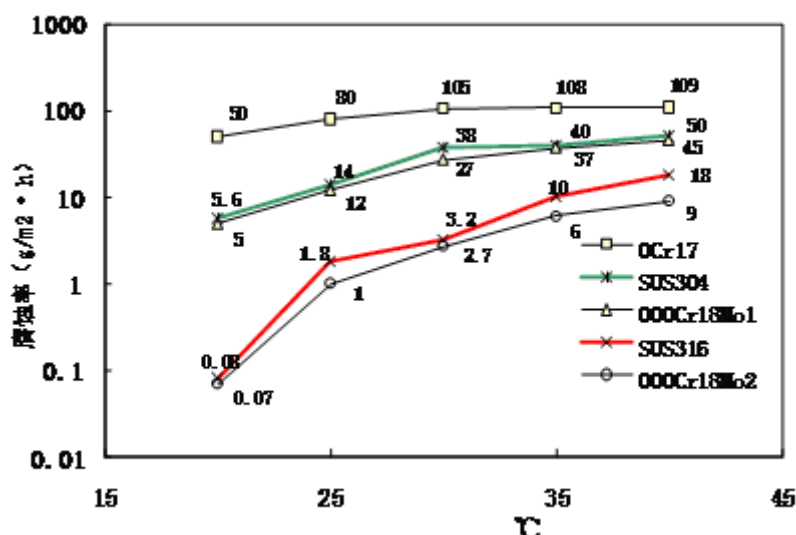
Figure 11: The pitting resistance of different stainless steel in 10%FeCl3·6H2O solution at different temperatures

It is clear that the addition of 1% Mo to 444 ferrite stainless steel results in better corrosion resistance than SUS304 stainless steel and the addition of 2% Mo leads to equivalent corrosion resistance with SUS316 stainless steel.

There is a higher grade of stainless steel called 445 ferritic stainless steel, i.e., ultra-low carbon Cr22Mo1-2Ti ferritic stainless steel. As having excellent corrosion resistance, formability and weldability, 445 ferritic stainless steel can be used for the decoration of coastal cities, such as the urban landscape, hotels, shopping malls, entertainment buildings, high-grade office buildings and other decorative plates or tubes as well as harsh corrosive environment, such as plant heat exchangers of inland power, water heaters, heat exchangers of chemical plant etc. Cr22Mo1Ti ferritic stainless steel is actually a steel saving Mo for Cr22Mo2 steel replacing 304L and 316L, which are prone to stress corrosion cracking. Cr22Mo2Ti is developed to substitute for 316L or Cr18Mo2Ti steels, which can not meet the coastal salt corrosion environment. Fig.12 indicat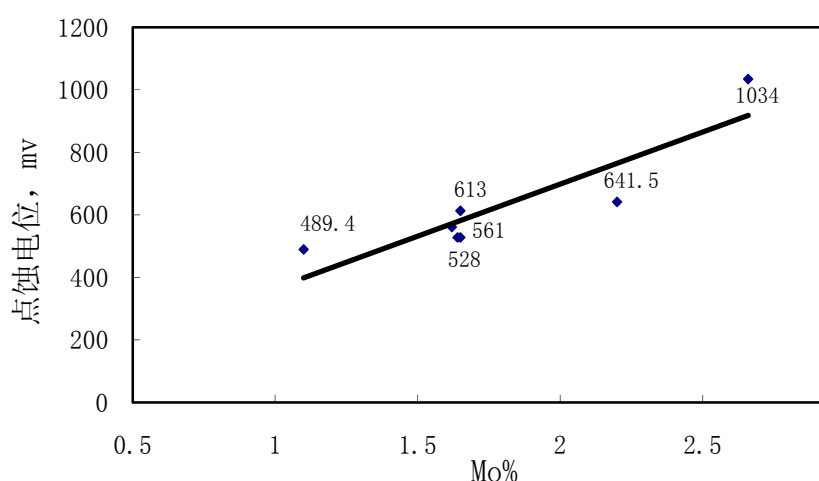es the pitting potential of Cr22MoTi ferritic stainless steel with different Mo content measured in 3.5% NaCl solution (30 ℃). The pitting

potential increases with the increase of Mo content. The pitting potential is 390mv for 00Cr17Ni12Mo2 steel and 489mv for 00Cr22Mo1Ti steel, whereas it is 641mv for 00Cr22Mo2Ti steel, around 100-250mv higher than 00Cr17Ni12Mo2 steel. The higher the pitting potential, the better the material pitting resistance is. The pitting potential of Cr22MoTi steel with different Mo content measured in 3.5% NaCl solution in 30℃, 40℃, 50℃ and 60℃ is shown in Fig. 13. The pitting potential of Cr22MoTi steel with different Mo content decreases with the increase of solution temperature. The pitting potential of Cr22MoTi steel with more Mo is higher than that with less Mo. The pitting potential curves of 00Cr22MoTi steel are higher than that of 00Cr17Ni12Mo2 steel.

Figure 12 The pitting potential of Cr22MoTi ferritic stainless steel with different Mo content in 3.5% NaCl solution (30 ℃)
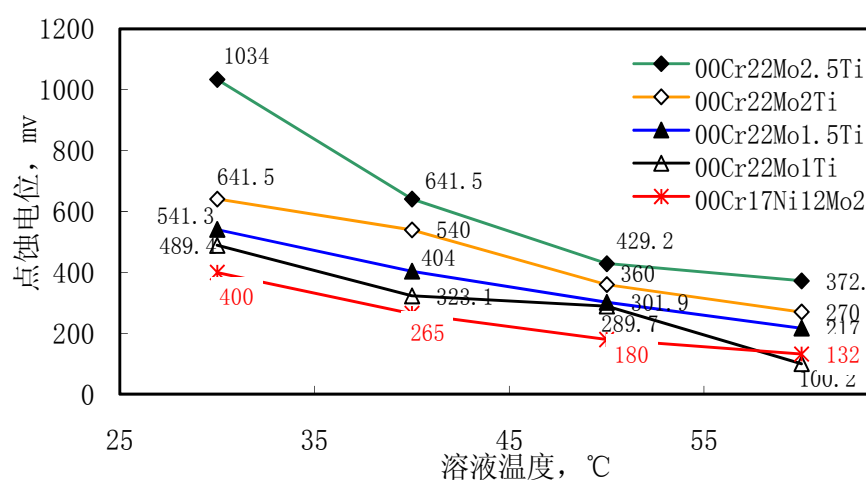
Figure 13: The pitting potential of Cr22MoTi steel with different Mo content in 3.5% NaCl solution at different temperatures

Fig. 14 shows immersion corrosion results of some stainless steel after immersed 4h in 10% FeCl3 · 6H2O solution at different temperatures. The pitting resistance of 00Cr22Mo1Ti steel is better than that of 00Cr17Ni12Mo2 in 10% FeCl3 · 6H2O solution at low temperature, whereas it is equivalent to 00Cr17Ni12Mo2 at high temperature. The pitting resistance of 00Cr22MoTi steel with more Mo is better than that of 00Cr17Ni12Mo2.
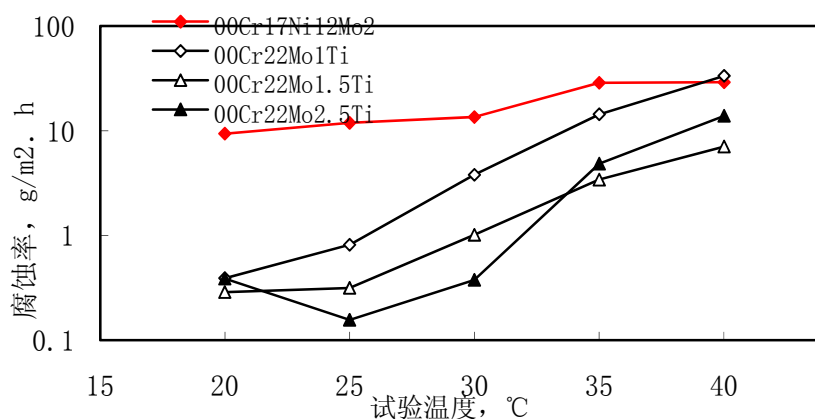

Figure 14: The pitting resistance of 00Cr22Mo1Ti, 00Cr22Mo1.5Ti, 00Cr22Mo2.5Ti and 00Cr17Ni12Mo2 steel in 10%FeCl3·6H2O solution

3. High strength martensitic stainless steel

Molybdenum, as one of the indispensable elements in high-strength stainless steel, has three main functions: first, the solid solution strengthening effect; second, the aging hardening effect or temper hardening effect; third, improvement in the corrosion resistance of steel. The most important effect of Mo is to increase tempering resistance and to strengthen by secondary hardening effect. The mechanism that Mo improves the tempering resistance is the formation of a fine Fe2Mo or Mo2C phase after the addition of Mo, which increases the second hardening effect [7]. In the high-strength stainless steel, the addition of Mo will generate the dispersed Fe2Mo Laves phase and this phase can significantly increase the strength of steel [8-11]. Some researchers believe that [12,13], the early molybdenum-rich precipitates in the aging also help the steel maintain a good resilience while they increase the strength of the steel. Mo, compared to Fe in terms of content, is a surface active element that displaces Ti or Cu from the interface region, thus reducing the possibility of precipitation of the excessive phase in the grain boundary. Mo-containing high-strength stainless steel is often enhanced by adding Co to increase its effectiveness. Studies show that [14], Co can reduce the solution of Mo in α-Fe [15, 16] (synergistic effect), thus more precipitation of the second phase

containing Mo is produced, leading to more effective increase of the steel strength during aging.

Table 3 and Table 4 respectively show chemical compositions and corresponding strength levels of high-strength stainless steels at home and abroad. Mo is a typical element for high-strength stainless steel alloy design as shown in Tables. The addition of Mo will be matched to C, Cr, Ni and other elements in steel to form a reasonable and orderly alloy system and achieve super high strength.

Table 3: Chemical compositions and corresponding strength of overseas typical high-strength stainless steels (wt%)

Steel designation	C	Cr	Ni	Mo	Co	Ti	Al	Rm,MPa
PH13-8Mo	≤0.05	12.2/13.2	7.5/8.5	2.0/2.5	-	-	1.2	1620
Custom450	0.035	14.9	6.5	0.8	-	-	-	1724
Custom465	≤0.02	11.0/12.5	11/11.2	0.75/1.2	-	1.5	-	1779
Pyromet X-23	≤0.02	9.5/10.5	6.5/7.5	5.0/6.0	9.5/11.0	-	-	-
Pyromet X-15	≤0.03	15.0	-	2.9	20.0	-	-	1550
Custom475	≤0.03	9.0	6.0	6.0	14.0	-	-	1979
D70	≤0.03	11.5/12.5	4.0/5.0	4.0/5.0	12.0/14.0	-	-	1656
03Kh11N10M2T	0.03	10.45	9.77	2.24	-	1.3	-	1720
VNS25	≤0.03	11.5/12.5	9.0/10.5	0.5/0.8	-	-	-	-
VNS65	≤0.02	13.4/13.6	2.2/2.6	3.9/4.0	16.1/16.3	-	-	1800
VNS59	≤0.03	9.5/10.5	8.8/9.8	3.2/3.6	6.5/7.5	-	-	1400
AM367	0.025	14.0	3.5	2.0	15.5	0.4	-	-
000KH14N4K14M3T	0.02	14.5	4.0	2.9	14.6	0.26	-	1620
03Kh11N10M2T2	0.03	10.5	9.7	2.0	-	-	-	1720
03Kh12N8K5M3TYu	0.028	11.5	7.8	2.3	5.3	0.95	0.33	1780
0Kh12N8MTYu	0.03	12.2	7.8	0.88	-	-	0.8	2097
11Cr9Ni2MoTi	0.015	11.0	9.0	2.0	-	1.5		-
FerriumS53	0.21	10.0	5.5	2.0	14.0	-	-	1980

Table 4: High-strength stainless steel grades and strength levels developed domestically

Strength level	Grade
850～920MPa	00Cr13Ni5M$_O$
950～1000MPa	00Cr13Ni6MoNb
1000～1200MPa	00Cr16Ni5Mo1
	00Cr14Ni6Mo2AlNb
1200～1300MPa	00Cr11Ni10Mo2Al
	00Cr16Ni6MoCuNb
1200～1400MPa	00Cr12Co12Ni4Mo4Ti
1300～1500MPa	0Cr11Ni10Mo2Ti0.6Al
1500～1700MPa	00Cr13Ni8Mo2TiNbAl
1600～1700MPa	00Cr11Ni10Mo2Ti1
1800～2000MPa	00Cr13Co13Ni4Mo5Ti（F863）

Mo content is up to around 5% in a new ultra-high strength stainless steel F863 steel. Its strength and KIC reaches 1940MPa and 90-100MPa·m1/2 respectively as a result of the strengthening effect of Mo.

The microstructure of samples (540℃/4h,600℃/4h) was observed using H800 transmission electron microscope, as shown in Fig. 15-16. The precipitates are Fe2Mo type Laves phase (a=0.474nm, c=0.772nm) which has a hexagonal structure (TCP topology closely packed structure). As a low carbon martensitic stainless steel, it rarely has carbide precipitates during aging. Fig. 15a, b respectively show the bright and dark field images of precipitate phase and Fig. 15c, d indicate the SAD map of precipitate phase and its calibration. The results show the orientation relationship

as: $$(1\ \overline{1}\ 0)_M\ //\ (2\ \overline{1}\ 2)_{L3}$$,

$$(\overline{1}\ 1\ 0)_M\ //(\overline{2}\ 1\ \overline{2})_{L1}//(\overline{2}\ 1\ \overline{2})_{L2}//(\overline{2}\ 1\ \overline{2})_{L3}$$,

$$[1\ 1\ 5]_M\ //[1\ 6\ 2]_{L1}//[2\ 6\ 1]_{L2}//[4\ 6\ 7]_{L3}$$. Incident direction of electron beam is following the martensite [115] M and Laves phase shows spherical shape.
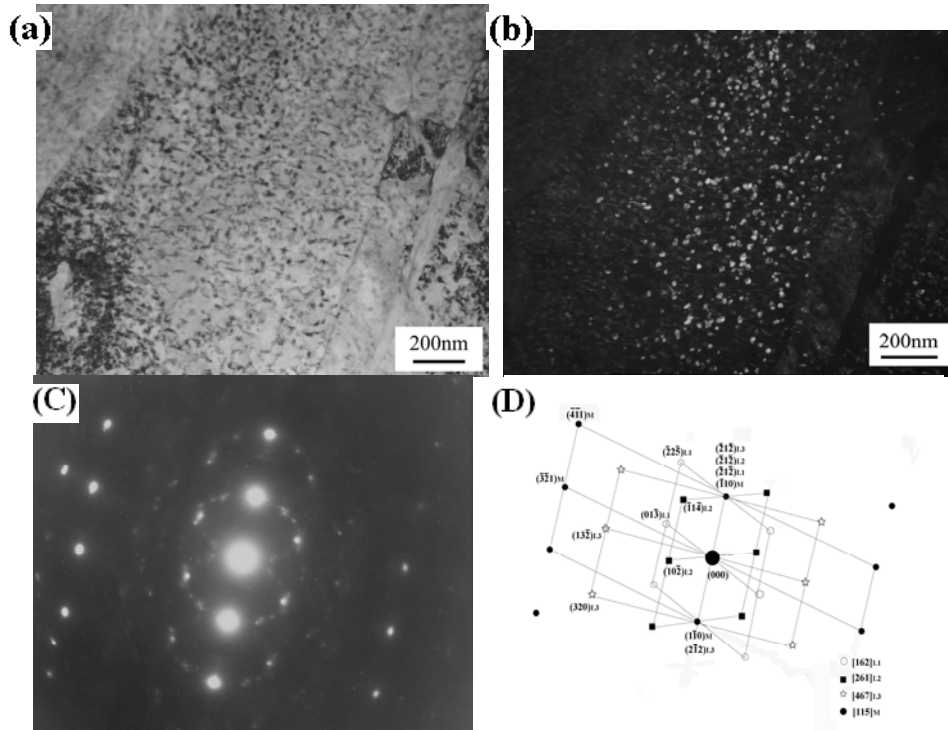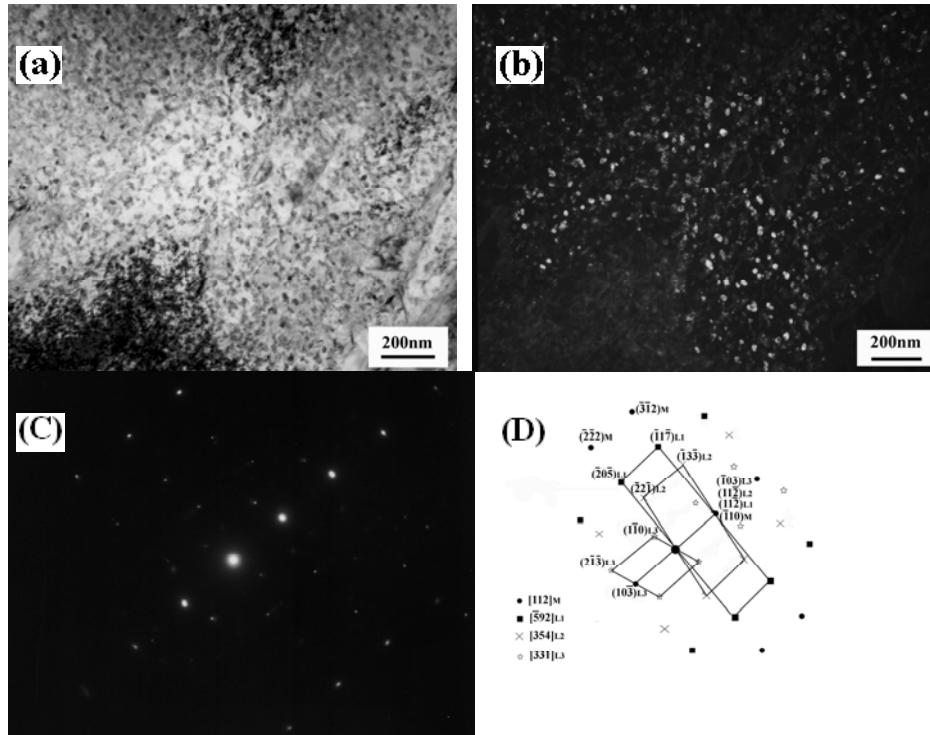

Figure 15: TEM micrographs and [115]MSAD pattern of Laves phase tempered at 540℃ for 4h a)BF;b)DF for$^{(10\overline{2})_L}$;c) [115]MSAD pattern; d) indexed patterns corresponding to (c)

Fig. 16 shows microstructure of 540℃/4h ageing precipitate phase which is produced by electron beam being incident along the martensite [115]M. The orientation relationship of fine and dispersively distributed precipitate phase is different leading to different contrast, that is, degrees of bright and dark images of precipitate phase. The results of calibration indicate:

$$[112]_M // [\overline{5}\,\overline{9}\,2]_{L1} // [354]_{L2} // [331]_{L3} ,$$

$$(\overline{1}10)_M // (11\overline{2})_{L1} // (11\overline{2})_{L2} // (\overline{1}03)_{L3}$$

Precipitates and matrix remain well coherent relationship and most of precipitates are formed near the dislocation line. Therefore, they obstruct dislocation movement and greatly improve the strength of steel.

Figure 16: TEM micrographs and [112]MSAD pattern of Laves phase tempered at 540℃for 4h. a)BF;b)DF for $(\overline{2}0\overline{5})_L$;c) [112]MSAD pattern; d) indexed patterns corresponding to (c)

Fig. 17 shows the 600℃/4h ageing TEM structure, SAD and its calibration. Laves phase obviously aggregates and grows up with the increase of ageing temperature, as shown in Fig. 17a, b. As incident direction of electron beam along [112]M, diffraction spots is obtained. The results of calibration show:

$[112]_M // [\overline{1}85]_{L1} // [232]_{L2} // [\overline{2}34]_{L3} // [\overline{1}22]_{L4}$, $(\overline{1}10)_M // (2\overline{1}2)_{L1} // (\overline{1}2\overline{2})_{L2} // (\overline{1}2\overline{2})_{L3} // (2\overline{1}2)_{L4}$, $(1\overline{1}0)_M // (1\overline{2}2)_{L3} // (\overline{2}1\overline{2})_{L4}$. The growth of precipitate phase results in the reduction of dispersion strengthening.
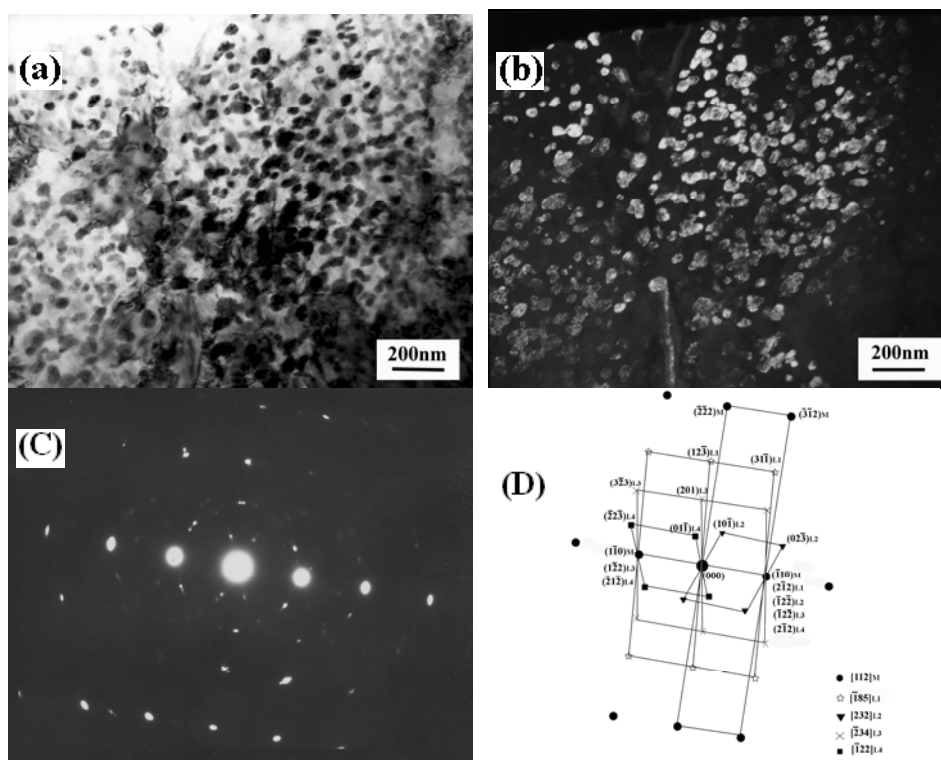
Figure 17: TEM micrographs and [112]MSAD pattern of Laves phase tempered at 600℃ for 4h. a)BF;b)DF for(201)ʟ;c) [112]MSAD pattern ;d) indexed patterns corresponding to (c)

4. Conclusions

1) The higher the Mo content, the more prominent is the effect on corrosion resistance in austenitic or ferritic stainless steels. Besides improvement in corrosion resistance, Mo has effects on the strength in high-strength martensitic stainless steels.

2) Mo has powerful effects, which is more significant when Mo interacts with chromium, on corrosion resistance in austenitic stainless steels. Mo promotes the development of super austenitic stainless steels with high performance. Due to the existence of Mo, the corrosion resistance of super austenitic stainless steels can be equivalent to that of Nickel-based alloy.

3) Adding 0.5%Mo in Cr17 ferritic stainless steel, which is used in automobile exhaust muffler system, will significantly improve its corrosion resistance in service environment. Particularly Mo improves pitting resistance and condensate corrosion performance.

4) The addition of 1% Mo to 444 ferrite stainless steel results in better corrosion resistance than SUS304 stainless steel and the addition of 2% Mo leads to equivalent corrosion resistance with SUS316 stainless steel.

5) The pitting resistance of 445 stainless steel with 1% Mo is better than that of SUS316L stainless steel at low temperature, whereas it is equivalent to SUS316L stainless steel at high temperature. The corrosion resistance of 445 stainless steel with 2% Mo is better than that of SUS316L stainless steel.

6) Mo increases tempering resistance and increases the strength by the secondary hardening effect. The strengthening mechanism is mainly that a fine dispersed Fe_2Mo type Laves phase is formed in high-strength martensitic stainless steel.

Reference

[1]. M.O.Speidel, Uggowitzer P.J. Proceedings of the Materials Week,1993. p.135, Lula, R.A.(Ed.). ASM International, Chicago.

[2]. J.Sedriks, Effects of Alloy Composition and Microstructure on the Passivity of Stainless Steel, Corrosion, Vol. 42(1986)7,376-389.

[3]. Yuping Lang. Effect on nitrogen on mechanical properties and corrosion resistace of austenitic stainless steels. Mater's Thesis. CISRI, 2000.4

[4] Mats Liljas. Superaustenitic stainless steel: develepment, fabrication and use[E]. Scandinavian Journal of Metallurgy, 1997,26(3):52-58.

[5] Yuping Lang, Xifan Kang. Corrosion resistance of super high nitrogen austenitic stainless steel and the effect of nitrogen. Journal of Iron and Steel Reserach，2001，vol.13，No.1。pp30-35

[6] Haitao Chen, Yuping Lang, Fan Yong. Development of ferritic stainless steel 439M for muffler. Proceedings of Stainless Steel and Heat Resistant Steel, 2009.

[7]Voznesenskaya N M, Kablov E N, Petrakov A F, et al.High-strength Corrosion-resistant Steel of the Austenitic-Martensitic Class[J]. Metal Science and Heat Treatment. 2002, 44 (7-8): 300-304.

[8] J.Koutsky, J.Jezek.Metal Treat. Drop Forging,1961,28:312~320.

[9] J.Koutsky, J.Jezek. J.Iron Steel Inst.,1962,200:938~942.

[10]K.J Irvine.The Development of High-strengh Steel[J].J.Iron Steel Inst.,1962,200:820~833.

[11]A. Kasak, V.K Chandhok,E. J Dulis. Development of Precipitation Hardening Cr-Mo-Co Stainless Steel[J]. Transactions of the ASM,1963,56:455~461.

[12]Peters D T,Cupp R.The Kinetics of Aging Reactions in 18 Pct Ni Maraging Steel[J].Trans.AIME.1966,236(10):1420-1428.

[13] Miner R E, Janckson J K, Gibbons D F.Internal Friction in 18 Pct Ni Maraging Steel[J].Trans.AIME.1966,236(11):1565-1561.

[14]D.J. Abson and J.A. Whiteman. Precipitation from iron-base alloys containing cobalt[J]. Journal of The Iron and Steel Institute, 1970, (208):594-600.

[15]L.E. Alekseeva, G.I. Koritskaya, and E.I.Talalakina.Stabilization of Small Deformations of Maraging Steel by Steel Relaxation[J].Metallovedenie i Termicheskaya Obrabotka Metallov, Dec,1987(12):12-15.

[16]S.V. Grachev, A.S. Sheyn, S.V. Pavlova and N.A.Rundkvist. Infl-uence of Quenching Programmes on Phase Compostistion and Effectiveness of Subsequent Aging of Maraging Steel[J]. Phys. Met. Metall., 1988, (66) 1:151-157.

The brief biography of Prof. Zhiyong Yang

Prof. Zhiyong Yang is deputy director of Institute for Structural Materials, Central Iron and Steel Research Institute (CISRI), and vice director of committee of Stainless Steels and Heat Resistant Steels, Chinese Specialty Steel Society. As a leading expert in the field of high strength stainless steels, Prof. Yang has been in charge of more than ten key research projects, especially for research and development in the stainless steels with military applications and hydro power station applications.

Application of Molybdenum in the Mould Steel

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Abstract: With wider and wider application of the mould, and its harsher and harsher service conditions, the properties requirements of the mould steel are increasingly improved, and molybdenum as an alloying element plays an important role in mould steel. The SD718 steel designed by addition of Mo in the AISI P20 + Ni can make 1 m thick plastic mould steel block all through quenched. Mo in the non-quenched prehardened plastic mould steel (SDFT) not only significantly inhibits proeutectoid ferrite transformation, but also facilitate the mould to obtain uniform hardness. When Mo is added into corrosion-resistant plastic mould steel, both corrosion resistance and polishing ability are improved. The SDC99 steel developed by modified Mo in the Cr12MoV steel, its secondary hardening capacity and toughness are improved by forming dispersive carbides M_2C and M_6C. Hot work steel (SDH8) containing Mo, precipitates Mo_2C and MoC in tempered martensite which change into M_6C with the tempering temperature increasing, and they all improve the heat resistance properties of hot work steel.

Key words: Molybdenum, Mould steel, Microstructure, Properties

Introduction

Mo, W and γ-Fe belong to the same space lattice structure, however the differences in atom radius between the former two elements and γ-Fe are 10% and 11% respectively. The substitutional solubility of Mo in α-Fe is 37.5%, which is higher than that of W, i.e. 35.5%. As one of important alloy elements, Mo improves the hardenability of steel and has strong carbide-forming tendency and precipitate strengthening effect. Addition of Mo in steel increases the diffusion active energy of carbon in austenite, and therefore decreases the diffusion coefficient, prolongs the incubation period of the ferrite-pearlite transformation, and enhances the austenite stability and driving force of transformation. The ferrite-pearlite and bainite regions in CCT curve are separated by a river bay area. Addition of Mo strongly retards the precipitatetion and growth of pro-eutectoid ferrite and pearlite, while it does not have apparent effect on bainite transformation. Mo is easy to form carbides of Mo_2C and MoC. Mo_2C has close-packed hexagonal structure, with 6 metal

atoms and 3 carbon atoms within unit crystal cell; MoC has single hexagonal structure, and 3 metal atoms and 3 carbon atoms within unit crystal cell with a small lattice constant. Both carbides have high hardness and decomposition temperature. Based on above characteristics, a wide application of molybdenum has been achieved in the mould steels.

1. Application of Molybdenum in the Plastic Mould Steels
1.1 Application of molybdenum in heat treatment pre-hardening plastic mould steel

Pre-hardening plastic mould steels achieves the required hardness and in-service properties for users at the delivery stage of metallurgical works. The moulds are directly manufactured with these steels by users without quenched and tempered treatment procedures, which tend to lead the defaults such as distortion, crack and decarburation followed the machining. At the same time, it is suitable for producing large, complex and precision plastic mould components due to the combination of excellent strength and toughness, machinability, polishing performance, dimension precision and cost performance, therefore, it accounts for a large market share of plastic mould steels. Excellent hardenability is required for mould steels due to the increasing development trends on large, complex, precision of plastic products, such as cylinder washer, refrigerator inner cavity, and shell of large TV-set and so on, and some with the size larger than 600 mm, especially for car safety bar weighted tens tons and with thickness of 1 m, which had been manufactured previously by AISI P20+Ni steel (DIN 1.2738，GB 3Cr2MnNiMo，Sweden designation is 718), the core of which can not be hardened completely. SD718 steel had been developed by us based on this type plastic mould steel, with the Mo content increasing from 0.30% to 0.40% but the Ni content constant, the compositions are given in Table 1. The dilatometric experiment showed that the proeutectoid ferrite transformation was not formed at the cooling rate of 0.01 ℃/s after austenitizing at 900 ℃, while the massive ferrite was observed for P20+Ni steel and 718 steel (Sweden designation), as shown in Fig. 1. This pre-hardened mould blocks can be fully hardened at a section of 1030×1140×2400 mm. Compared with the conventionally large plastic mould steel P20+Ni, the C curve of SD718 steel transfers towards the right side by the increase of Mo content, especially for ferrite and pearlite transformation within the high temperature transformation region, as a result, the formation of ferrite in the core is avoided due to the dramatic increase of hardenability.

Table 2 the compositions ofP20+Ni and SD 718 steels (mass, wt %)

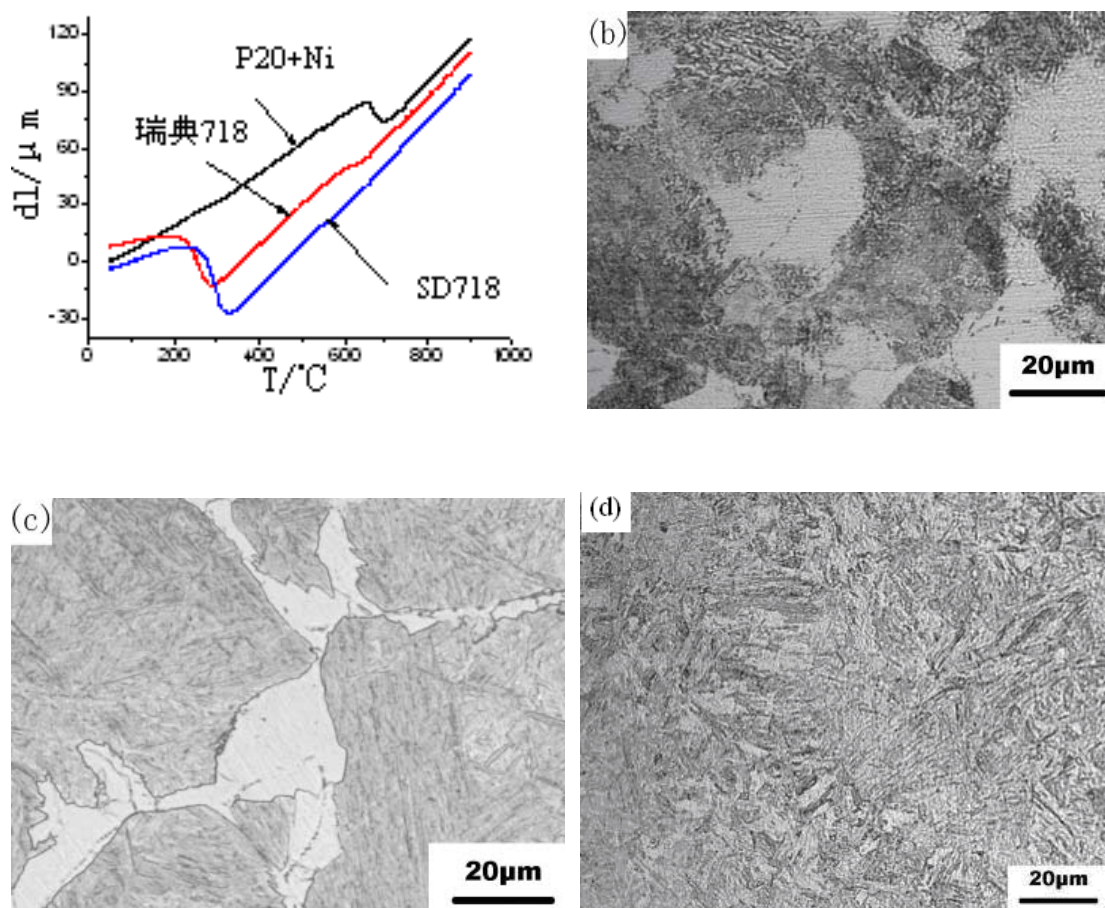| Steels	C	Si	Mn	Ni	Cr	Mo	P	S
P20+Ni	0.32-0.40	0.20-0.80	1.00-1.50	0.85-1.15	1.70-2.00	0.25-0.30	≤0.03	≤0.03
SD718	0.27	0.28	0.80	0.69	1.67	0.40	0.008	0.002

Fig. 1 (a) The dilatometric curves of SD718, P20+Ni and 718 steels at the cooling rate of 0.01 ℃/s after austenitizing at 900 ℃, and microstructure of (b) P20+Ni steel,   (c) 718 steel and (d) SD718 steel.

1.2 Application of molybdenum in non-quenched and tempered pre-hardening plastic mould steel

In order to save the energy resources, to reduce cost, and to shorten the period of manufacture of pre-hardening plastic mould steels, the aspects of mechanism of alloying, microstructure properties and machinability have been studied systematically for non-quenched and tempered plastic mould steels since 1992. With independent innovation, we have developed FT type plastic mould steel. The experimental results showed that FT steel has bainite-ferrite duplex phases microstructure after hot forging or hot rolling followed by cooling in air, and exhibits high strength and toughness, however it can be fabricated into plastic mould only with a diameter smaller than 150 mm[1-7]. In order to

extend the application of non-quenched and tempered on plastic mould with larger section size and uniform hardness. Conventional development idea of plastic mould steels has been broken through by the author, and a non-quenched and tempered pre-hardening plastic mould steel has been developed by adding different amounts of Mo under given Mn and Cr content, and the steel is suitable for manufacture of mould with section size range between 300 mm and 600 mm.

The results showed that the critical cool rate of ferrite drastically decreases with a Mo content higher than 0.3%, on which a very strong effect of Mo content between 0.4% and 0.5%. Based on above research achievements, Baosteel Co. has produced non-quenched and tempered plastic mould steel (designation is SDFT) with a thickness of 300~600 mm, and a width of 800~1200 mm, the pre-hardening harness ranged from HRC 28~42, and section hardness variation was less than HRC 1.5. Fig 2 and Fig. 3 show the CCT curves and section hardness distribution of SDFT steel with a section of 460 mm×800 mm [8-12].
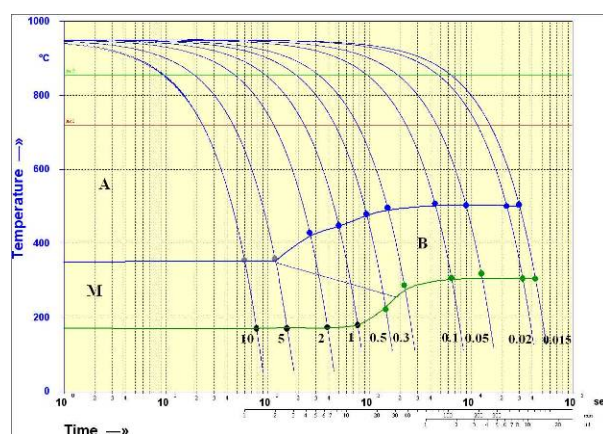
Fig.2 CCT curves of SDFT steel   Fig. 3 Section hardness distribution of experimental steels.
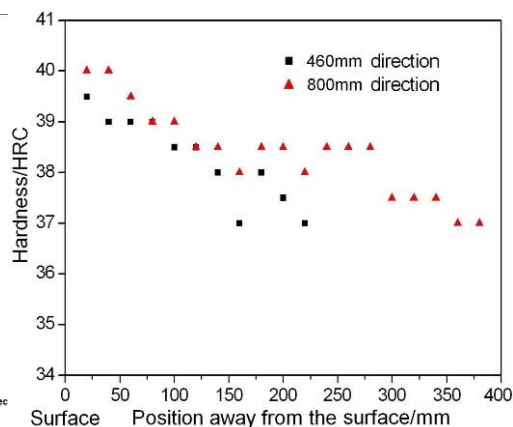
1.3 Application of molybdenum in stainless plastic mould steels

Mo element makes steel surface passivate both in the reduced acid (hydrochloric acid, sulfuric acid, sulfite) and in the salt solute with strong oxidizability (especially for chlorine ion), and so it is realized universally that Mo improves corrosion resistance of steel. The pitting corrosion tendency is inhibited or avoided by the addition of Mo alloy element, such as the common pitting corrosion of materials in the medium of chlorine[1]. For example, 9Cr18Mo (Mo addition into 9Cr 18) is more suitable for using in environment than 9Cr18, a high carbon and high Cr martenite stainless steel. Zhang

Honggui in our group compared the polishing properties of Mo-contained 4Cr16Mo steel with that of 4Cr13 steel. Fig. 4 shows that the former has a higher surface finish under same polished conditions[1].

(a) 4Cr16Mo steel   (b) 4Cr13 steel
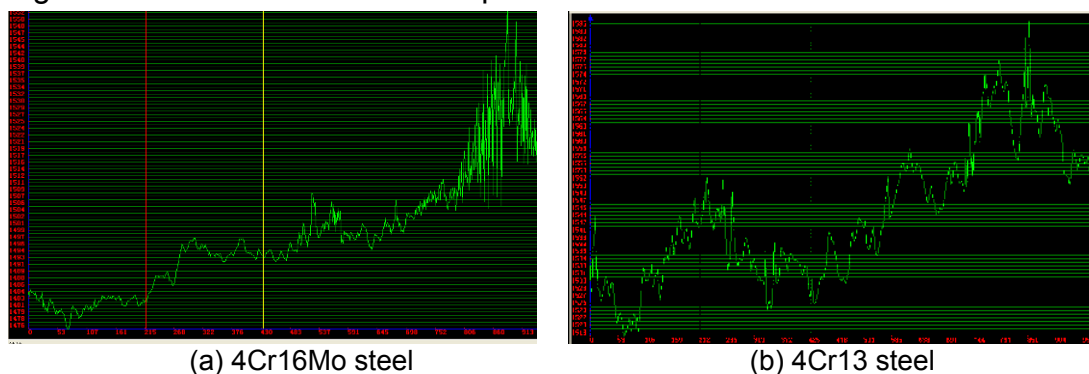
Fig.4 SEM micrograph of polished specimens.

2. Application of Molybdenum in Cold Work Steels

The plastic deformation of cold work mould steels are examined at room temperature by different methods such as bending, extrusion, punching, extruding, cold upsetting, thread rolling and so on. Cold work moulds are loaded by various mechanical forces, such as tension, compression, impact fatigue, and turbo. The failure modes include wear, fracture, plasticity deformation, and adhesion. For cold work mould steels, high wear resistance, fatigue resistance, adhesion resistance and enough strength and toughness are commonly required. Wear-resistance cold work moulds are usually manufactured with Cr12 steels with high hardness and wear-resistance, while it also has low strength, due to large amounts of carbides and serious segregation. Cr12MoV steel contains a small amounts of Mo and V content (0.15~0.60%) and has been applied widely in China. The addition of Mo and V decreases the carbides segregation; and the alloy carbides, precipitated during tempering at high temperature, have secondary hardening effect. Compared with Cr12 steels, Cr12MoV steels have higher toughness and similar wear-resistance due to the finer and more uniform dispersion carbides. In recent years, our research group have developed cold work mould steels SDC90 and SDC99 based on Cr12MoV steel, with an appropriately decrease of the content of C and Cr and an increase of Mo and V content for a fine microstructure, the compositions are given in Table 2[2].

Table 2 the compositions of cold work mould steels (mass, wt %)

Steels	C	Si	Mn	Cr	Mo	V
Cr12MoV	1.45~1.70	≤0.40	≤0.35	11.0~12.50	0.40~0.60	0.15~0.30
SDC90	0.90～1.0	0.90～1.0	0.20～0.40	9.0～10	1.90～2.20	0.8～1.0
SDC99	0.90～1.0	0.40～0.60	0.20～0.40	8.50～9.0	1.40～1.60	0.20～0.40

The effects of tempering temperature on quenched hardening of Cr12MoV steel and SDC99 steel are shown in Fig. 5. It can be seen that both steels have the same level of quench hardening. The Cr12MoV steel achieved a higher hardness at the tempering temperature below 300℃ due to a large amounts of undissolved carbides; however, SDC steel had a higher secondary hardening effect than Cr12MoV steel attributed to a higher Mo content in the former, in which a major reason for secondary hardening effect is because most contained Cr carbides were Ledebrite carbides, as shown in Fig. 5. The matrix was strengthened by the Mo_2C carbides, which precipitated during tempering and not easily to grow, indicating high thermal stability and hardness.
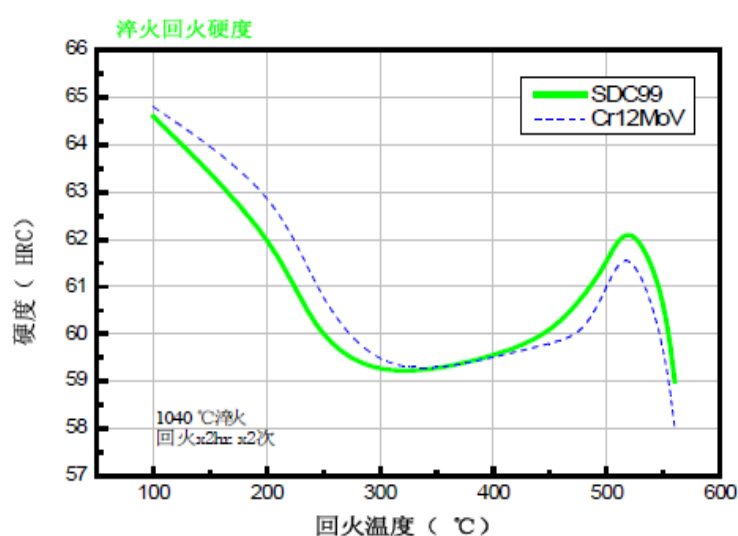
Fig. 5 The strong role of Mo on secondary hardening effect.

At the same time, the mechanical properties of three steels after quenched at 1040 ℃ twice and tempered at 210 ℃ for 2 h are shown in Fig. 6. It can be seen that raising Mo content can increase the toughness under the same hardness level. The microstructures in Fig. 7 show that the carbides in SDC99 steel were finer than that of Cr12MoV, and which had a benefit effect on strength and toughness properties of steels.
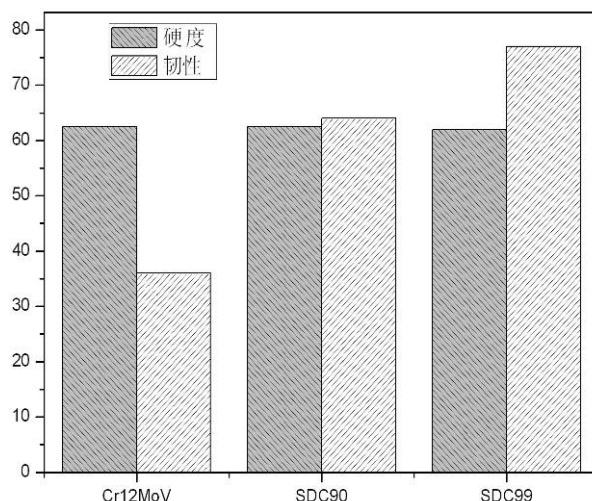
Fig. 6 The hardness and toughness after quenched and tempered at relative low temperatures.
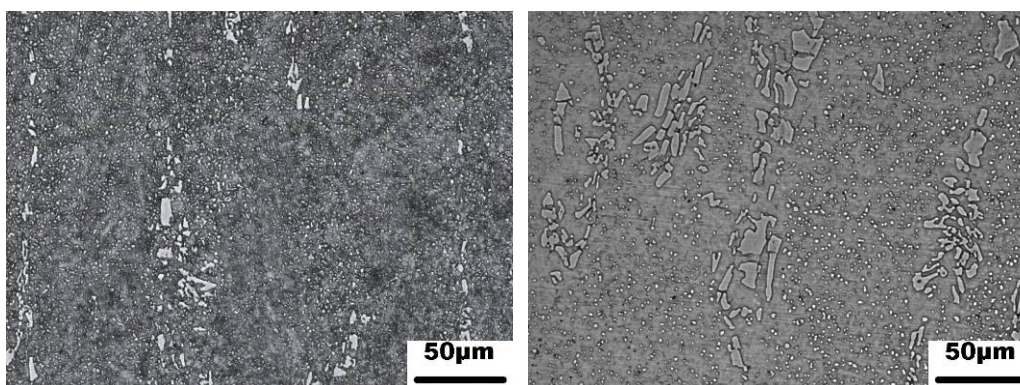
Fig. 7 The microstructure of (a) SDC steel and (b) Cr12MoV steel.

The carbides sizes between SDC steel and Cr12MoV steel were further compared by electrolysis phase extraction, as shown in Fig. 8. For Cr12MoV, most carbide sizes are between 4 μm and 30 μm, and the amounts with sizes ranging from 10 μm and 30 μm are high with an average size of 12.03 μm. Large eutectic carbides are distributed in matrix, and they are piled up and undissolved. The carbide size distribution after tempering at 210 ℃was similar to those of the as-quenched one. Although, the hardness and wear resistant of steels were improved by the large eutectic ledebrite carbides distributed in matrix, however they made the steel crack prematurely due to lower toughness.

Fig. 9 shows the carbide size distribution of SDC steel after quenched at 1040 ℃.The size universally ranged from 0.1 μm to 10 μm with an average size of 1.23 μm, it was found that those carbides were secondary carbides. The carbide size distribution of steel after tempering at 210 ℃was similar to

those of the quenched steel. It indicated that the carbide average size of SDC99 steel was much smaller than that of Cr12MoV. The crack propagation resistance of steels, the toughness and the life in service were improved attributed to the large amounts of dispersed carbides in the matrix. SDC99 steel not only exhibited a good wear resistance but also had a much higher toughness than that of Cr12MoV

Average size: 12.03µm   Average size: 11.37µm
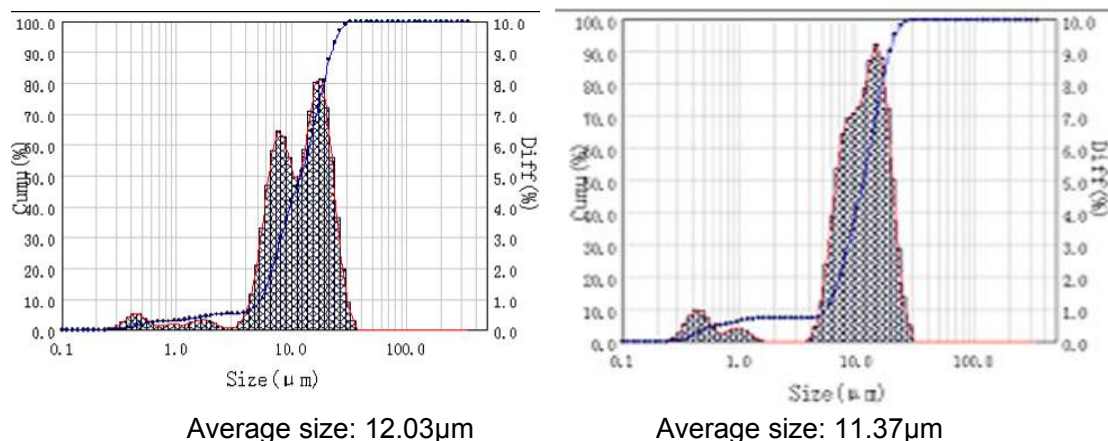
Fig. 8 The carbide size distributions of Cr12MoV steel (a) quenched and (b) tempered

Average size:1.23µm   Average size: 1.21µm
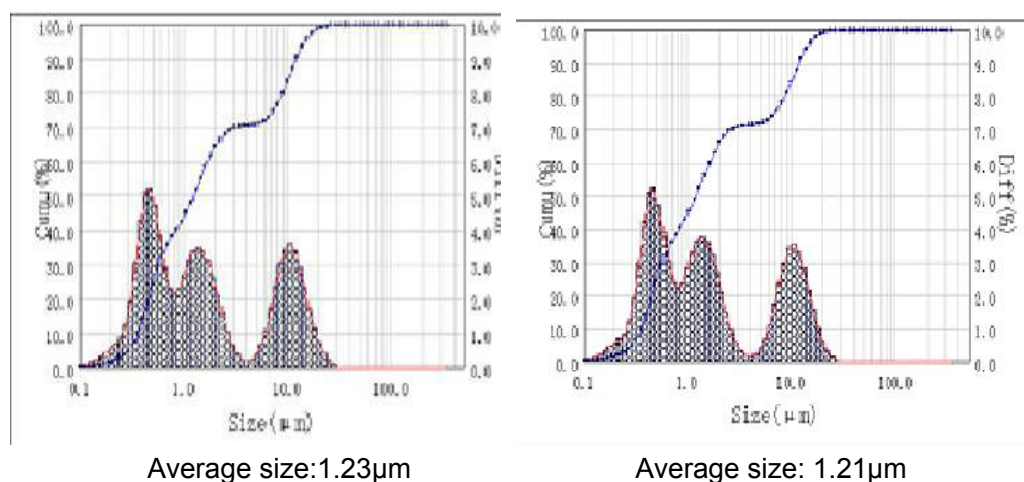
Fig. 9 The carbide size distributions of SDC steel (a) quenched and (b) tempered.

The carbide size distributions of two steels were studied by statistics method, and the Fig. 10 showed the carbides with size of 0.25~1 µm accounting for 45.5% of the total carbide populations in SDC99 steel, whereas 91% carbides were bigger than 5 µm in Cr12MoV steel.
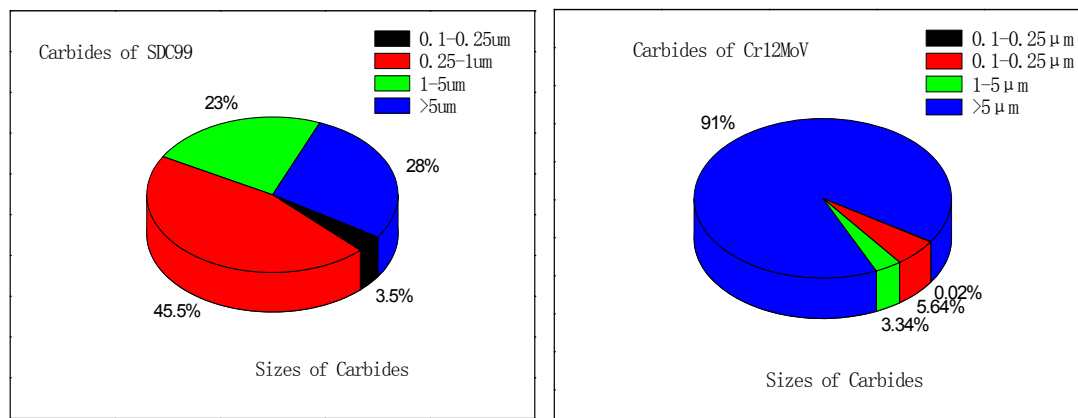
Fig. 10 The size distribution of carbides for (a) SDC steel and (b) Cr12MoV steel.

SDC steel with extra Mo addition in the base composition of Cr12MoV, which improved the carbides size distribution. The combination of excellent wear resistant and higher toughness was mainly attributed to the fine dispersive carbides. TEM observations showed the fine secondary carbides with sizes between 0.25 μm and 1 μm. Those distributed carbides were confirmed to be M23C6 in SDC99 steel by the diffraction patterns, as shown in Fig.11. It is found that most secondary carbides were M23C6, and eutectic carbides were M7C3, which is similar to that of Cr12MoV steel.
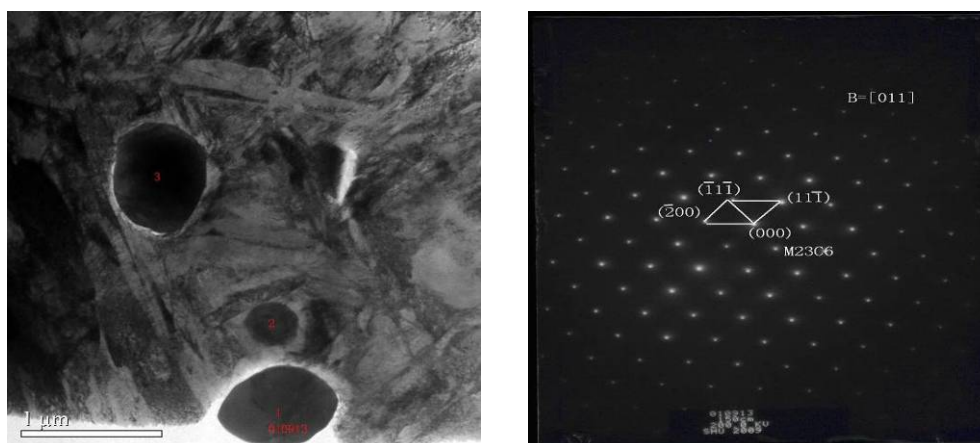
Fig. 11 The secondary precipitated carbides and its TEM diffraction pattern for SDC steel.

The carbide type and amount of SDC steel were calculated as a function of Mo content by Jmatpro software, and the results were plotted in Fig. 12.

0.5% Mo   1.5% Mo

3.0% Mo   5.0% Mo
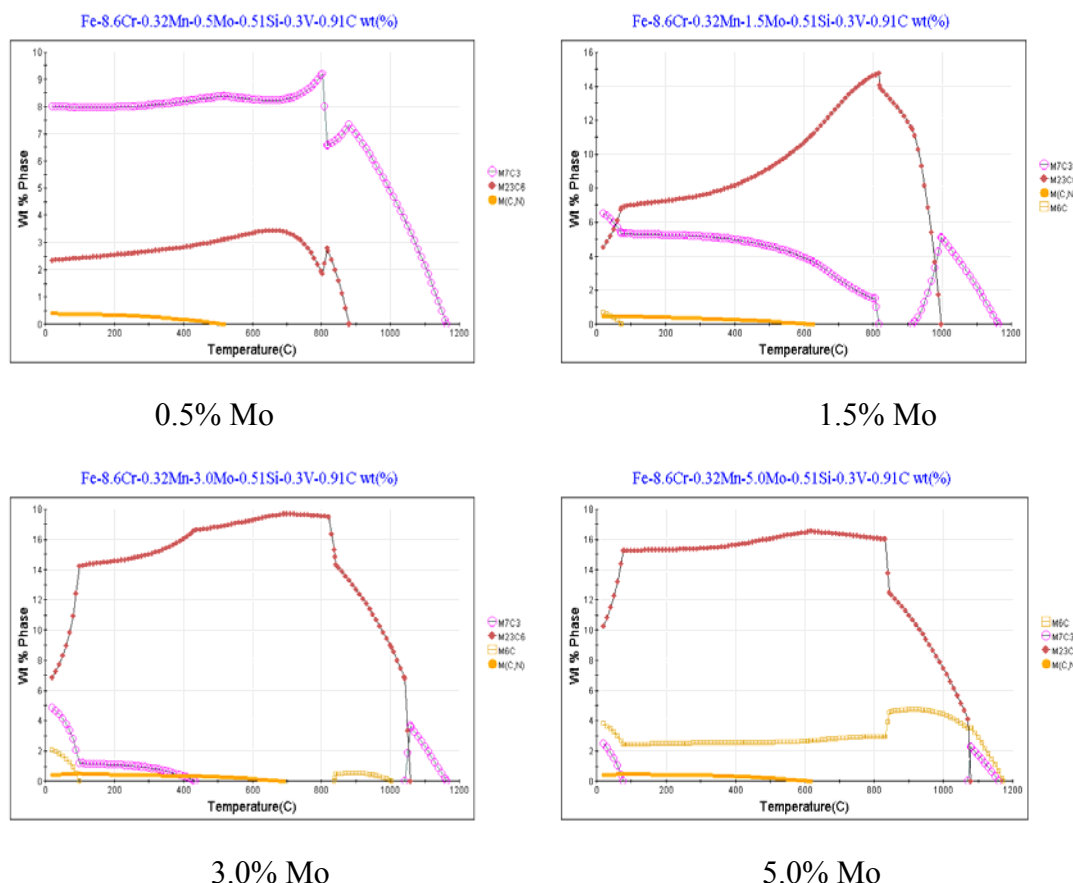
Fig. 12 The dependence of type and content of carbide on temperature for SDC steel.

With the increase of Mo content in steel, the amounts of M7C3 carbides decreased and those of M23C6 increased. M6C carbides began to form in SDC99 steel when the Mo content was higher than 3.0%. The comprehensive properties of steel were improved by large amounts of secondary carbides precipitated in matrix. High wear resistance was dependent not only on high hardness and also on microstructure of steel. Large amounts of dispersive secondary carbides in martensite produced secondary hardening effects. The common strengthening phases were M2C (i.e. W2C、Mo2C), MC(i.e. VC) and M23C6 (Cr23C6) so on. Those carbides have very high hardness and also do not have a tendency to grow at high temperature, for example, the hardness of VC is HV2700~2900. Wear resistance was improved efficiently by alloy carbides, which can contribute for the better comprehensive properties of SDC99 than that of Cr12MoVsteel.

3. Application of Mo in Hot-Work Mould Steels

High thermal stability and creep, high toughness, enough hardness and thermal-fatigue resistance are required for Hot Work Mould Steels [1]. Mo

addition improves both the hardenability and thermo-fatigue resistance, prevents secondary temper embrittlement, and enhances high temperature strength and tempering stability. It is concluded that Mo is a major alloy element for secondary hardening due to the precipitates of Mo2C in marstenite during tempering. The formation Mo2C and MoC alloy carbides by Mo and C elements, they can transform to M6C with increase of tempering temperature. Fine and parallel needle-shaped (lamellae in two-dimensional space) Mo2C carbides are precipitated in laths in martenite or sub-grain boundary, they belong to hexagonal system. In addition, addition of Cr and Co can strengthen the secondary hardening effect. The steels need to be reheated at higher temperature to make the W and V carbides to dissolve into austenite, but they cause the formation of coarse austenite grains and a detrimental effect. And so, Mo is commonly chosen as the best element for secondary hardening effect. The addition of Mo can produce the secondary hardening effect at a Mo content higher than 1.0% and achieve the best effect at 3%. It achieves the best economic and efficient effect at 2.0%~2.5% Mo [2]. SDH8 steel has been developed by our research group through increasing Mo content and decreasing V content. Compared with H13, SDH8 steel has an excellent thermo-stability and thermo-fatigue resistant, as shown in Fig. 13 and Fig. 14. Fig.14 shows the surface cracks and section cracks after thermo-cycle for 3000 cycles, for SDH8 and H13 steels. The surface cracks in SDH8 steel were fine, and large cracks were not found; for H13, several wide and large major cracks were found through the specimen surface. And the crack depths of SDH8 were fine and shallow, distributed sparsely at the specimen surface, while the cracks were deep in H13 steel, which exhibited a lower thermo-fatigue resistance. Fig.15 shows the variation of section hardness of both steels after 3000 cycles thermo-fatigue, indicated that the decrease of surface hardness of SDH8 was smaller than that of H13, and it indicated that the former have more excellent high temperature thermo-strength properties and a higher thermo-fatigue resistance. The results of microstructure stated that the improved thermo-stability was dependent on the large amounts of carbides contained Mo element, as shown in Fig.16 [1].
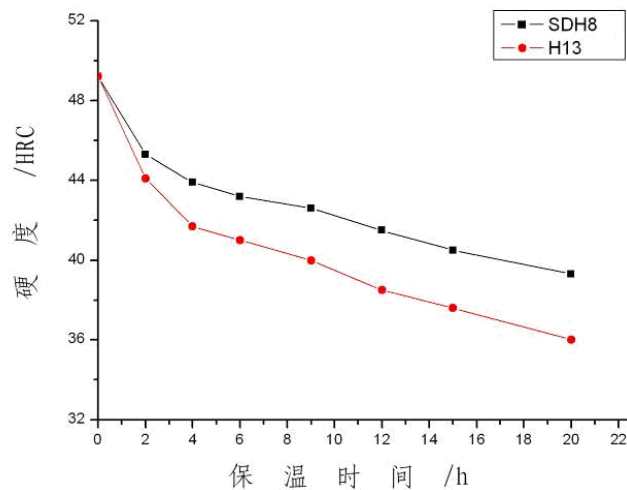
Fig. 13 The comparison curves of thermal stability for SDH8 steel and H13 steel at the same quenched and tempered conditions.
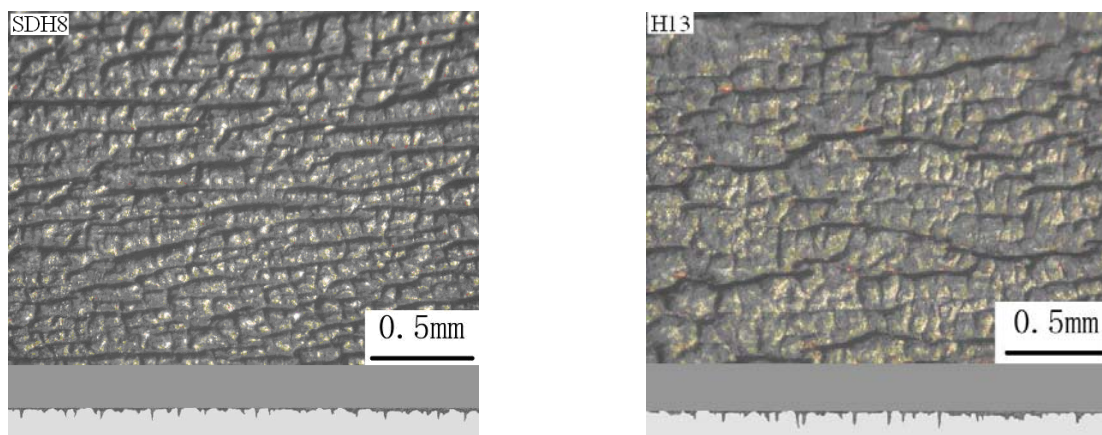

Fig. 14 The comparison of surface cracks and depths of crack after thermal fatigue test for SDH8 steel and H13 steel.
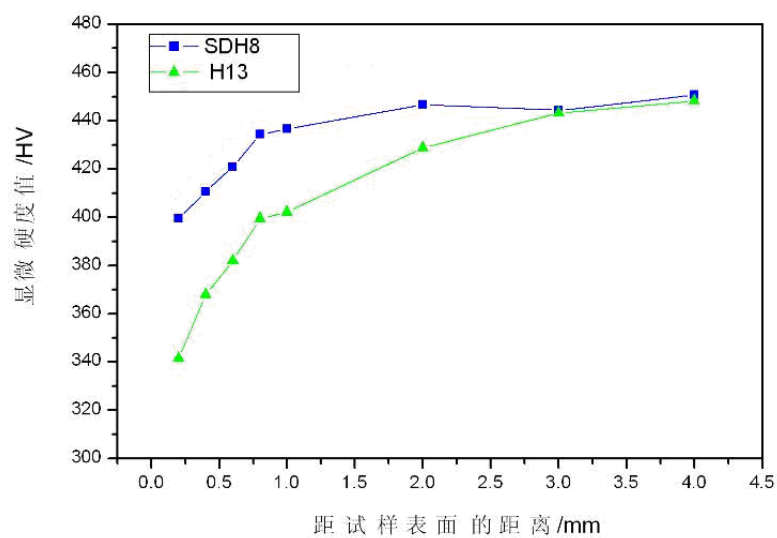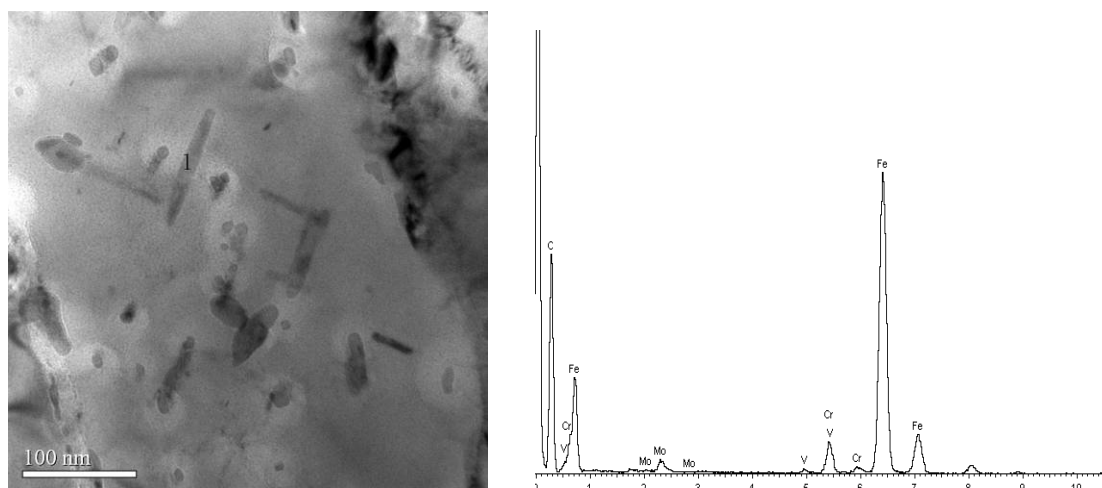

Fig. 15 The section hardness distribution curves for SDH8 steel and H13 steel after 3000 thermal fatigue cycles.

(a)TEM micrograph of microstructure   (b) The EDS of point 1 in (a)
Fig. 16 The TEM micrograph and EDS of carbides for SDH8 steel quenched and tempered.

4. Conclusions

（1）SD718 steel has been developed by modification of Mo content based on AISI P20+Ni steel. The plastic mould block can be completely hardened at a thickness of 1 m. Mo prevents the proeutectoid ferrite transformation in non-quenched and tempered pre-hardening plastic mould steels (SDFT), and it has benefit for achieving a uniform section hardness distribution for mould blocks. The corrosion resistance and the polishing performance were improved by addition of Mo in plastic mould steels.

（2）The secondary hardening effects has been largely improved by Mo alloying based on the Cr12MoV steel. The matrix was strengthened by the dispersion of carbide M2C, which also improved the wear resistance and toughness of cold work mould steels.

（3）For Mo-contained hot-work mould steel（SDH8）, the thermal stability and creep of hot-work mould steels have been improved by precipitates, i.e. the alloy carbides of Mo2C and MoC precipitated in tempered martensite, and the formation of M6C with the increase of tempering temperature.

References

[1]   Chen ZZ, Ma DS. Hand Book of Plastic Mould Steels and Their Applications [M]. Beijing: Chemical Industry Press, 2005.

[2]   Lu Y, Wu XC. Research progress in pre-hardened plastic mould steels [J]. Heat Treatment of Metals, 2007, 32(12): 22-25.

[3]   Wu Xiaochun, Zhang J, Cui K. Machinability of non-quench platstic mould steels[J]. Journal of Huazhong Univeristy of Sciencen and Technology, 1995, 23(12): 7-12.

[4] Wu XC, Cui K. Study on free-cutting non-quench plastic mould steels [J]. Journal of Iron and Steel Research, 1996, 8(1): 29-33.

[5] Wu XC, Cui K. Study on precipitates of microalloying elements in non-quench plastic mould steels [J]. Iron and Steel, 1998, 33(6): 50-53.

[6] Wu XC, Zhou H, Wu XY, et al. Machinability of free-cutting non-quench plastic mould steels [J]. Mechanical Engineering Materials. 1996, 20(1): 39-42.

[7] Wu XC, Lou DC, Cui K. Microstructure and mechanical properties of free-cutting non-quench plastci mould steels [J]. Special Steels, 1996, 17(1): 15-18.

[8] Wu XC, Lou DC, Cui K. Effect of V and Ti on microstructure and mechanical properties of non-quench bainitic steels[J]. Iron and Steel Research, 1996, 3: 25-29.

[9] Wu Xiaochun, Cui Kun. The machinability of unquenched and untempered die steels for plastic moulding[C], Proceeding of an International Conference on Tools Steel for Dies and Molds, Shanghai, China, 1998, 12-14.

[10] Luo Yi, Wu Xiaochun, Wang Hongbin, Min Yong'an. Study on the microstructure and properties of prehardened plastic-mould SWFT steel for big section[J]. Key Engineering Materials, 2007, 353-358: 1629-1632.

[11] Luo Yi, Wu Xiaochun, Wang Hongbin, Min Yong'an. Study on microstructure and hardness uniformity of non quenched prehardened plastic mould steel for large section[J]. Material Science and Engineering A, 2008, 492: 205-210.

[12] Luo Yi, Wu Xiaochun, Wang Hongbin, Min Yong'an. Development of a non-quenched prehardened steel for large section plastic mould[J]. Journal of Iron and Steel Research, international, 2009, 16(2): 61-67.

[13] Luo Yi, Wu Xiaochun, Wang Hongbin, Min Yong'an.A comparative study on non-quenched and quenched prehardened steel for large section plastic mould[J]. Journal of Material Processing Technology, 2009, 209: 5437-5442.

[14] Luo Y, Wu XC, Zhang HK. Microstructure and mechanical properties of large section non-quench pre-hardened plastic mould steels [J]. Heat Treatment of Metals, 2008, 33(3): 28-30.

[15] Zhang HK. Study on new corrosion resistant free-cutting plastic mould steels [D]. Master's Thesis of Shanghai University，2007.

[16] Luo Y, Wu XC, Min YA, et al. Comparison of microstructure and mechanical properties of Cr12Mo1V1 steels produced domestically and abroad [C]. Proceedings of Mould Materials, Chendu, 2005.9, 111-116.

[17] Xie YZ. Research and development of high strength high toughness cold-work moudl steels [D]. Master's Thesis of Shanghai University, 2010.

[18] Luo Y, Wu XC, Min YA, et al. Microstructure and hot fatigue behavior of SDH13 steel. Heat Treatment, 2006, 21(1):25-30.

[19] Pan XH, Zhu ZC. Improvement on chemical composition of H13 hot work mould steel. Mould Production Technology [J]. 2006, 4: 78-85

[20] Song WW. Study on microstrucutre control and mechanical properties of Nb-containing hot work mould steels [D]. Master's Thesis of Shanghai University，2009.3

The brief biography of Prof. Xiaochun Wu

Prof. Xiaochun Wu is working with School of Materials Science and Engineering, Shanghai University. As a famous expert in mould steels, Prof. Wu has long been involved in fundamental research and technical development in the field of mould steels and in charge of more than 10 research and development projects.

The roles and applications of molybdenum element in low alloy steels

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Abstract: The mechanisms and applications of molybdenum (Mo) in low alloy steels were elucidated in this paper. Mo can promote the transformation of acicular ferrite and bainite through its retardation effect on the proeutectoid ferrite transformation, and therefore improve the strength and toughness of low alloy steels. Mo can increase the solubility of microalloying elements (Nb, V and Ti) in austenite and retard the precipitation of microalloying carbonitrides, so that more microalloying elements can be preserved at relatively low temperature and then precipitated from ferrite, which can bring about strong precipitation hardening effect. Mo can occupy a fraction of lattice sites of microalloying carbonitrdes precipitated from ferrite to form the precipitates with the chemical formula of $(M,Mo)(C,N)$ (M is the microalloying element). This can not only increase the volume fraction of precipitates, but also refine the size of precipitates, so its precipitation hardening effect is improved remarkably. The microalloying carbonitrides containing Mo are hard to be coarsening during holding at high temperature and have a strong thermal stability. Finally, some examples of applications of Mo in high grade pipeline steel, high strength engineering machinery steel, fire-resistant steel and hot-rolled strip for automobile were briefly introduced.

1 Introduction

The trend of low alloy steels is to pursue high strength, high toughness, high plastic, excellent process performance and service performance.   Mo addition plays an important role in the development of low alloy steels. On 1957, Irvine and Pickering[1] presented that a small amount of Mo and B additions can inhibit the formation of proeutectoid ferrite, but has little effect on the bainite transformation kinetics. Thus, bainite could be acquired by a wide range of cooling rate, consequently increasing the strength and toughness of steels. Since then, Climax Molybdenum Company has developed a lower C steel with the addition of Mo-B, so-called Climax steel. Its typical composition is 0.04% C-2.0% Mn-0.4% Mo-0.05% Nb[2]. Due to the lower carbon equivalent, its

weldability and toughness has been greatly improved. Therefore, the role of Mo addition on transformation strengthening in low alloy steel was found early and was continuously developed and applied. In addition to transformation strengthening, there are at least other effects of Mo addition in low alloy steels as follows: 1) to improve the solid solubility of microalloying elements Nb, V, Ti in austenite and to promote precipitation of microalloying carbonitride in ferrite; 2) to increase the thermal stability of microalloying carbonitride and to improve the high temperature performance; 3) to delay the recrystallization of austenite and to expand the areas of non-recrystallization of austenite in the rolling process. These effects above were to some extent applied in low alloy steel production.

This paper first reviewed the basic principles of physical metallurgy of Mo in low alloy steel, emphasizing the effects of Mo on→phase transformation, and on the solid solubility, precipitation, thermal stability of microalloy carbonitride. Several examples on the application of Mo addition in low alloy steels were then given. Finally, some comments on the future research were presented.

2 Effects of Mo addition on → phase transformation in low carbon low alloy steels

The main effect of Mo addition on→phase transformation is significantly delaying proeutectoid ferrite transformation, resulting in obtaining bainite. The reasons are the coupled effects of solute drag and decreasing the carbon diffusivity at the interface, which result from the strong tendency to segregation of Mo at the interface in steels.

Figure 1 shows the continuous cooling transformation (CCT) curves of two different test steels (0.056Nb steel, 0.057Nb +0.23 Mo steel). Austenitizaition, austenite deformation and CCT measurement were carried out by Gleeble. It can be seen in Figure 1 that fully bainitic microstructure was obtained in 0.057Nb +0.23 Mo steel at the cooling rate exceeding 1 ℃/s. However, fully bainitic microstructure was only obtained in 0.057Nb steel without containing Mo when the cooling rate exceeding 50 ℃/s. Furthermore, the transformation start temperature of 0.056Nb steel (Ar3) is more sensitive to the cooling rate than the Mo-added steel (Bs). Figure 2 (0.056Nb) and Figure 3 (0.057Nb +0.23 Mo) show the microstructure forming at different cooling rates[3]. As shown in Figure 2, when the cooling rate was lower tan 10 ℃/s, the microstructure was polygonal ferrite and a small amount of quasi-polygonal ferrite; when the cooling rate was higher than 10 ℃/s, granular bainite formed. However, as

shown in Figure 3, granular bainite formed at the cooling rate higher than 1 ℃ /s in 0.057Nb +0.23 Mo steel; when the cooling rate higher than 10 ℃/s, lath bainite was acquired. Figure 4 (a) summarized the results of Vickers hardness of test steels at different cooling rates. It is seen that the hardness of the Mo-added steel was higher than the Mo-free steel. In addition, the more Mo addition, the hardness difference is greater. As shown in Figure 4(b), the hardness (or strength) of test steels increased linearly as the transformation start temperature decreased. Combined with the CCT curve in Figure 1, it is indicated that Mo not only increases the strength of steel, but also decreases the heterogeneity of microstructure and performance along the thickness of the thick plate, where the cooling rate varies along the thickness.

Much attention was also paid attention to the addition of B in low carbon bainitic steels. It was found that the segregation of B at the grain boundary significantly inhibited the proeutectoid ferrite transformation. However, it was shown that only the coupled addition of B with Mo, Nb played a better role as shown in Figure 5[4]. In the case of the single addition of B, the solution of B is decreased by the formation of Fe23 (C, B)6 at the austenite grain boundary due to segregation of B and C. However, in the case of coupled addition of B, Mo and Nb, clusters of Mo-C or Nb-C forms and decreases the segregation tendency of C, consequently avoiding the precipitation of Fe23 (C, B)6, as shown in Figure 6[5].
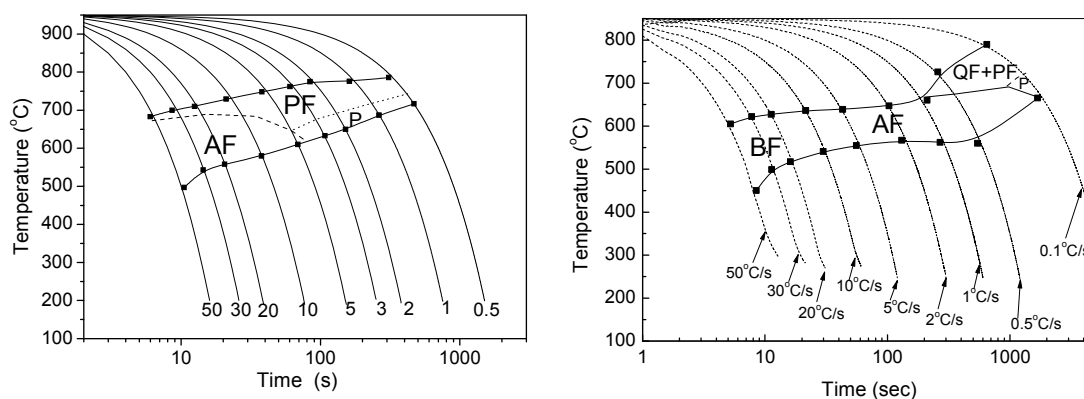
Figure 1 Dynamic CCT curve of test steels[3]:

(a) 0.056Nb steel: 0.04C-0.26Si-1.65Mn-0.056Nb-0.014Ti;

(b) 0.057Nb +0.23 Mo Steel: 0.062C-0.25Si-1.53Mn-0.057Nb-0.23Mo-0.019Ti

Austenitization at 1200 ℃ for 5min, then compressed by 40% at 850 ℃
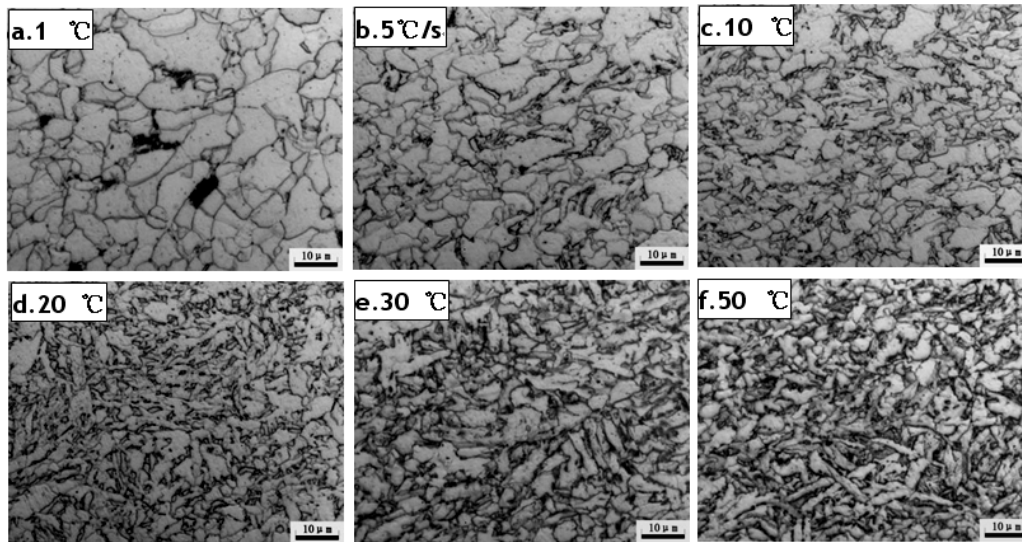
Figure 2 Optical micrographs showing the microstructure obtained under different cooling
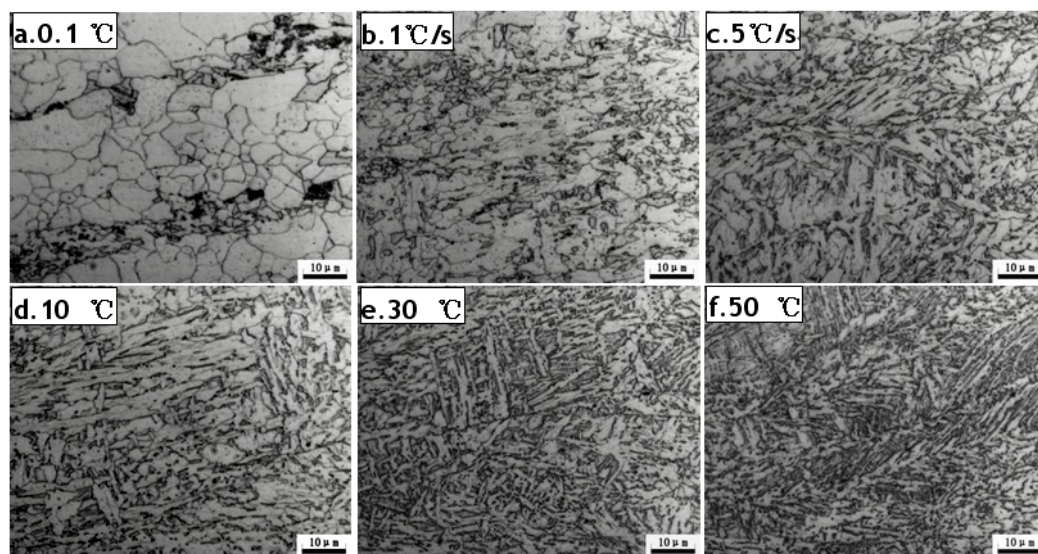
rates in the 0.056Nb steel[3]

Figure 3 Optical micrographs showing the microstructure obtained under different cooling

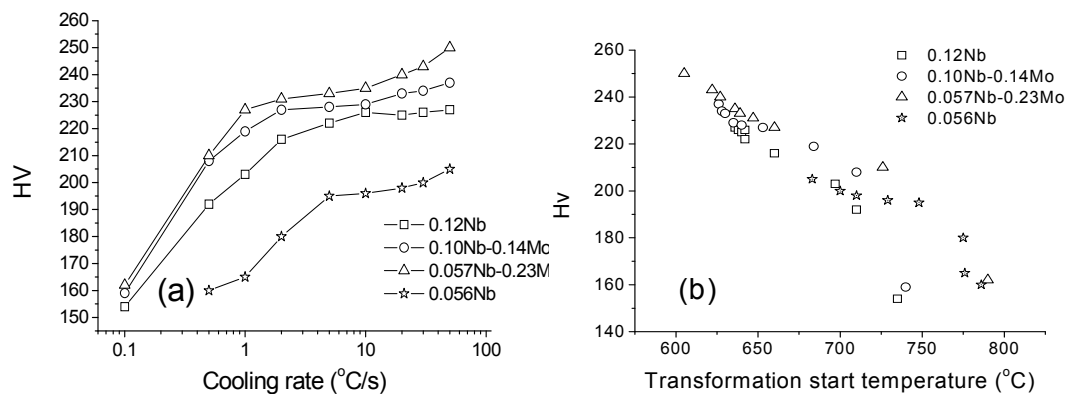rates in the 0.057Nb +0.23 Mo steel[3]

Figure 4 (a) Variations of Vickers hardness (HV) with cooling rate, (b) relationship of HV
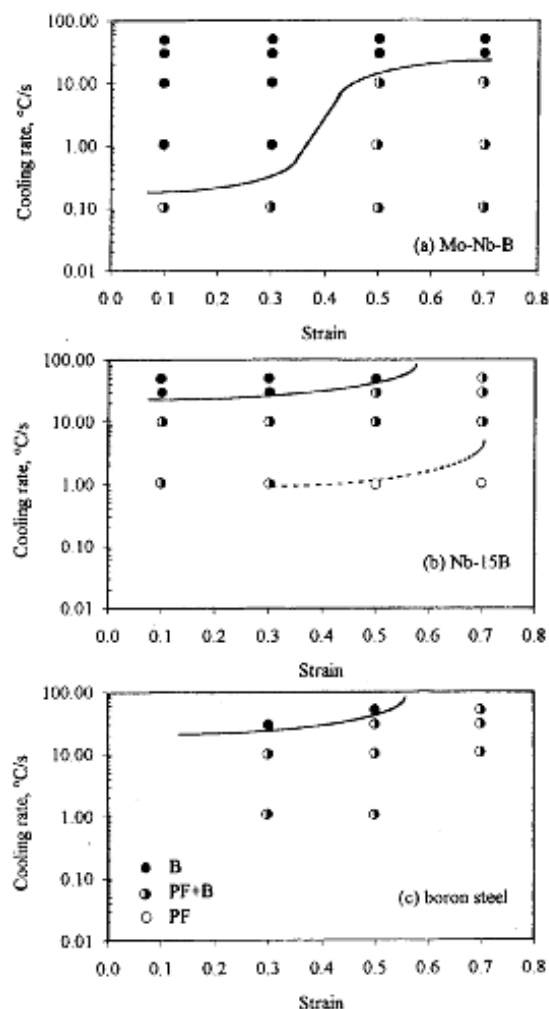
and transformation start temperature[3]

Figure 5 The critical strain and cooling rate to avoid the formation of polygonal ferrite in

different steels: (a) Mo-Nb-B, (b) Nb-15B, (c) a single B[4]

65
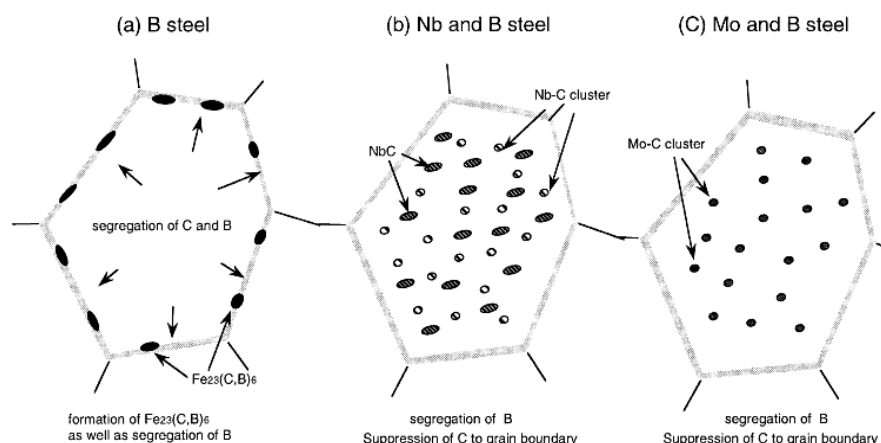
Figure 6 Schematic diagram showing the mechanism to inhibit precipitation of Fe23(C,

B)6 in the case of coupled addition of B and Mo or Nb[5]

3 Influence of Mo addition on the precipitation of microalloying carbonitride and the thermal stability of precipitates

Solid solution and precipitation of microalloying carbonitride are of great importance for adjusting the austenitic state, refining grain and strengthening by precipitates. The precipitation of microalloying carbonitride includes the precipitation from austenite and from ferrite (including interphase precipitate), and the coarsening behaviors during soaking or slow cooling after precipitated. All stages mentioned above will be greatly influenced by the addition of Mo.

3.1 Precipitation from austenite

Mo dissolved in austenite reduces the activity of microalloying and C, N elements, increases their solubility product and decreases the supersaturation of precipitation and the driving force of nucleation, hence delaying the process of precipitation[6]. Figure 7 shows the influence of Mo and V on the PTT (precipitation amount - temperature - time) curves of Nb(C, N) from austenite according to Bacroix et al.'s work[7]. Nb microalloyed steels containing Mo has the most typical features of C-curve and the precipitation reaction was delayed by the addition of Mo.
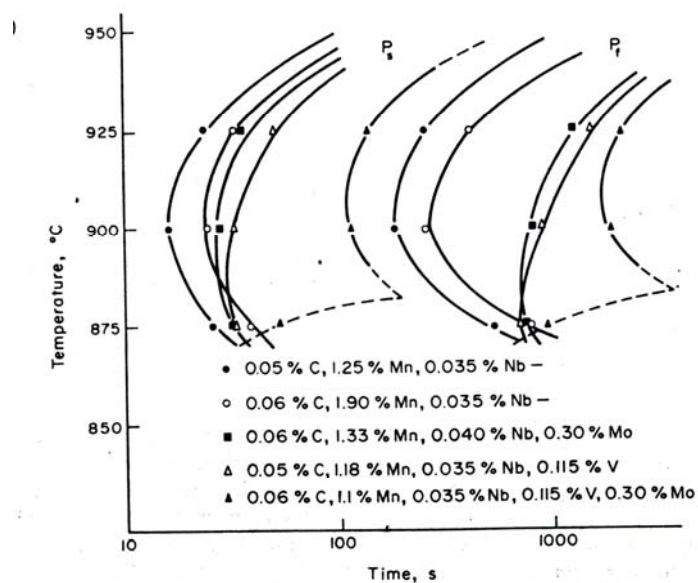
Figure 7 Effect of Mo on PTT diagram of Nb(C,N) precipitation from austenite[7]

Following the calculation method used in the literature[8], the effect of Mo on PTT curve when Nb (C, N) precipitates from austenite was calculated. The calculation results are shown in Figure 8[6]. It is seen that the precipitation start time is almost delayed by one order of magnitude after adding 0.14% Mo. Thus, more microalloying elements are held and precipitates during ferrite transformation. The precipitates in ferrite are small and hold semi-coherent relationship with neighboring ferrite, resulting in greater strengthening effect.
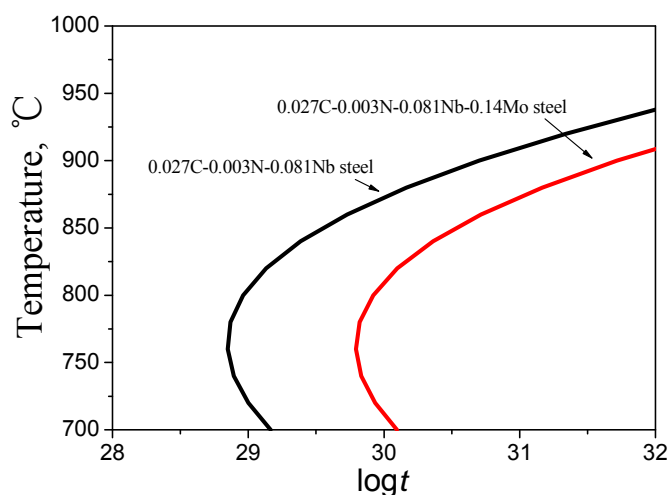
Figure 8 Calculated effects of Mo on Nb (C, N) precipitation PTT curve from austenite[6]

3.2 Precipitation in ferrite

It has been clarified that microalloying elements would not precipitate solely but co-precipitate with Mo in the Mo-added steels, i.e., (M, Mo) (C, N) with a NaCl-type fcc structure[9].

Figure 9 shows the high resolution TEM image and EDS spectra after completion of ferrite transformation in the test steel with 0.027C-0.20Si-1.11Mn-0.081   Nb-0.14Mo-0.003N   (wt%).   The   ferrite transformation was conducted at 750 ℃ for 316 s after austenite deformation. It is seen that the precipitates are very fine with a circular sheet of about 3 nm in diameter. It is thus indicated that they were precipitated from ferrite according to the following feature. When the microalloying elements precipitate from ferrite, Nb(C, N) always holds Baker-Nutting relationship with ferrite. The mismatch between the precipitate and the substrate mismatch varies with direction. In order to the make the total interfacial energy minimum, the shape of precipitate should keep the circular sheet, of which the bottom is parallel to (110)[8]. The spectroscopy analysis confirmed that the precipitates phase contains Mo, illustrating Mo and Nb precipitates together from ferrite.
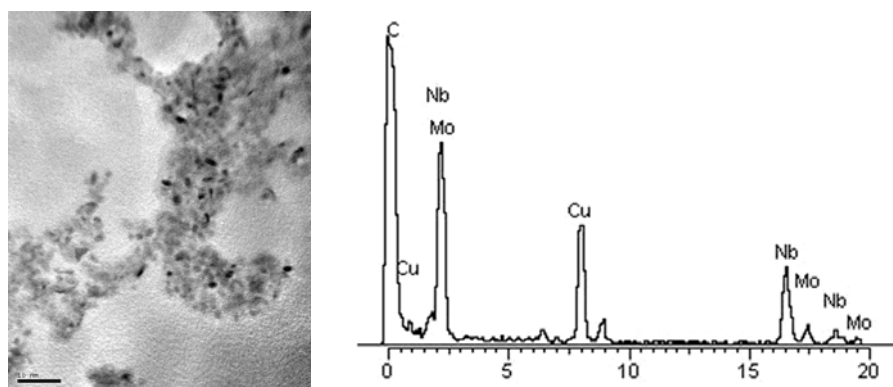

Figure 9 High resolution TEM image and EDS spectra after completion of ferrite

transformation at 750 ℃ for 316 s after austenite deformation in the

0.027C-0.20Si-1.11Mn-0.081 Nb-0.14Mo-0.003N (wt%) steel[6]

In order to predict the chemical formula at different precipitation temperature, it is necessary to build the corresponding thermodynamic model. Microalloying precipitation containing Mo can be assumed to be regular solution consisting of microalloying carbide MC, nitrides MN and substable molybdenum carbide MoC, which have the same crystal structure-NaCl type face-centered cubic. According to the double sublattice model of regular solution, M and Mo occupy a sublattice but C and N occupy the other sublattice. The complex precipitate can be expressed as (M1-x, Mox) (C1-y, Ny), where x and y respectively

denote Mo and N mole fractions in their sub-lattice and $0 \leq x \leq 1$, $0 \leq y \leq 1$. The thermodynamic calculation methods related see the reference[10]. Figure 10 shows the calculation results of test steel above. It is seen that the calculation results agree very well with the spectrum analysis results at different temperatures.
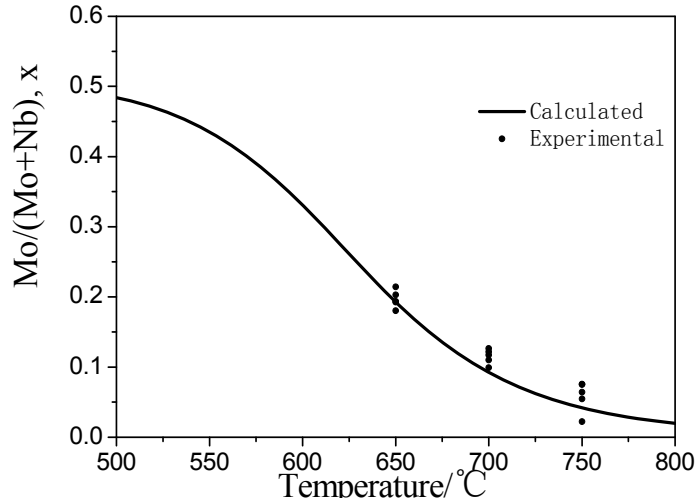

Figure 10 The relationship of Mo site fraction in complex precipitates and precipitation
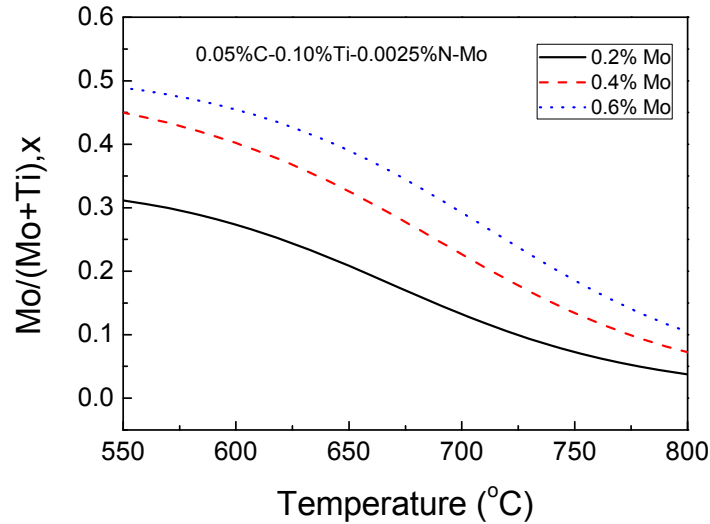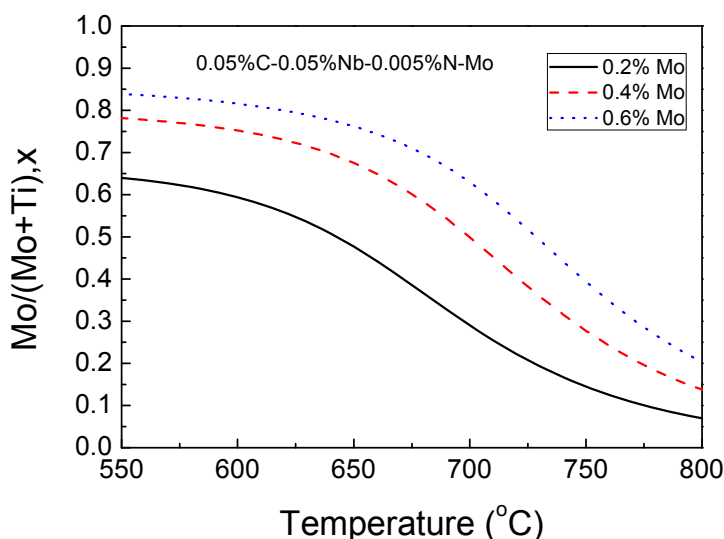
temperature in the test steel[6]

Figure 11 The relationship of Mo site fraction in complex precipitates and precipitation

temperature in the Nb microalloyed steels with different Mo contents

Figure 12 The relationship of Mo site fraction in complex precipitates and precipitation

temperature in the Ti microalloyed steels with different Mo contents

Figure 11 and Figure 12 respectively show the calculation results of Mo site fraction in its sublattice in the Nb and Ti microalloyed steels with different Mo contents. According to those two figures, the site fraction of Mo increases with the increasing of Mo content but with the decreasing of precipitation temperature. More Mo precipitates at the lower temperatures. Such complex precipitation increases the volume fraction of precipitates. On the other hand, the diffusion coefficient of Mo is smaller than the other microalloying elements. Therefore, both the growth of precipitates and coarsening after the completion of precipitation would be inhibited. Consequently, the size of the complex precipitation is small. It is expected that the complex precipitates containing Mo have a greater precipitation hardening effect than the simple microalloying precipitates.

3.3 Thermal stability

The coarsening of Mo-containing precipitates requires the diffusion of both Mo and other microalloying elements from ferrite to ferrite/precipitate interface. Since the diffusion rate of Mo is slower than other microalloying elements, the coarsening rate of precipitates is controlled 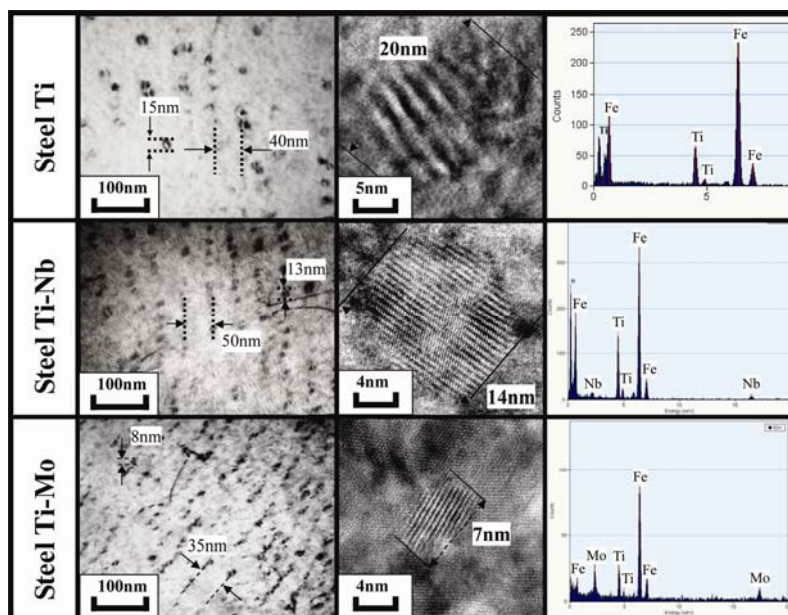by the diffusion of Mo and thus is slow. Fig.13 presents a group of TEM images and EDX data showing the particle morphology and compositions of interface precipitation for single Ti-bearing steel, Ti-Nb-bearing steel and Ti-Mo-bearing steel after isothermal holding at 750℃ for 60min [11]. Fig.14 shows the average particle sizes
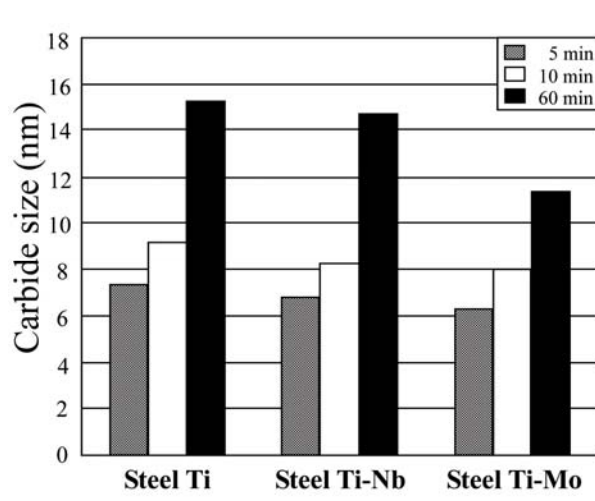
measured for the three steels with different holding times [11]. For the three steels, the contents of Ti, Nb and C are 0.20%, 0.04% and 0.10% respectively. It is clear that the particles containing Mo and Ti are much finer and more thermally stable than those containing Ti and Nb and only containing Ti.

The above mentioned characteristics of Mo-containing steel can weaken the coarsening tendency of precipitate during the coiling process of hot strip production, and can also help to improve the properties at high temperature for some steels (For example fire-resistant steel).

Fig.13 TEM images and EDX data showing the particle morphology and compositions of interface precipitation for single Ti-bearing steel, Ti-Nb-bearing steel and Ti-Mo-bearing steel after isothermal holding at 750℃ for 60min [11]

Fig.14 The average sizes of particles measured for the three steels with different holding times [11]

4 Applications of Mo in low alloy steels

So far, Mo has been widely applied in the productions of high grade pipeline steel, high strength engineering machinery steel and fire-resistant steel. Most of the pipeline steels with grade X70/X80/X100 are alloyed with 0.10-0.30% Mo, especially for the thick plate. The microstructure of pipeline steel is composed of a mixture of acicular ferrite and granular bainite. With the increase in strength grade, the microstructure is refined and the fraction of GB is increased. Combined Mo-B addition is used for X120 steel to further improve the hardenability, and the microstructure obtained consists of lath bainite (or lower bainite). Combined Mo-B addition is also used for non-quench typed engineering machinery steel and the microstructure is composed of granular bainite or lath bainite. All these steels largely make use of the phase transformation strengthening resulted from the enhancement of B on the bainite transformation.

Combined addition of Mo-Nb is usually adopted for the fire-resistant steel, which can improve the high temperature properties of the steel, making use of fine and highly thermal stable particles containing Mo.

In recent years, JFE corporation has developed a kind of automobile hot rolled strip with a combination of high tensile strength, high elongation to failure and high hole-expanding ratio with the typical values of 780Ma, 24% and 120% respectively, which are much superior to conventional high strength steels, as shown in Fig.15 [12]. The combined addition of Ti-Mo was used to obtain a large amount of very fine precipitates in this steel, which enhances the precipitation hardening. On the other hand, the pearlite microstructure, which is harmful to the hole-expanding property, can be eliminated by means of the combination of Ti and Mo with carbon atoms..
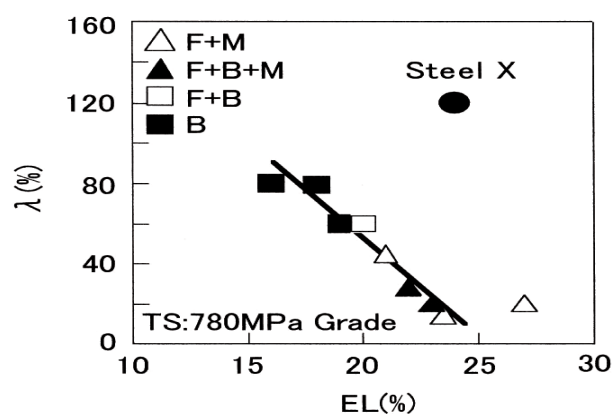

Fig.15 Comparison of hole-expanding ratio and elongation of developed steel with those

of conventional hot-rolled high strength sheet steels [12]

5 Outlook

More recently, there appears a trend in China's steel industry to reduce the addition of expensive elements, such as Mo, by means of low temperature rolling and super-rapid cooling. However, Mo still plays an irreplaceable and unique role in the production of thick plate. Mo can overcome the inhomogeneity of microstructure and properties resulted from the inhomogeneous deformation and cooling to a great extent in thick plate and thus improve the strength and toughness of steel. This is the reason why Mo is still widely applied in the production of high grade thick pipeline steel. In this sense，it is necessary to enhance the research works on physical metallurgy of Mo with emphasis on thick plate steel.

Mo possesses a unique advantage in refining the precipitates size, increasing the precipitation hardening and improving the thermal stability of precipitates, but the research activity and applications with respect to this field are very limited now. It is necessary to profoundly study the role of Mo in the microalloying precipitation, and to broaden its application range.

References

[1] Irvine K J, Pickering F B. J. Iron Steel Inst., 1957, 187:292.

[2] He X L, Shang C J et al. High Performance Low Carbon Bainite Steel- Chemistry, processing, microstructure, property and application. Beijing: Metallurgical Industry Press, 2008.

[3] Yang J H. Investigation on Microstructure Control of Low Carbon High Nb-bearing Steel. Dissertation, University of Science and Technology Beijing, 2009.

[4] Bai D Q, Yue S, Maccagno T M and Jonas J J. ISIJ Int., 1998, 38:371-379.

[5] Hara T, Asahi H, Uemori R and Tamehiro H. ISIJ Int., 2004, 44:1431–1440.

[6] Cao J C. Study on the Precipitation of Carbonitride in Nb-Mo-bearing Steel. Dissertation, Kunming University of Science and Technology, 2006.

[7] Bacroix B，Akben M G，Jonas J J．Thermomechanical Processing of Microalloyed Austenite．Warrendale：A Publication of the Metallurgical Society of AIME，1982：293~316.

[8] Yong Q L. Secondary Phases in Structural Steels. Beijing: Metallurgical Industry Press, 2006.

[9] Miyata K, Omura T, Kushida T, et al．Metallurgical Materials Transactions A，2003，34A：1565~1573.

[10] Luo H，Karjalainen L P，Porter D A，et al．ISIJ International，2002，42（3）：273~282.

[11] Chen C Y. Study on the Precipitation Behavior of Nano-sized Carbide in the Novel HSLA Steel. Dissertation, National Taiwan University, 2007.

[12] Funakawa Y, Shiozaki T, Tomita K et al. ISIJ Int., 2004, 44:1945-1951.

The brief biography of Dr. Xinjun Sun

Dr. Xinjun Sun is a senior engineer in Institute for Structural Materials, Central Iron and Steel Research Institute, and entitled "Taishan Scholar". Dr. Sun has long been involved in fundamental research and technical development in the field of low alloy high strength steels.

Principal effects of Mo in HSLA steels and cross effects with microalloying elements

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Molybdenum is typically alloyed to high strength low alloy (HSLA) steels when mechanical properties of the highest level are demanded. Such steel grades find increasing application in the oil & gas, automotive and construction industry as more performance with less steel is targeted. Most prominently, molybdenum promotes the formation of bainitic or martensitic microstructures depending on the processing conditions. Yet, molybdenum can also precipitate as fine carbides and provide thus secondary precipitation hardening. Besides of its direct metallurgical effects, molybdenum has interesting cross effects and synergies with microalloying elements such as niobium. The combination of these elements can reinforce molybdenum's principal effects on the one hand side but also optimize the effect of the microalloying elements on the other side. The paper will describe such effects and demonstrates how these can be utilized to obtain intriguingly improved properties in HSLA steels.

1. More performance with less steel

Increasing attention is being paid to the economic advantages that high-strength low-alloy steels have to offer. These advantages include lower cost structural components, increased resistance to brittle failure, economies during construction and transportation as a result of lower cost in handling lighter sections, fewer man-hours of welding and lower electrode consumption as a result of lighter sections (Fig. 1). The advantages listed are of primary interest to the transportation and materials handling industry where the ratio of payload to dead weight load is of paramount importance. Fringe benefits resulting from this are greater speeds, less fuel consumption per load and smaller sized propulsion units. In addition to strength properties, structural steel selection is concerned with ease of forming, welding and other fabrication procedures. Service conditions require that the steel exhibits good toughness at the temperature of service, thus the candidate steel should possess adequate impact resistance at the lowest temperatures anticipated in service.

Traditional high strength structural steel is produced based on a carbon-manganese alloy concept having a ferritic-pearlitic microstructure and obtained by either normalizing or thermomechanical rolling. Such steel covers a yield strength range of up to around 460 MPa. To make the desired strength, different strengthening mechanisms are employed (Fig. 2). The base strength originates from the carbon content ranging up to 0.2%. However increasing the carbon content severely deteriorates the steel's toughness. Solid solution strengthening is mainly obtained by manganese and silicon bulk alloying. The most important contribution to increasing the strength is grain refinement and the most effective way to achieve this is by microalloying in combination with thermomechanical rolling. Grain refinement is the only strengthening mechanism that also improves toughness. Niobium is in that respect by far the most effective element followed by titanium. The dispersion of fine precipitates, typically carbides or nitrides of the microalloying elements further increases the strength.
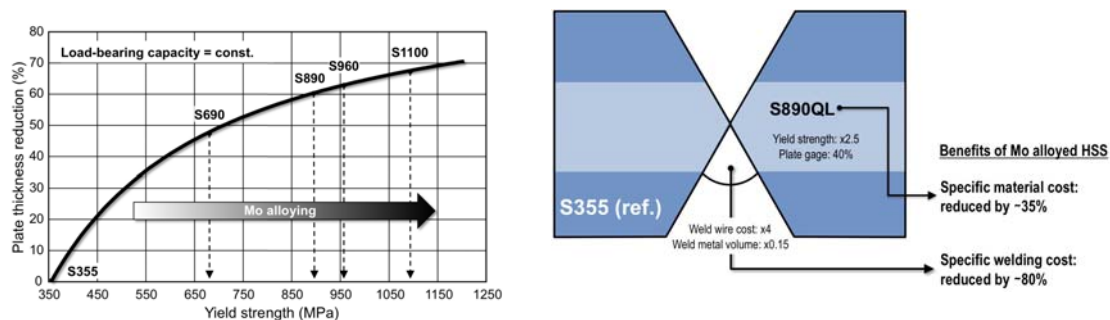

Figure 1: Benefits of using high strength steel with regard to steel consumption and processing efforts.

In modern high strength structural steels with strength levels above 460 MPa, it is necessary to modify the nature of the ferrite matrix and to avoid pearlite formation. One method is to force the austenite-to-ferrite transformation to occur at temperatures below 700°C and thereby increase the dislocation density and refine the subgrain size. The resulting microstructure is bainite or degenerated ferrite. The two alloying elements that prominently assist this transformation strengthening are molybdenum and boron. To a lesser extent chromium and niobium are also effective in that respect. With such alloy concepts a yield strength level of up to around 800 MPa can be achieved.

The highest strength is yet obtained with a martensitic microstructure. This microstructure is the result of quenching form the austenite, which can be done by a separate heat treatment or directly after finish rolling (Fig. 3). In order to

obtain a fully martensitic structure, the cooling speed must be sufficiently high. Alloying of molybdenum and/or boron effectively help to reduce the critical cooling speed for martensite formation. The amount of alloys depends finally on the gage to be produced as well as on the cooling capacity of the production line. The strength of quenched martensite is controlled by the carbon content. With applicable carbon contents in the range of 0.1 to 0.2 %, the tensile strength ranges from 1200 to 1600 MPa. However, the toughness of fully quenched martensite is quite low, so that this type of material is only use for thinner sheet applications for instance in car bodies. For heavier gauged structural applications quenching and tempering is necessary in order to produce steels with minimum yield strength from 690 to 1100 MPa with simultaneous high toughness and good processing behavior. Quenched and tempered steels can be alloyed with chromium, molybdenum, nickel, niobium, boron and vanadium at carbon contents up to 0.2%. During heat treatment this leads to a fine bainitic-martensitic microstructure with optimum strength and toughness properties.
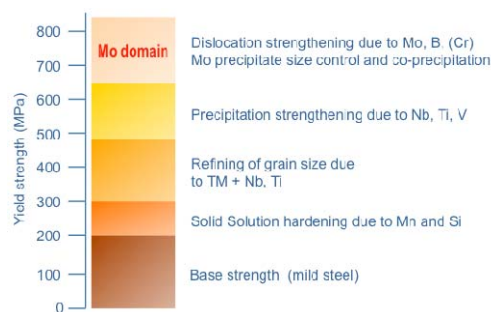

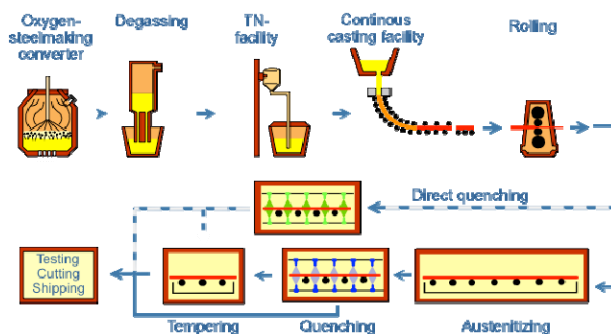
Figure 2: Strengthening effects in HSLA steel.

Figure 3: Processing routes for quenched & tempered steel.

2. Effects of molybdenum during hot rolling
2.1. Recrystallization

Adding molybdenum to (microalloyed) steel has important effects during all stages of the hot rolling process as is schematically shown in Figure 4. Thereby Mo acts directly as a solute atom and indirectly by influencing the behavior of microalloying elements such as Nb, Ti and V.
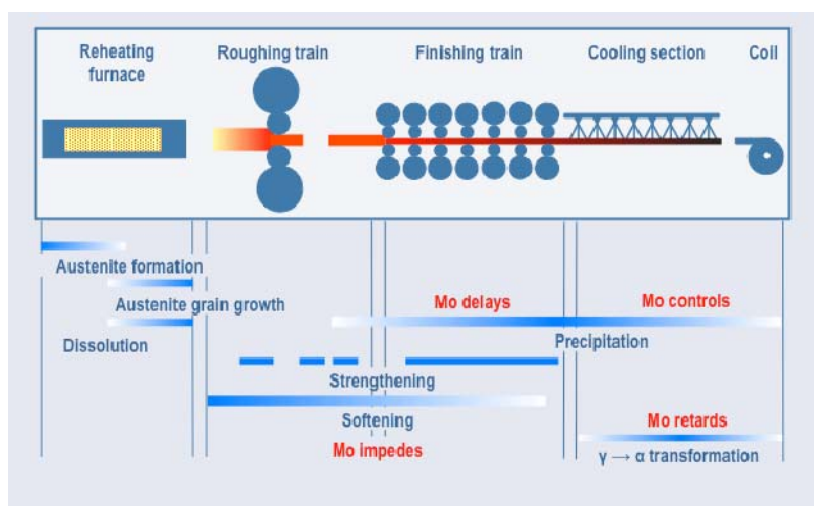
Figure 4: Principal effects of Mo alloying during the hot-rolling stage.

The addition of Nb to low carbon steel significantly retards the rate of static recrystallization (SRX). For instance, by microalloying of 0.04%Nb the time for 95% recrystallization (t95) at 1060°C is around 20 seconds, whereas it takes over 50 seconds to complete the SRX if the Nb content of the steel is increased to 0.095%. Also an increase in the Mo content from 0.1% to 0.6% leads to a significant retardation of the SRX kinetics (Fig. 5). Since it is the aim of roughing rolling to obtain a homogeneous, fully recrystallized austenite microstructure this effect of Nb and Mo has to be taken into account when designing the rolling schedule. Taking the maximum interpass time in the roughing mill being 20 seconds, full recrystallization must occur within that period, i.e., t95 must be less than the interpass time. This demand determines the temperature level of roughing rolling. On the other hand, the slab discharge temperature has to be considered that has typically maximum values of 1150°C and 1250°C or plate mills and strip mills, respectively. Thus the processing window, where fully recrystallizing roughing rolling passes can take place, is 80-180°C for the 0.1%Mo-0.04%Nb alloy, whereas it is reduced to 30-l30°C for the 0.6%Mo-0.04%Nb alloy.
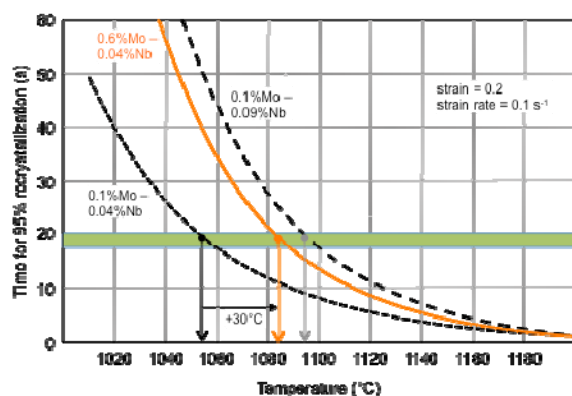
Figure 5: Influence of Mo-Nb alloy combinations on static recrystallization at high temperature.
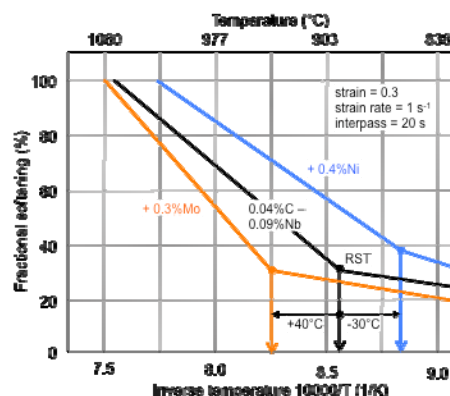

Figure 6: Effects of Mo and Ni addition to a low-C high-Nb base alloy on fractional softening behavior.

From stress-strain curves obtained in multi-pass tests, the interpass fractional softening (FS) was determined following a procedure described by Liu and Akben [1]. From the plot of fractional softening vs. the inverse temperature (Fig. 6) two characteristic temperatures with respect to recrystallization can be derived. The recrystallization limit temperature (RLT) indicating the temperature below which softening is less than 100%, and the recrystallization stop temperature (RST) indicating the temperature below which no softening is observed between deformation passes. Figure 6 shows the behavior for 0.04%C-0.09%Nb steel as a reference having a RST of around 900°C. Adding 0.3% Mo to such a steel has little influence on the RLT but further raises the RST by about 40°C to around 940°C. The influence of Mo can be understood as retarding recrystallization by solute drag. On the contrary adding 0.4% Ni reduces the RLT as well as the RST significantly. Since the recrystallization retarding effect of Nb saturates above 0.06%Nb [2] addition of Mo can effectively help to further raise the RST with respect to non-recrystallizing finish rolling without negative impact on the RLT with respect to recrystallizing roughing rolling.

2.2. Strain induced precipitation

Earlier experients performed by Akben et al. [3] revealed the effect of Mo additions on the dynamic recrystallization (DRX) of microalloyed steels based on hot compression tests. When microalloyed steels are deformed above the solution temperature of their respective carbonitrides, the addition of Mo leads to a distinct retardation in the initiation of dynamic recrystallization. The solute retarding effect of Mo alone is intermediate between that of Nb, which has the greatest and that of V, which has the least effect on an equal atom fraction

basis. The relative influence of these elements in solution is consistent with the relative magnitudes of their atomic size and electronic differences with respect to -iron. When such steels are deformed below the solution temperatures of their respective carbonitrides, in-situ precipitation of small particles results in a further component of retarding recrystallization. In this case the addition of Mo involves two opposing effects. One is an increased retardation of recrystallization due to its effect as a solute. The other is a decrease in the amount of precipitation due to a reduced activity of C and N by Mo. It was observed that the onset of precipitation of Nb in a 0.05%C-0.04%Nb steel takes twice as long once 0.3% Mo is added as shown in Figure 7. It is evident that especially during hot strip rolling with short interpass time a large portion of Nb can be retained in solid solution. Microalloying elements prevailing in solid solution after finish rolling have the capability of reducing the austenite-to-ferrite transformation temperature (Fig. 8). This effect is most pronounced for solute Nb followed by that of solute Ti while solute V has only a weak influence. The effect becomes more significant when accelerated cooling is applied. Such a delay of transformation effectively results in a further grain refinement due to enhanced ferrite nucleation and reduced grain growth.
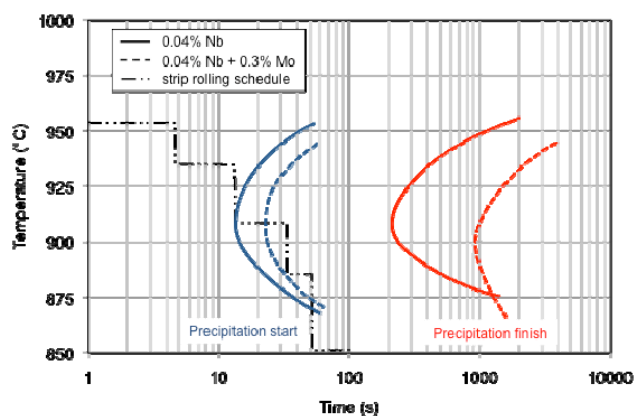

Figure 7: Influence of Mo addition on the dynamic precipitation behavior of Nb (schematic hot strip rolling schedule).
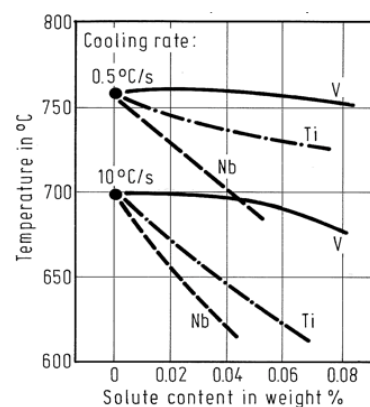
Figure 8: Effect of solute microalloying elements on transformation temperature.

Hara et al. [4] have explained the effect of reduced carbon activity by adding Mo as being a consequence of Mo-C cluster formation. Earlier Tanaka et al. [5] reported already the diffusion of C in austenite to be slowed down by Mo addition. This effect of Mo makes carbon less available for forming carbides with Nb or Ti. In other words, the amount of microalloying atoms being preserved in solid solution during austenitic rolling is increased. Microalloying

elements that are in solid solution after finish rolling have two important effects. They delay the transformation from austenite to ferrite to a lower temperature. This delay increases with the cooling speed (Fig. 8). Secondly, solute microalloying elements have the potential to precipitate during or after the phase transformation to a much finer particle size than that of precipitates formed in austenite. The finer the particle size the higher is the strengthening effect as will be discussed later in detail.

2.3. Hardenability

The molybdenum effect of reducing the carbon activity was also found beneficial with respect to boron-alloyed steels. Boron is a very powerful hardenability element that is added to steel in minute amounts, usually not more than 50 ppm. As such it is used in (ultra-) low carbon bainitic steels as well as in quench-hardening steels. The effectiveness of boron to provide hardenability lies in its segregation to the austenite grain boundary where it obstructs the formation of grain boundary ferrite at transformation temperature. This mechanism is however only possible if B is in solid solution. Since B is a strong nitride former, Ti is usually added at around stoichiometric ratio (Ti = 3.4×wt.%N) to protect B. However, B can still be lost by forming a complex $Fe_{23}(C,B)_6$ precipitate. This happens in the austenite grain boundary particularly when increased amounts of B and C are present due to segregation. Asahi [6] and Hara et al. [4] have identified this phenomenon for steels with ultra-low as well as over-peritectic carbon contents. In both cases the addition of Mo to the alloy improved the effectiveness of B since intragranular Mo-C cluster forming reduces the carbon diffusion into the austenite grain boundary (Fig. 9). Niobium microalloying was found to have a similar effect of avoiding $Fe_{23}(C,B)_6$ precipitation, which however is rather related to NbC precipitation removing solute carbon.
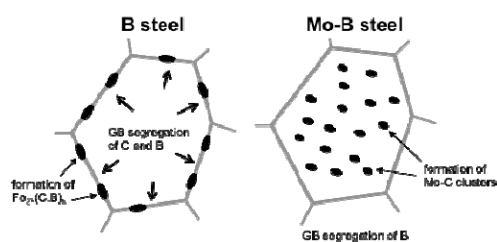

Figure 9: Schematic of boron grain boundary (GB) segregation and precipitation in B and Mo-B steel.
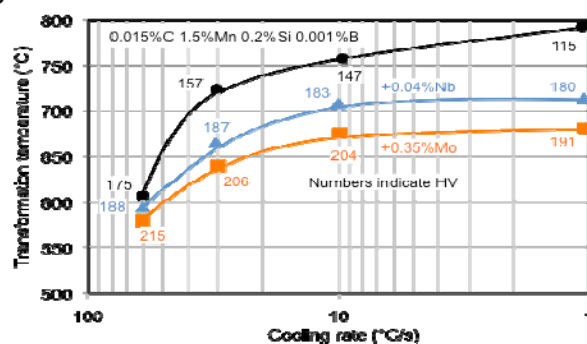

Figure 10: Effect of cooling rate on transformation temperature and hardness in ULCB steel with B, Nb-B and Mo-B alloying.

Besides of rendering a better effectiveness of boron in preventing grain boundary ferrite formation, molybdenum acts as a hardenability element by itself. This Mo effect additionally enhances the B effect as becomes evident from Figure 10 [4]. Compared to the Nb-B steel where only B acts as hardenability agent the Mo-B steel shows lower transformation temperature as well as higher hardness at any cooling rate.

Figure 11 exemplifies the hardenability effect of molybdenum by adding different levels of Mo to a constant low carbon Mn-Cr base alloy [7]. Each alloy was heated to a temperature of 50°C above the Ac3 temperature and held for 10 minutes. Afterwards the alloy was cooled at various rates and the microstructure was evaluated. Adding 0.25% Mo to the base composition significantly delays pearlite formation and lowers the transformation temperature. Simultaneously, the bainite field is largely extended. As such, practically at all technically relevant cooling rates a ferritic-bainitic microstructure is obtained. Increasing the Mo content further to 0.5% leads to a delay of ferrite formation and a complete suppression of pearlite formation. At cooling rates of above 30 K/s a fully bainitic microstructure exists.

More detailed analysis of the bainitic phase revealed that the block size decreases with increasing Mo content whereas the misorientation angle between bainite laths as well as the dislocation density increases. These effects in an increased hardness (strength) of bainite as the Mo content is raised. Increasing the cooling rate at a constant Mo content leads to the same effects. Simplified this means that raising the Mo content in such low carbon steel can substitute for lack of cooling rate. This is relevant to mills equipped with less powerful accelerated cooling devices. On the other hand, Mo helps to achieve bainitic transformation and sufficient strengthening for heavier gauged strip or plate material.
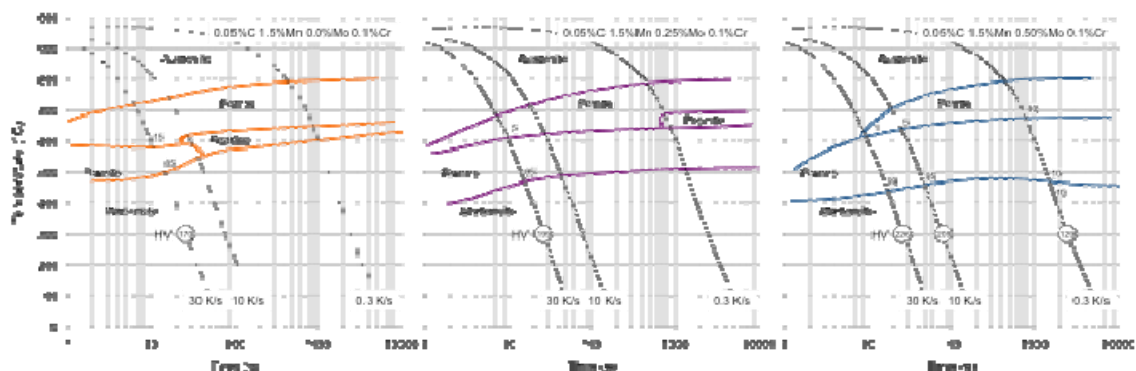

Figure 11: Effect of Mo alloying on the transformation behavior of a low-carbon base alloy (heating to Ac3+50°C – holding for 10 minutes without deformation – cooling at various rates).

Industrial alloys for HSLA steel applications are usually composed of different alloying elements to combine several effects as discussed before. A standard element in such steel is niobium, which in more recent alloy design is added in the order of 0.1%. Combining a low-carbon high-niobium alloy with Mo leads to a synergetic effect on the transformation behavior. For this alloy pearlite formation is suppressed and the onset of ferrite formation is significantly delayed (Fig. 12a). The critical cooling rate to obtain full bainite formation in the 0.04%C-1.4%Mn-0.1%Nb-0.3%Mo alloy is around 10 K/s. Modifying this alloying concept by increasing carbon and manganese levels, reducing the molybdenum content and adding chrome results in a further improved hardenability (Fig. 12b). The critical cooling rate for full bainite transformation in this alloy variant is in the order of only 4 K/s.

In yet another alloy variant molybdenum was substituted by a combination of nickel and copper. Although this alloy also results in fully bainitic microstructure at cooling rates of above 4 K/s, several differences in the transformation behavior can be observed (Fig. 12c). The start temperature of bainite transformation is increased by around 50°C. At slower cooling rate (1 K/s) such as occurring by air-cooling, no bainite is formed anymore but a small fraction of pearlite appears, which is detrimental to toughness. At high cooling rates (95 K/s), as they can occur after welding, martensite formation is possible.

These three examples particularly underline the effect of molybdenum in promoting bainite and avoiding pearlite formation, respectively. With regard to mechanical properties, all three alloys reach a strength level of 650 MPa tensile and 550 MPa yield under suitable rolling conditions and fully bainitic microstructure.
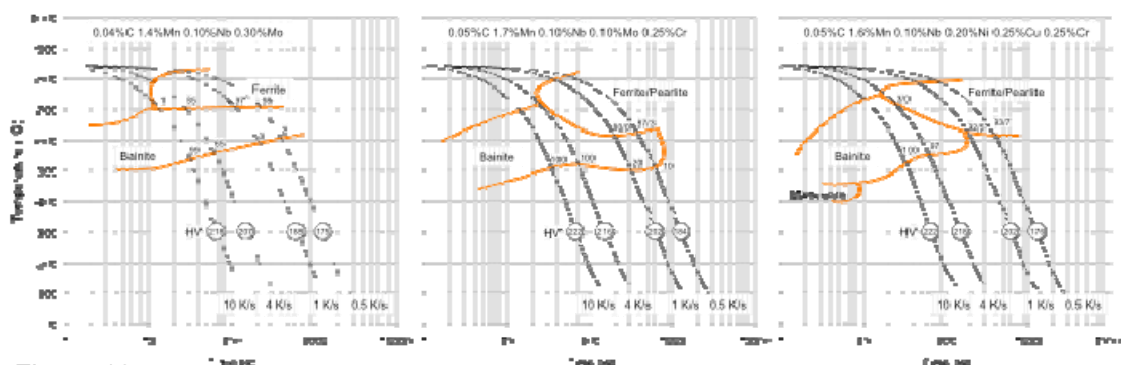

Figure 12:

Transformation behavior of various low-carbon alloys of similar Pcm and strength level (holding at 1200°C for 10 minutes – deformation   = 0.6 at 1050°C – deformation   = 0.6 at 850°C – cooling at various rates).

For continuously cooled molybdenum-boron steels, the main effect of bulk alloying elements such as manganese or chrome is to lower the temperature at which the transformation to bainite begins. In carbon-manganese steels, the addition of molybdenum in combination with solute titanium or niobium reduces the critical cooling rate for producing bainite, i.e., suppresses transformation to polygonal ferrite.

2.4. Interphase precipitation

Any microalloying element being in solid solution after finish rolling has the potential of precipitating during or after the austenite-to-ferrite transformation. During austenite decomposition so-called interphase precipitation occurs by a mechanism of periodical particle nucleation at the moving austenite/ferrite interface during transformation [8]. The austenite side of the movin phase boundary enriches with carbon and microalloying elements due to their lower solubility in ferrite. At certain intervals supersaturation leads to precipitation manifesting itself by row arrangement of precipitates (Fig. 13). Since the entire process is diffusion controlled, interphase precipitation is most effective at a comparably slow cooling rate. Increasing the alloy content progressively lowers the temperature of transformation at a given cooling rate, reducing the diffusivity of the solute elements, which finally becomes insufficient for interphase precipitation. Hence, interphase precipitation is mostly feasible for ferritic microstructures, unless the bainite start temperature is pushed upwards by suitable alloy design. From a practical point of view, one would cool down the material after finish rolling to a temperature that is providing efficient precipitation and hold the material isothermally until the phase transformation is completed. This temperature should not be too high since particle ageing (Ostwald ripening) leads to coarsening and a corresponding loss of particle strengthening effect. Most suitable for precipitation hardening is the temperature range between 630 and 650°C.

For particular applications it is not favorable to have pearlite phase in the final microstructure. Therefore it is important to delay the pearlite formation to times longer than the isothermal holding period. Molybdenum alloying is efficient in achieving this delay as discussed above. Furthermore, in practice coiling in a hot strip mill naturally provides isothermal holding since the cooling rate in the coil is slow (around 30°C/h). In fact the coil is still at high temperature after precipitation is complete and this promotes particle coarsening by Ostwald ripening. In this respect molybdenum is found to inhibit

particle coarsening by segregating to the particle matrix interface and blocking the diffusion of carbide forming elements between particle and matrix. This mechanism results in a much-reduced loss of particle strengthening even for extended isothermal holding at 650°C (Fig. 14) [9]. In reality, the temperature continuously drops by natural coil cooling. At temperatures below 550°C diffusion is so limited that particle coarsening does not take place effectively. This situation would be reached in the example of Figure 14 after around 12,000 seconds. The molybdenum alloyed steel shows after that time almost no loss in hardness (strength). In absence of molybdenum, particle coarsening of TiC would lead to a hardness drop of approximately 30 HV (corresponding to 100 MPa strength).
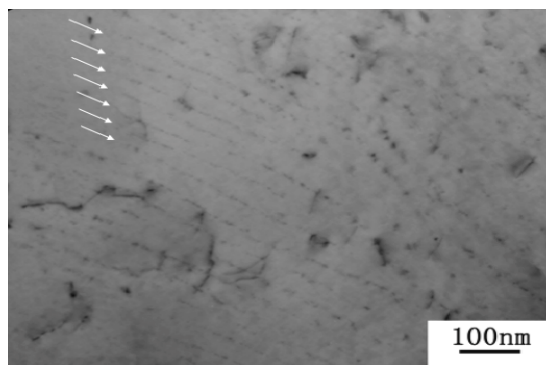

Figure 13: Example of row-like precipitate arrangement (arrows) in a 0.05%C Mo-Nb-Ti steel coiled at 630°C.
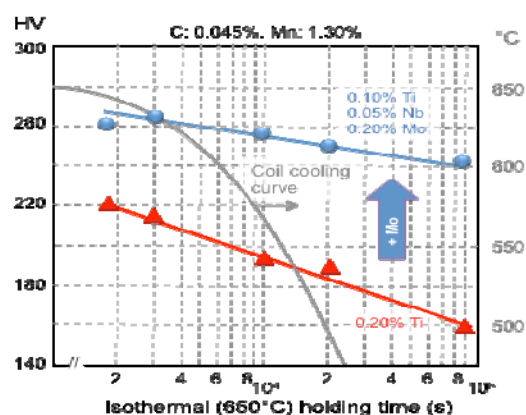

Figure 14: Influence of isothermal holding at 650°C on precipitation hardening (typical coil cooling curve is indicated).

If the coiling temperature is set below the range allowing efficient interphase precipitation and / or rapid cooling is applied, microalloying elements will remain in solution and can only precipitate during a secondary heat treatment.

Figure 15 summarizes the strengthening effects by transformation and / or precipitation hardening for the Mo-Nb and Mo-V alloy system respectively [10]. The precipitation strengthening, having a maximum in the range of 630 to 650°C, adds to the strengthening effect in the matrix. The latter one increases with decreasing coiling temperature. For the Mo-Nb system this strength increase continues below 600°C whereas it levels of at that temperature for the Mo-V system. This is because the synergetic effect of Mo and Nb effectively promote the forming of a bainitic microstructure providing transformation hardening. It appears that the gain in transformation hardening nearly equals the loss of precipitation hardening at lower coiling temperature. Hence the total

strength being the sum of the two strengthening components remains nearly constant. This constitutes a considerable advantage as in a hot strip mill one can encounter considerable drifts of the actual coiling temperature along the strip. In the Mo-V system such a temperature drift would necessarily reflect in substantial scattering of the final yield strength.
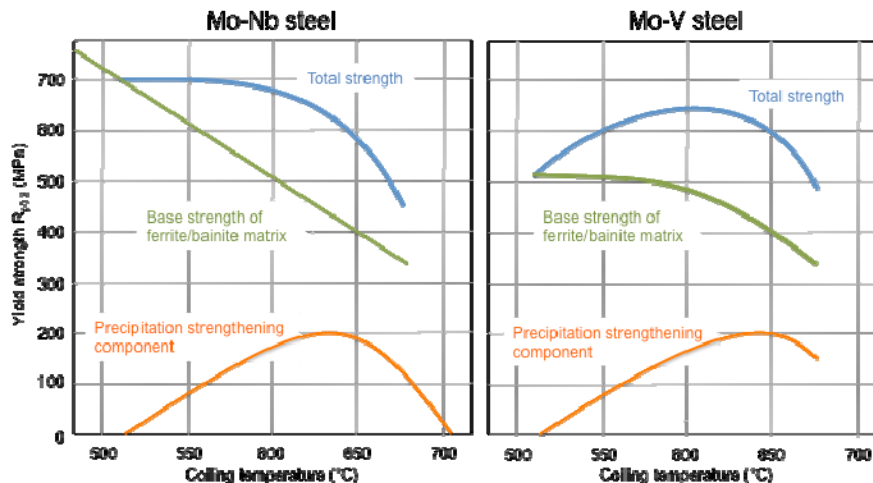

Figure 15: Effect of coiling temperature on yield strength in low-carbon Mo-Nb and Mo-V steel.

3. Effects of molybdenum in advanced processing concepts
3.1. Direct quenching of plate

When producing steels of the highest strength level quenching & tempering is the traditional treatment. The rolled material after down cooling from the rolling heat is re-austenitized and then quenched (Fig. 3). This results in a very strong but often brittle material. Subsequent tempering provides a much better toughness and ductility on the expense of strength. Molybdenum effectively enhances the so-called tempering resistance, which counteracts the loss of strength as described by Krauss [11].

In more recent processing concepts, the rolled material is fast cooled immediately after finish rolling. Depending on the cooling severity and the cooling stop temperature, the following cooling variants can be distinguished for plate mills [12]:

●ACC (Accelerated cooling) results in cooling with ideal cooling rate, i.e. difference of cooling rate between surface and center is kept low.

●HACC (Heavy ACC) is a special variant of the classical ACC but with lower final cooling temperature and somewhat higher cooling rate.

●DQ (Direct Quenching) with fastest possible cooling of the surface, similar to conventional quenching. The center of the plate is also cooled to below the martensite-start temperature by means of continuation of cooling.

●DQST (DQ + Self Tempering) means that the center heat still present is exploited after an extremely short cooling time and self-tempering is achieved. Compared to the traditional Q&T procedure, DQ or DQST has the decisive difference that the steel only goes once through the ˜ phase transformation (instead of 3 times in Q&T). That means the microstructure of the finish-rolled austenite has an influence on the properties of the quenched material, as it will not be normalized. The microstructure before direct quenching depends on the hot-rolling schedule. If the finishing temperature is above the recrystallizing stop temperature (HR = hot rolling), the austenite shape will be equiaxed and relatively coarse. On the contrary, if finish rolling is done below the recrystallization stop temperature (CR = controlled rolling), the austenite grain is elongated in the rolling direction and flattened in the normal direction.

Applying either of the rolling schedules to a 0.15%C-Mn-B steel without and with 0.25% Mo leads to the following results [13]:

●Strength and toughness are better for the HR/DQ than for the CR/DQ route in the Mo-free steel. The strength of the CR/DQ material is particularly low since ferrite has formed along the boundaries of the former austenite grains.

●The strength of the Mo-added material is nearly equal for the HR/DQ and CR/DQ material and in both cases significantly better than for the Mo-free steel.

●When comparing the toughness of HR/DQ treated steels, the Mo-free material performs better.

●The toughness of the Mo-added steel considerably improves when applying the CR/DQ route.

These differences can be explained by the cross effects between Mo and B as indicated before in Figure 9. In the Mo-free steel part of the boron precipitates as $Fe_{23}(C,B)_6$ and is not available for hardenability. In absence of free B at the austenite grain boundary, ferrite nucleation is facilitated particularly when the finish rolling temperature is coming close to the Ac3 temperature. Based on experiments by Asahi [6] with 0.15%-Mn-B steels the critical cooling rate to obtain 90% of the full martensite hardness is thus higher in Mo-free steel especially when the B-content is below 20 ppm (Fig. 16).
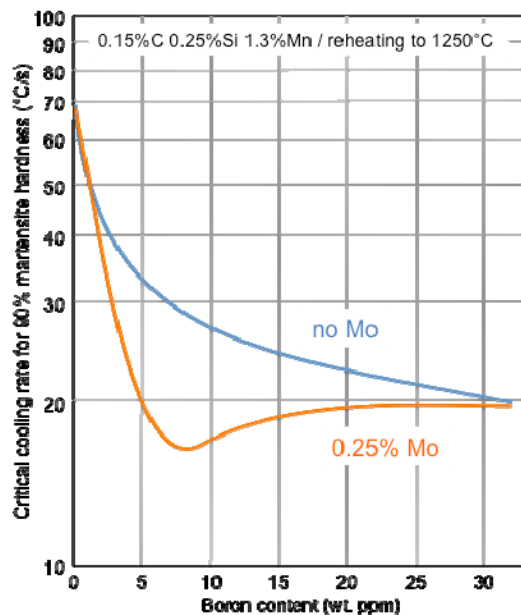
Figure 16: Influence of Mo on the effectiveness of B alloying with regard to the critical cooling rate to obtain 90% martensite hardness.
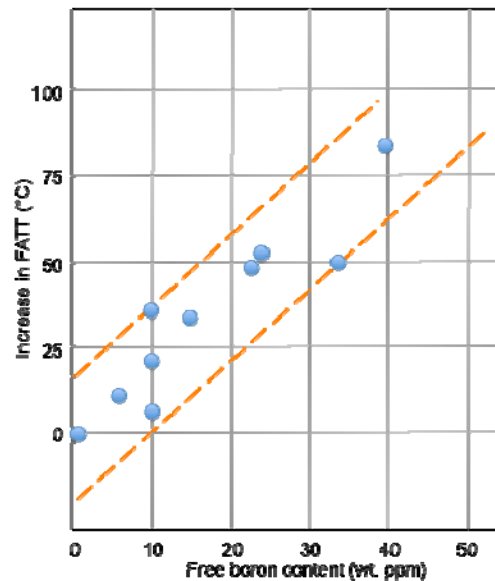
Figure 17: Influence of the free B content (not fixed as BN) on the fracture appearance transition temperature (FATT) in 0.10-0.12%C steels.

On the other hand, solute boron at grain boundaries, reduces the cohesive forces that hold neighboring grains together, and thereby reduces impact toughness through grain boundary decohesion. This is seen as an increase in the fracture appearance transition temperature (FATT) with increasing free boron content in the steel (Fig. 17) [10]. Consequently, grain boundary precipitation of borocarbide and boride particles improves toughness by essentially removing boron from (segregated) solid solution in the vicinity of the grain boundary, which explains the better HR/DQ toughness of the Mo-free steel. The toughness improvement in the Mo-added CR/DQ steel is related to obstructing crack propagation by the elongated austenite grain structure.

An alternative alloy design for good quench hardenabilty is Mo-Ni steel. When subjecting such an alloy concept to HACC or DQ cooling the obtained base microstructure is granular bainite being a mixture of irregular ferrite with second phases (MA, bainite, or pearlite) distributed between the irregular ferrite grains [14]. Due to molybdenum's effect of retarding pearlite formation, actually only martensite-austenite (MA) or bainite are expected to appear as second phase. Figure 18 shows the yield-tensile behaviour for the two cooling concepts. It is obvious that the DQ route leads to the highest tensile strength, yet the yield strength is lower than in the HACC route. Considering the yield ratio the DQ route results in a particularly low value, as it is typical for

ferritic-martensitic dual phase steel. Therefore it is reasonable to assume that the second phase is MA in the DQ route. In the HACC route the yield ratio is much higher indicating that bainite is the second phase. Adding Nb at different levels to this Mo-Ni alloy the strength significantly increases for both routes. In the HACC route the yield ratio stays nearly constant whereas in the DQ route it increases. This indicates that by adding Nb the microstructure of the second phase is changing towards bainite. Toughness is lowest for the Mo-Ni steel without Nb produced via the DQ route and significantly increases with the addition of Nb. In the HACC route toughness is on a high level for all alloys.
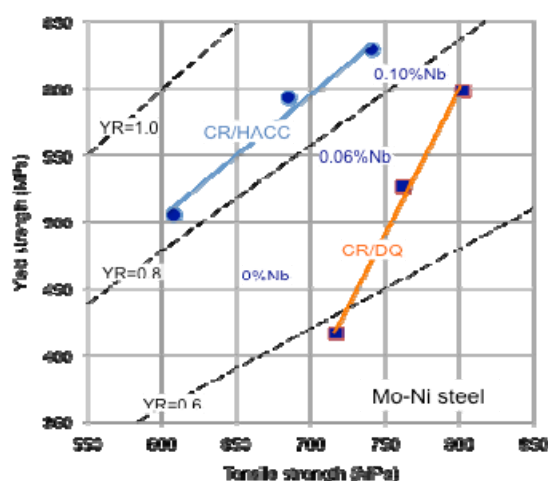
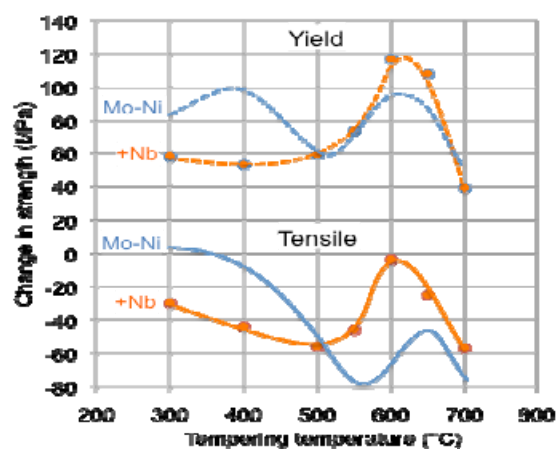| Figure 18: Influence of the cooling route on the yield-tensile strength of 0.07%C-0.2%Mo-0.3%Ni steel and cross effects of Nb alloying. | Figure 19: Influence of tempering temperature (30 minutes) on the yield-tensile strength of 0.07%C-0.2%Mo-0.3%Ni steel and cross effects of Nb alloying. |

When applying a tempering treatment to the DQ route produced material, competing mechanisms such as the Cottrell effect, recovery and secondary precipitation are leading to a modified strength as shown in Figure 19. The tensile strength is decreasing for tempering temperatures up to around 550°C, which is mainly due to a reduction of strength of the second phase. The regain of strength in the tempering range of 550 to 650°C is due to secondary precipitation, which is more pronounced in a Mo-Ni+Nb steel. The yield strength however shows a significant increase at low tempering temperature due to pinning of mobile dislocations by carbon diffusion (Cottrell effect). This effect is most pronounced in the low yield ratio (Mo-Ni) steel. Secondary precipitation hardening is stronger in the Nb-added steel, indicating that a substantial amount of Nb is in solid solution. It is widely known that solute Mo and Nb have effects of retarding the climb motion and recovery of dislocations

as well as grain boundary migration. In low-carbon HSLA steel these solute elements retard dislocation recovery at temperatures of up to 550°C [15]. This can explain the moderate loss of strength of the Nb-added steel when tempering in the range of 400-500°C. The retention of dislocation networks has also a beneficial effect secondary precipitation since such defects act as a nucleation site during tempering [16].

3.2. Dual phase hot rolled strip

Compared to a multi-purpose cooling device in a plate mill the cooling profile in a strip mill is much less flexible. The limits are set by the exit speed of the strip at the finishing stand, the length of the run-out table, the configuration of the cooling headers as well as the coiling temperature. Therefore, it becomes necessary to modify the CCT diagram in an appropriate manner by alloying to obtain a particular microstructural mix. To produce a dual phase (F-M) steel the challenge is to avoid any bainite or pearlite formation and to have the right share of ferrite in the microstructure (typically 75-85%). The remainder must be pure martensite. Two principal cooling strategies can be practiced depending on the capabilities on the run-out table (Fig. 20). Single-step cooling aims for a coiling temperature between 600 and 500°C. It is here important not cooling too sharp in order to avoid bainite formation. On the other hand, cooling too slowly may result in pearlite formation. In two-step cooling fast cooling to a temperature of around 700°C is applied right after finish rolling. Then cooling is interrupted and a phase of quasi-isothermal holding allows sufficient ferrite formation. Finally the second cooling step aims for a coiling temperature of around 200°C. It is apparent from Figure 20 that increasing the time gap between the initial bainite-martensite phase field and the pearlite phase field enhances the processing window regardless of the cooling strategy. Yet, the two-step cooling process is the preferable strategy. Molybdenum alloying can most efficiently open the gap between the phase fields [17]. Figure 21 indicates the effect of Mo on the relevant times of ferrite start, pearlite start and 75% ferrite formation. It is clear that for the given base alloy the addition of only 0.1% Mo sufficiently delays the pearlite start to beyond 75% ferrite formation. Thus Mo addition increases the window of allowable cooling rates very significantly. The small delay in ferrite start by Mo can be counteracted by more severe austenite pancaking, for instance by a small amount of adding Nb to the alloy.
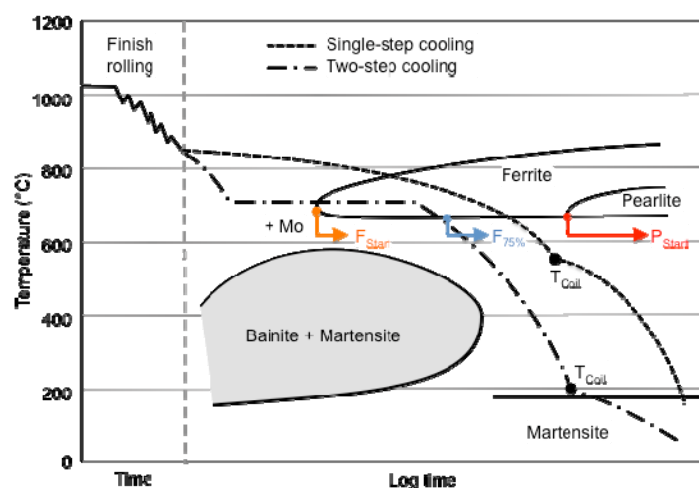
Figure 20: Cooling strategies for producing dual phase steel out of the rolling heat and schematical influence of Mo in modifying the CCT diagram.
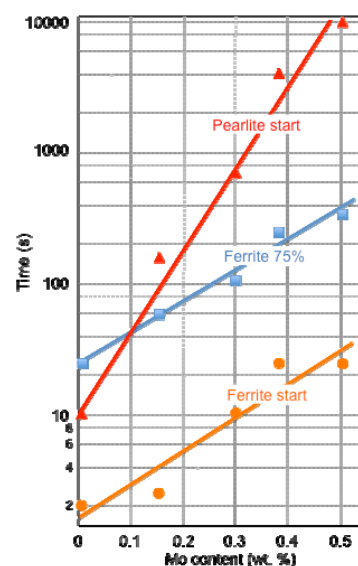
Figure 21: Effect of Mo on the phase formation times in a 0.05%C-1.2%Si-0.9%Mn-0.5%Cr alloy.

3.3. Cold rolled multiphase steels

High strength - cold formable automotive steels often rely on achieving a combination of relatively low yield strength and high tensile strength. This behavior typically requires a multiphase microstructure consisting of soft ferrite and hard martensite (DP steel) or optionally containing additional phases such as bainite and retained austenite (TRIP steel). Therefore the hot rolled strip is adjusted to a ferritic pearlitic microstructure that is easy to cold roll. The cold rolled strip is the subjected to an intercritical annealing cycle according to Figure 22, be it in a continuous annealing line (CAL) or a hot-dip galvanizing line (CGL). During the intercritical annealing phase a determined amount of austenite is adjusted, while the remaining ferrite is recrystallized and the pearlite is being dissolved. During a slow cooling phase to the so-called quenching temperature new ferrite is formed and the amount of intercritical austenite is correspondingly decreased but further enriched with carbon.

In the DP production route the carbon-enriched austenite is then rapidly cooled below martensite start temperature without formig any other phases. Obviously, for the DP steel route it is important to apply a high cooling rate to avoid bainite formation. This becomes particularly relevant for low-carbon DP alloys, which are preferred by carmakers due to the better weldability. Figure 23 indicates the critical cooling rate for 0.05%C-Mn steel [18]. Increasing the Mn content indeed reduces the critical cooling rate. However, a too high Mn

content can cause significant centerline segregation, which is detrimental to some forming properties. Therefore it is common to add other hardenability elements such as Cr or Mo or a combination of both. Molybdenum is approximately 3 times more effective than Cr in reducing the critical cooling rate at a constant Mn level of 1.2%. It allows producing DP steel even on older galvanizing lines that are not particularly equipped with high power cooling devices. Furthermore, a small addition of Mo tremendously widens the process window making the process more robust against line speed and cooling rate variations.
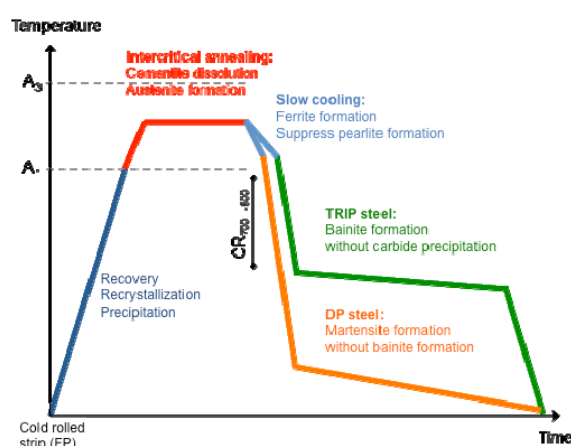
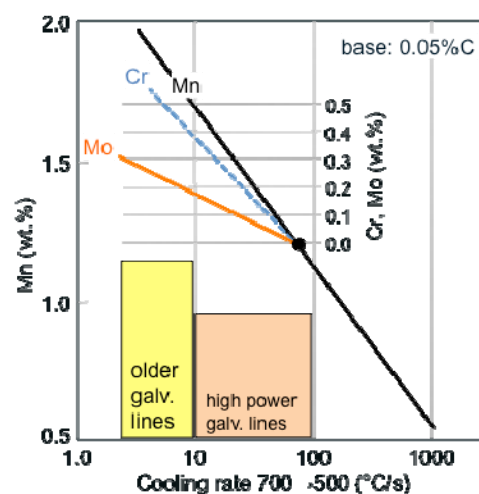Figure 22: Principal intercirtical annealing cycles for DP and TRIP steel processing.

Figure 23: Influence of Mn, Mo and Cr on the critical cooling rate of a low-carbon DP590 steel grade.

Another trend in automotive steel production is to further increase the tensile strength of low-carbon DP steel from the mainstream level of 590 MPa towards 980 MPa. This can only be achieved by increasing the martensite share in the microstructure and requires thus a higher intercritical annealing temperature to produce the correspondingly increased amount of austenite precursor phase. However, the average carbon content in the autenite will be reduced and the tendency of forming bainite on the expense of martensite is enhanced. Figure 24 demonstrates the capabilities of different alloying concepts in that respect. The base alloy added with Cr is capable of achieving a strength level of around 650 MPa only. Adding Nb in a small amount lifts the strength level to around 780 MPa, yet over a narrow range of intercritical annealing temperatures. The combined addition of Mo and Nb provides a strength level of around 900 MPa over a much wider range of intercritical annealing temperatures. Several

synergetic effects, amongst them grain refinement and delayed bainite formation contribute to this improvement [19].

In TRIP steel processing rapid cooling to a temperature of around 500°C is followed by isothermal holding allowing bainite formation (Fig. 22). During bainite formation the remaining austenite further enriches with carbon content so that it can finally exist as metastable austenite at room temperature. Thereby it is important not losing carbon by cementite precipitation. If the baintic holding time is too short the material tends to show mechanical characteristics resembling rather those of DP steel. A long bainitic holding time bears the risk of pearlite formation. Aluminum as a standard alloying element in TRIP steel suitable for galvanizing lines has the effect of delaying pearlite formation. Yet, at somewhat increased holding temperature as is necessary when producing galvannealed coatings the amount of retained austenite drops drastically for a mere Al-based alloying concept (Fig. 25) [20]. On the contrary, the Al-Mo-Nb concept demonstrates a much higher amount of retained austenite after annealing at increased holding temperature. Thereby, Mo further delays pearlite formation and Nb prevents carbide precipitation in the bainite phase [21]. The interaction Mo with carbon at the ~. interface affects the activity of carbon at the interface making the bainite transformation extremely sluggish.
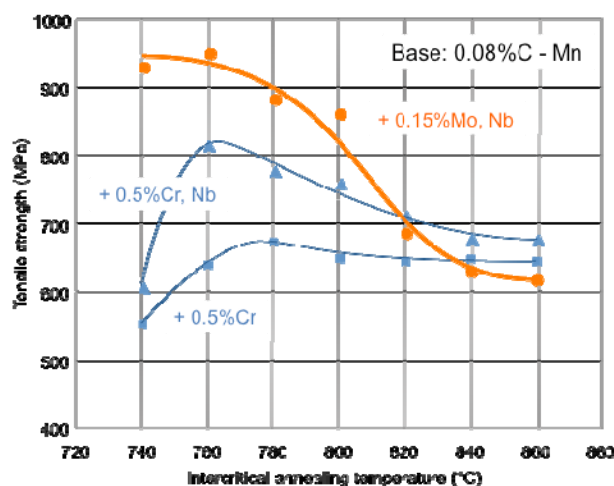

Figure 24: Influence of intercritical annealing temperature on the tensile strength of DP steel for Cr, Nb and Mo alloying.
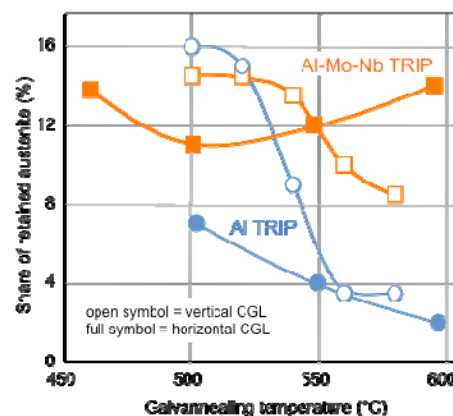
Figure 25: Influence of galvannealing (bainitic holding) temperature on the amount of retained austenite in TRIP steel for Al and Al-Mo-Nb alloys.

In a vertical CGL the highest amount of retained austenite is obtained. In addition the carbon content in retained austenite is at its highest level here. This is caused by the longer bainitic holding time compared to a horizontal

CGL. In a horizontal CGL this alloying concept offers the possibility of producing strong TRIP-aided DP steels. With increasing intercritical annealing temperature the work-hardening characteristic is shifted from RA to DP behavior, noticed by the reduction of the yield strength ratio. Raising the intercritical annealing temperatures leads to higher amount of austenite, which, on the other hand, is less carbon-enriched and consequently the amount of retained austenite at room temperature is lowered.

According to the above statements about the influence of Mo on the bainite transformation, TRIP aided DP steel in the tensile strength level 900 MPa can be reached. Reducing the holding time in the bainitic region, typical for horizontal CGL leads to a DP 1000, caused by a higher amount of martensite. With 10.5 % retained austenite good forming behaviour can be expected. In a vertical CGL a TRIP 800 is obtained with this alloying concept. With a modified CAL cycle using an increased bainitic holding temperature a TRIP steel of the same tensile strength class can be produced. The characteristic tensile curves of these variants are shown in Figure 26 [22].

It can be concluded that Mo additions can be used in order to achieve higher amounts of martensite and less retained austenite after processing. Hence the tensile strength level can be increased remarkably without deteriorating weldability in terms of carbon equivalent too much. Nb has been proven to stabilise retained austenite. Furthermore the grain refining effect of Nb precipitates is known to facilitate higher strength levels.
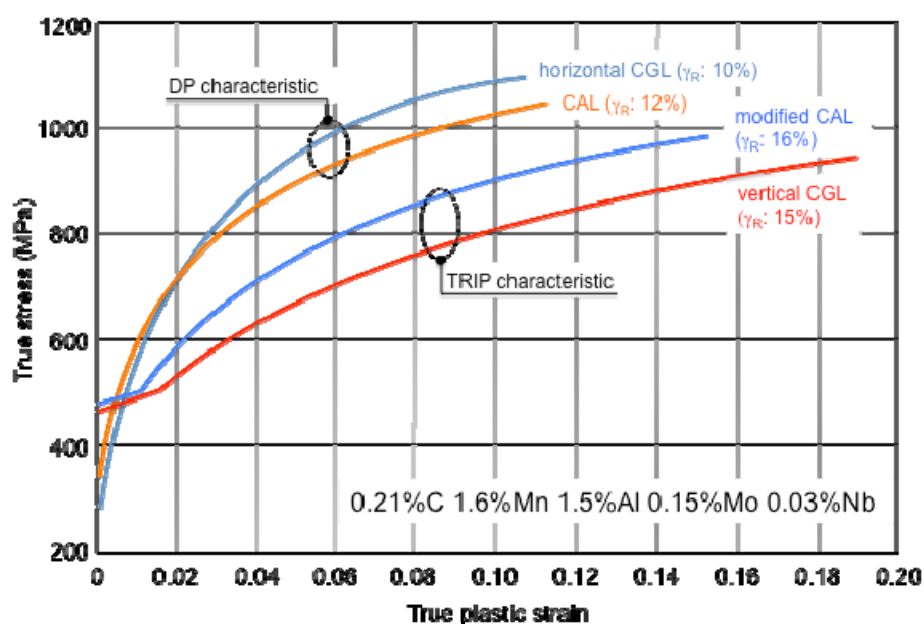

Figure 26: Tensile characteristics of a C-Mn-Al-Mo-Nb alloy processed by various intercritical annealing cycles (amount of retained austenite is indicated in parentheses).

4. Conclusions

Molybdenum as an alloying element in low-carbon steels has powerful effects with regard to the recrystallization behavior and hardenability. Its full potential, however, is developed when molybdenum interacts with other alloying elements leading to synergetic effects. In combination with Cr, Ni or B the hardenability is much increased. Interaction with the microalloying elements results in clearly improved precipitation strengthening. Particularly in combination with Nb, molybdenum shows a very interesting potential in producing some of the highest strength steels for structural, pipe and also automotive applications. A pre-requisite of utilizing these advantages is the design of suitable processing route, which necessitate a thorough understanding of molybdenum's metallurgical effects.

References

1. W. J. Liu and M. G. Akben, Can Metall. Q., 26 (1987), p. 145.
2. L. J. Cuddy, "The Effect of Microalloy Concentration on the Recrystallization of Austenite During Hot Deformation," Thermomechanical Processing of Microalloyed Austenite, Warrendale, PA: TMS-AIME (1984), p. 129.
3. M.G. Akben, B. Bacroix and J. Jonas, Acta Met., 29 (1981), p. 111.
4. T. Hara, H. Asahi, R. Uemori and H. Tamehiro, ISIJ International, Vol. 44 (2004), No. 8, p. 1431.
5. T. Tanaka and T. Enami, Tetsu-to-Hagané, 58 (1972), p. 1775.
6. H. Asahi, ISIJ International, Vol. 42 (2002), No. 10, p. 1150.
7. M. Masimov and N. Kwiaton, A study of Mo-induced bainitic transformation in continuously cooled steels by X-ray and electron diffraction, Euromat 2009, Glasgow.
8. R.W. Honeycombe, Trans A.I.M.E., 7A (1976), p. 915.
9. Y. Funakawa and K. Seto,Tetsu-to-Hagane, 93 (2007), p. 49
10. A. P. Coldren, R. L. Cryderman and N.L. Semchysheh, Strength and Impact Properties of Low-Carbon Structural Steel Containing Molybdenum, Climax Molybdenum Company.
11. G. Krauss, Heat-Treated Low-Alloy Carbon Steels: The Benefits of Molybdenum, these proceedings.
12. H.J. Kirsch, P. Fluess, W. Schuetz and A. Streisselberger: New Property Combinations in Heavy Plate via the Accelerated Cooling Process, Stahl und Eisen 119 (1999) No. 3, p. 57.
13. C.S. Lee and W.Y. Choo, Proc. from Materials Solutions '97 on Accelerated Cooling/Direct Quenching Steels, ASM (1997), p. 51.
14. V. Schwinn, P. Fluess and D. Ormston, Proceedings of Recent Advances of Niobium Containing Materials in Europe, Verlag Stahl Eisen (2005), p. 43.
15. Mizutani et al., Nippon Steel Technical Report No. 90 (2004), p. 45.
16. C. Klinkenberg, K. Hulka and W. Bleck, steel research 75, No. 11 (2004), p. 744.
17. A.P. Coldren and G.T. Ellis, Journal of Metals, Vol. 32, No. 3 (1980), p. 41.

18. T. Irie, S. Satoh, K. Hashiguchi, I. Takahashi and O. Hashimoto, Kawasaki Steel Technical Report, No. 2 (1981), p. 14.
19. O.A. Girina, N.M. Fonstein and D. Bhattacharya, Proceedings of New Developments on Metallurgy and Applicactions of High Strength Steels, Buenos Aires (2008).
20. T. Heller, I. Heckelmann, T. Gerber and T.W. Schaumann, Proceedings of Recent Advances of Niobium Containing Materials in Europe, Verlag Stahl Eisen (2005), p. 21.
21. W. Bleck, A. Frehn and J. Ohlert, Nobium Science & Technology – Proceedings of the International Symposium Niobium 2001, TMS (2001), p. 727.
22. B. Ehrhardt, T. Gerber and T.W. Schaumann, Proceedings of the International Conference on Advanced High Strength Sheet Steels for Automotive Applications, Winter Park (2004), p. 39.

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