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The Developing Prospect of Air-cooled Bainitic Steels

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Abstract
The unique properties of air-cooled bainitic steels have been described. A series of Mn containing air-cooled bainitic steels invented by authors is presented in this paper: including low carbon granular bainitic steels, low carbon grain-boundary allotriomorphic ferrite/granular bainite duplex steels, medium and medium high carbon bainite/martensite duplex steel, and low carbon carbide free bainite/martensite duplex steels. The development of ultra-low carbon bainitic steels in China is also introduced.

Keywords: Bainitic steel; Bainite; Strength and toughness

The Source of Mn Series and Mn-B Series Air-Cooled Bainitic Steel

In the late 1920's, Roberson [1)] first found a mid-temperature transformation product named bainite later. Bainite structure exhibits a good combination of strength and toughness. Accordingly, it attracts more attention. However, the development of bainitic steel was limited due to the complicated technique of isothermal treatment. Pickering and Irvine invented an air-cooled low carbon bainitic steel of Mo-B series in the late 1950's [2)]. In the early 1970's, Hong-Sheng Fang found that a certain content of Mn may change the shape of TTT-curve. Mn has a special redistribution role in overcooling austenite transformation. To illustrate this rule, define $R_{\alpha/\gamma}$ as enrichment factor of Mn in α/γ interface: $R_{\alpha/\gamma}=X_{Mn}(\text{interface})/X_{Mn}(\text{average})$, while X_{Mn} (interface) represents the content of Mn in α/γ interface, and X_{Mn} (average) represents the average content of Mn in alloy. Correspondingly R_α and R_γ denote the enrichment factors of Mn in ferrite and austenite respectively. The experimental results of Mn enrichment factors in a Mn-B steel are shown in Table 1 [3)]. No visible difference is found concerning Mn concentration between α and γ phases, whereas there is a distinct enrichment in the α/γ interface, in accordance with negligible partition local equilibrium (NP-LE)[1)]. The concentration spike of Mn is bound to cause pining-up effect on α/γ interface movement, i.e. solute drag effect, greatly delaying ferrite growth. In addition, Mn enrichment in the α/γ interface causes the decrease of carbon activities and activity gradient in the austenite matrix around the α/γ interface [4)], and thus causes the decrease of carbon diffusion rate in austenite and further restricts the to ferrite growth, that is the so-called solute drag-like effect. It is solute drag and drag-like effects that prompt to form the "bay" shape at 600°C or so of $\gamma\rightarrow\alpha$ transformation curve (see Figure 1). The effects also depress bainite transformation temperature and driving force, resulting in fine bainite grain size.

Table 1. Mn enrichment ratio at different temperature.

Temperature (°C)	R_α	R_γ	$R_{\alpha/\gamma}$
475			1.03
500		1.04	1.07
525	1.01	1.03	1.12
550	1.00	1.00	1.15
575	0.99	1.03	1.19
600	1.00	1.02	1.29
625	1.04	1.00	1.20
650	1.03	0.99	1.24
675	0.97	0.97	1.16
700	1.00	1.00	1.13

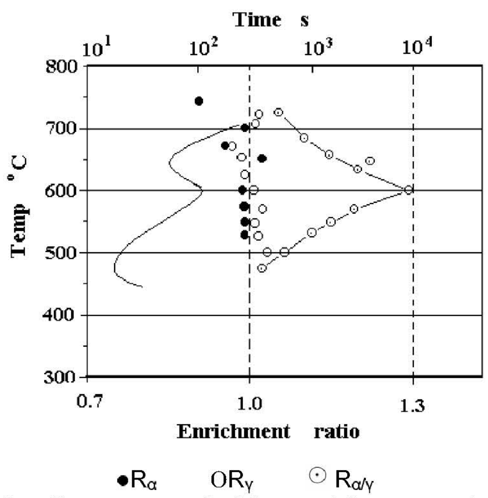

Fig.1. C curve and Mn enrichment ratio vs temperature (Steel: 0.13C%, 2.32%Mn).

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According to the above idea, the authors invented bainitic steels of Mn-series and Mn-B-series, which broke through: 1- the traditional idea that air-cooled bainite can only be obtained by the addition of expensive Mo, W etc. 2- Moreover, compared with bainitic steel of Mo-series, that of Mn-series has so many advantages as follows: higher air-cooling hardenability, lower bainite transformation temperature (B_s), good combination of strength and toughness, simple alloying and cost saving. 3- Mo-B series bainitic steel is limited mainly to low carbon field, the present invented steels are low-carbon, medium-carbon, medium-high carbon Mn-series and Mn-B-series bainitic steels with different properties and applications [5,6].

The Strengthening and Toughening Approaches and the Development of Bainitic Steels

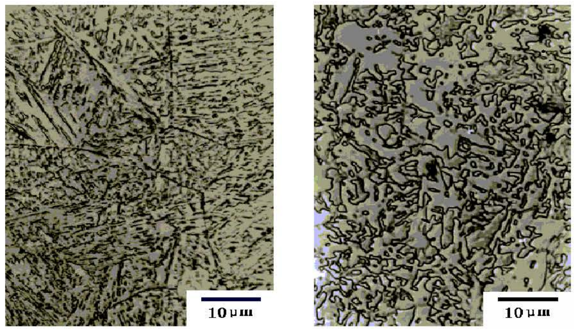
1. Granular-bainitic steel.

The authors have proven that good combination of strength and toughness can be obtained by controlling the size, quantity and distribution of the M/A islands in granular bainite microstructure. A kind of granular bainitic steel was invented and became a new kind of non-moderating steel.

After the late 1950s, Habraken [7] suggested the microstructure of granular bainite, which consists of ferrite matrix and M/A islands. It was popularly observed in low carbon and medium carbon alloy structural steels. It is found by the authors that the so-called "granular bainite" includes two kinds of microstructure which are not identical essentially. One accompanies apparent surface relief, where ferrite matrix possessing lath packets belongs to upper bainite ferrite, and semi-continuous island strips are distributed almost parallel in ferrite lath matrix. The islands are also distributed preferentially in grain boundary of former austenite, which makes the parent austenite grain boundary apparent. This kind of microstructure is called granular bainite. For the other kind, the striped surface relief effect is invisible, the ferrite matrix is irregular massive pro-eutectoid ferrite; the ferrite matrix may grow up across the parent grain boundary which is not easy to reveal, and the irregular islands are randomly distributed in ferrite matrix. This kind of microstructure is called granular structure [8] (Figure 2). The above two kinds of microstructures may be separated or mixed, while the strength and toughness of the granular bainite is superior to that of granular structure.

Research by Mangonon [9] indicated the granular bainite should be avoided as a harmful microstructure with which the toughness of steel is diminished. However, the authors' work suggests the granular bainite should not be generally defined as a harmful microstructure [10]. Under some circumstances, the steels with granular bainite may possess a good combination of strength and toughness, and the decisive factor is the microstructure parameter of granular bainite as follows:

1- The strength rises with the increase in the number of islands, and with the decrease in sizes; 2- The toughness is improved with the decrease in the number and sizes of islands; 3- The toughness of the steel can be further increased after tempering. (Figure 3)



(a) (b)

Fig.2. Microstructure of granular bainite (a) and granular structure (b), 12Mn2VB.

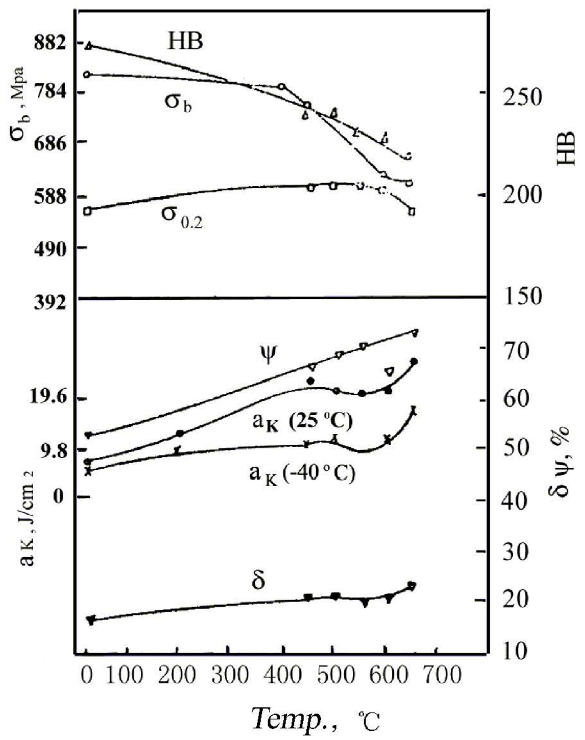


Fig.3. The effect of tempering temperature on mechanical properties of granular bainitic steel 12Mn2VB.

Experiments show that the number of the islands increases with the increase in carbon content in steel, the sizes of the islands decrease with the increase of cooling rate and with the decrease of prior austenite grain size. For example, the properties of a kind of low carbon granular bainitic steel 12Mn2VB invented by authors based on the above principle are performed as the following: $\sigma_b \geq 800$MPa, $\sigma_{0.2} \geq 500$MPa, $\delta_5 \geq 14\%$, $\psi \geq 45\%$, $a_{ku} \geq 60 J/cm^2$.

Tempering at a medium or high temperature causes the decomposition of the M/A islands, which is similar to the moderating microstructure in which the granular particles of carbides disperse on the ferrite matrix (Figure 4), and further improve the combination of strength and toughness: $\sigma_{0.2}\geq580$MPa, $\sigma_b\geq760$MPa, $\delta_5\geq18\%$, $\psi\geq60\%$, $a_{ku}\geq160$J/cm^2. After going through the process of "forging or rolling—air cooling—medium temperature tempering", this type of steel can substitute for medium-carbon alloy moderating steel to make moderating articles such as truck front axles and connecting rods. This type of steel without quenching also has been used to manufacture sucker rods for oil fields. The properties can be obtained as follows: $\sigma_b\geq900\sim1100$MPa, $\sigma_{0.2}\geq750\sim850$MPa, $\delta_5\geq14\%$, $\psi\geq45\%$, $a_{ku}\geq90$J/cm^2. Low carbon granular bainitic steel can be steadily used as bainite-type non-moderating steel.

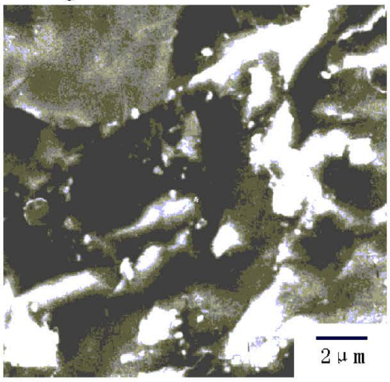


Fig. 4. Microstructure of granular bainite after tempering at 600°C, 12Mn$_2$VB.

2. Grain boundary allotriomorphic ferrite/granular bainite duplex steel (F_{GBA}/B_g Steel).

According to the classic strengthening-toughening theory of aggregated structure [11], the strength of duplex microstructure increases as the volume fraction of the stronger phase increases, and the plasticity and toughness increases as the softer phase increases. Since the strength of granular bainite (B_g) structure is much higher than that of pearlite structure, substituting pearlite with B_g in ferrite-pearlite (F/P) steel will evidently increase strength. On the other hand, the proeutectiod ferrite in F/B_g steel is able to obtain the better plasticity and toughness with allotriomorphic ferrite except the net ferrite and widmannstaten ferrite. So the small grain-size discontinuous F_{GBA} as one constituent phase is used to improve the toughness of F_{GBA}/B_g steel. The model of F_{GBA}/B_g duplex microstructure is schematically illustrated in Figure 5 [12] and Figure 6. The CCT curve of the steel (Figure 7) shows that such microstructure can be obtained in a wide range of cooling rate. Table 2 shows that the mechanical properties of F_{GBA}/B_g steels JB785 have much better toughness than B_g steel B71.

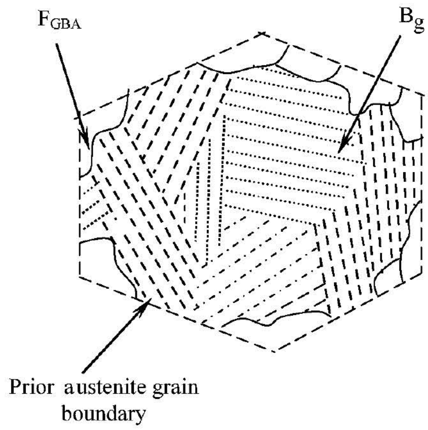


Fig. 5. Schematic illustration of F_{GBA}/B_g duplex microstructure.

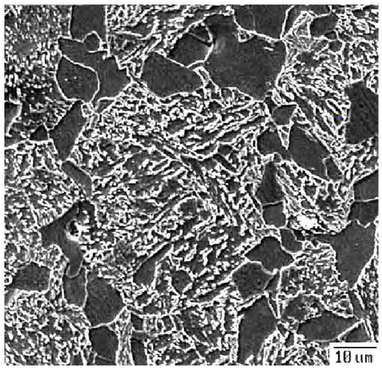


Fig. 6. F_{GBA}/B_g duplex microstructure of 0.1%C-MnCrSi Steel.

In the course of crack propagation in F_{GBA}/B_g microstructure, the following factors cause the increase of toughness [12]: (1) The softer phase F_{GBA} causes large plastic deformation to relax local stress concentration of crack tip in F_{GBA}/B_g duplex microstructure and reduce three-dimensional tensile stress. Thus it results in the blunting effect on the crack tip and the stop of crack propagation (Figure 8); (2) Some cracks have to pass through many B_g and F_{GBA} repeatedly to continue propagation since F_{GBA} does not always connect each other, which lead to the higher toughness.

Table2. Effect of microstructures on the mechanical properties of 12mm thick plate.

Symbol	Microstructure	σ_b /MPa	$\sigma_{0.2}$ /MPa	δ_5 /%	ψ /%	Cold bending 180°	A_{kv} /J	Crack initiation energy /J	Crack propagation energy /J
B71	B_g	895	660	15	39	d=3a	24.3	18.1	6.2
JB785	F_{GBA}/B_g	865	546	20	45	d=2a	60.1	28.5	31.6

Notice: d-bending diameter, a- steel plate thickness.

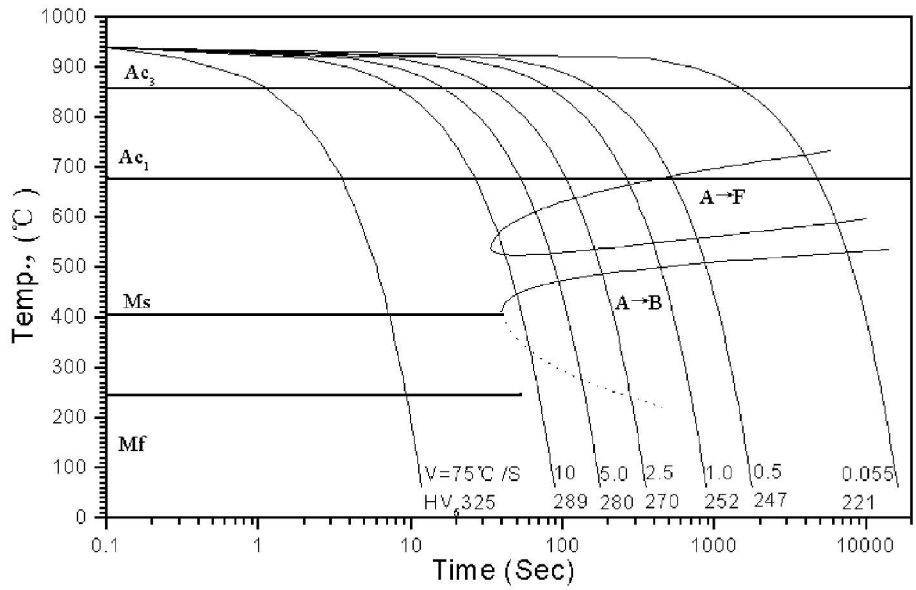


Fig.7. CCT curve of typical F_{GBA}/Bg experimental of 0.1%C-MnCrSi steel.

Under the conditions of no-supplementary refinement and controlling rolling, without using heat-treatment and adding precious alloy elements, low carbon air-cooled F_{GBA} / B_g steel plates of 12, 16, 20mm-thickness were successfully turned out in steel plate production line with the properties of $\sigma_b \geq 850$MPa, $\sigma_{0.2} \geq 550$MPa, $\delta_5 \geq 16\%$, A_{KV} value of 60J at 20°C 27J at -40°C, especially with good weldability. It is obvious that the strength and toughness of this steel will be further improved with supplementary refinement, controlling rolling and heat treatment. Besides high strength steel plate, this steel can be used for high strength reinforcing rods, non-moderate articles, etc.

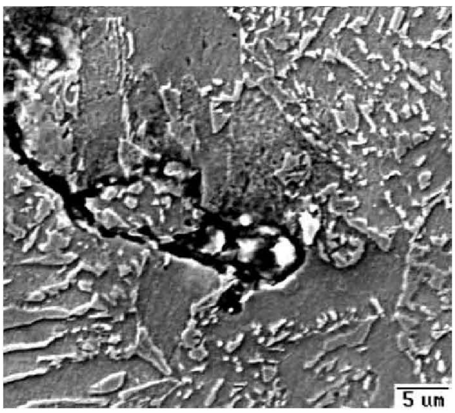


Fig. 8. The effect of F_{GBA} on crack branching, deflecting and blunting in F_{GBA}/B_g steel.

3. Medium-carbon lower bainite/martensite duplex steel.

The lower bainite/martensite microstructure can be obtained from medium carbon Mn series bainitic steel by air cooling. The strength and toughness of this kind of steel is inferior to that of single martensitic steel when it is with low temperature tempering, but while tempered at 440°C, it exhibits superior strength and toughness to that of tempered martensite with identical hardness, which is shown in Figure 9. The authors' work [13] shows that a small semi-continuous carbide film is formed along the interface during air cooling. Crack is induced by stress concentration accompanying dislocations aggregating in front of carbide film, and brittleness is increased. So the superiority of lower bainite is restricted. After it is tempered at medium temperature, the carbide in grain boundary coarsens and spheroidizes to decrease crack source that induces intergranular crack. At the same time, the volume of twin martensite of the B/M microstructure is less than martensite steel, and the grain is divided by lower bainite to refine the martensite (Figure 10), so that the toughness is improved, and the air cooled medium carbon B/M steel is preferred with medium or high temperature tempering.

Considering the good comprehensive properties of this kind of steel after high temperature tempering, for example, after tempering at 630°C, the following properties can be obtained: σ_b 900MPa, $\sigma_{0.2}$ 780MPa, δ_5 20%, ψ 55% and a_{KU} 110J/cm^2. It is applicable to a most all kinds of moderating articles or surface induction heating quenching required articles such as axles, cam shafts and crank shaft, etc. This kind of steel has also been successfully developed for the spring steel to make leaf spring and spiral spring. The following properties can be obtained: σ_b 1900MPa, $\sigma_{0.2}$ 1650MPa, δ_5 7%, ψ 40% and a_{KU} 40J/cm^2. The air-cooling hardenability is more than 30mm thickness of leaf spring.

4. Carbide free bainite/martensite (CFB/M) duplex phase steel.

It is well known that the delayed fracture due to the entering of hydrogen in steel has greatly decreased the performance life of articles made up of high strength steel with yield strength of over 1000MPa [14].

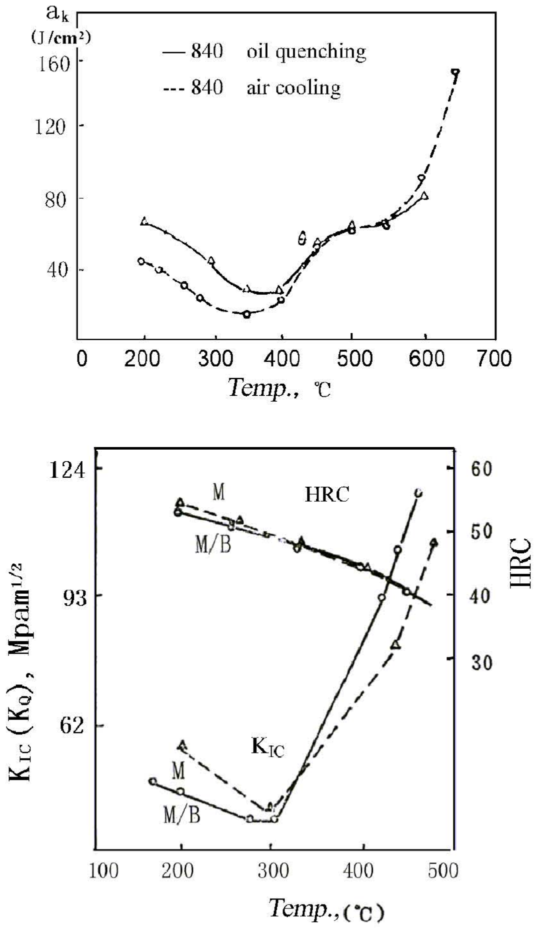


Fig.9. The effect of tempering temperature and microstructure on a_{kU} (a) and K_{IC} (b), M/B from air-cooling.

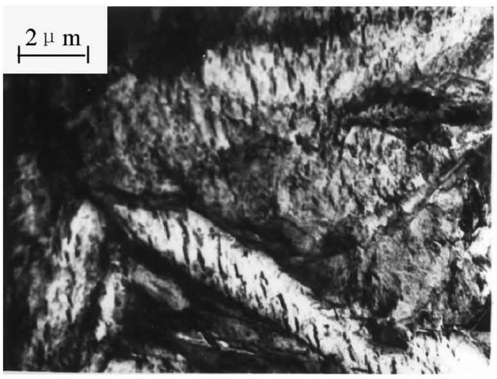


Fig.10. The bainite/martensite mixed microstructure.

The CFB/M microstructure with an ultra-fine structure can be obtained in air cooled condition when Si is added into the bainitic steel of Mn or Mn-B series. The former austenite grains are divided and the martensite is refined by CFB plates. The generally believed fine structures of bainite are as follows: lower bainitic plate is composed of sub plates; sub plate is composed of sub units; sub unit is the smallest structure unit; while the detail of sub unit remains unknown. The authors found that sub unit of CFB plate is composed of sub-sub units by the first time using high vertical resolution (0.01nm) scanning tunneling microscopy (STM), atomic force microscopy (AFM) and also by TEM. Sub units and sub-sub units of bainite are surrounded by retained austenite film in air-cooled low carbon Mn-Si series bainite steel. Take Figure 11 as an example: the width of bainite plate is 1~2μm, composed of 2~3 sub plates with 400~500nm in width; while the sub plate is composed of mass sub units with size of 200~400nm. The width of retained austenite film between sub plates and sub units is about 15~30nm and the film of about 7nm in sub unit divides sub unit into sub-sub units. With high thermal and mechanical stability (Table 3 and Table 4), the retained austenite film substitutes carbide and performs as hydrogen trap to slow the aggregation of hydrogen to the tip of crack, refines the microstructure unit of matrix, acting as large angle boundary between fine structure and retained austenite film. Thus ultra high strength CFB/M steel is provided with high delayed fracture resistance, high toughness and fatigue strength (Table 5).

The strength and toughness of air-cooled low carbon Mn Series bainitic steel increase with added Si shown in table 6 [15]. The toughness of the CFB/M steel with a 1.8% Si was improved after tempering at 340~380°C while the strength remains constant (Figure 12).

The susceptibility to hydrogen embrittlement E_H is further improved with the increase of tempering temperature in steel with 1.8%Si content (Table 7). The threshold value of stress corrosion strength factor K_{ISCC} of the low carbon CFB/M steel U20Si (1.8%Si) is 54.5MPa m$^{1/2}$ which is much better than 40CrNiMoA [16] and 30CrMnSiA steel under similar strength (Table 8).

Low carbon CFB/M steel can be used for high and ultra high strength structure articles such as high strength bolt, rail frog and high strength steel plate, etc. Medium carbon carbide free bainite/martensite duplex steel can be used for different kinds of spring, etc. Medium-high carbide free bainite/martensite duplex steel can be used for wear resistance articles, grinding balls, etc.

Recent Development of Ultralow Carbon Bainitic Steel in China

Due to the development of petroleum pipe line, marine facilities and shipbuilding industries, as well as the high strength and toughness and good weldability, ultralow carbon bainitic steel has been developed rapidly in China, and has been manufactured in many steel works such as WH Steel, Bao Steel, AS Steel and WY Steel with a series of yield strength of 500MPa, 600MPa, 700MPa and 800MPa. [17-20]

Table 3. Variation of the amount of retained austenite(%) in low carbon CFB/M duplex microstructure with tempering temperature of U20Si (1.8%Si).

	Tempering temperature, °C						
	As-quenched	220	280	340	360	380	420
Tensile specimen	8.7	8.2	7.2	7.3	5.9	5.8	
Impact specimen		7.2	7.3	7.3	6.0	5.9	4.4

Table 4. The effect of 3% plastic deformation and tempering temperature on the amount of retained austenite (%) in CFB/M duplex microstructure of U20Si.

	Tempering temperature °C					
	As - quenched	220	280	340	360	380
Before deformation	8.7	8.2	7.2	7.3	5.9	5.8
After deformation	-	5.2	6.9	7.2	5.9	3.8

Table 5. The comparison of fatigue strength σ_{-1} between CFB/M steel and other kind steels.

Steel		σ_b, MPa	$\sigma_{0.2}$, MPa	σ_{-1}, MPa
U20Si	CFB/M	1540	1340	700
	M	1540	1340	635
30CrMnSi	M	1510	1350	600

Table 6. The effect of Si on the strength and toughness of bainitic steel.

Symbol	Si (%)	Tempering temperarure (°C)	K_{1C} MPa $m^{1/2}$	HRC	σ_b (MPa)	$\sigma_{0.2}$ (MPa)	δ_5 (%)	ψ (%)
LF1BB	0.6	250	105	47	1547	1143	12.1	57
LF1BC	0.6	300	82	46	1539	1265	12.3	54
LF2BB	1.4	250	114	48	1566	1185	10.0	43
LF2BC	1.4	300	96	47	1524	1230	10.2	53
BSC	1.5	280	101	49	1550	1220	15	51
LF3DC	1.8	300	119	50				

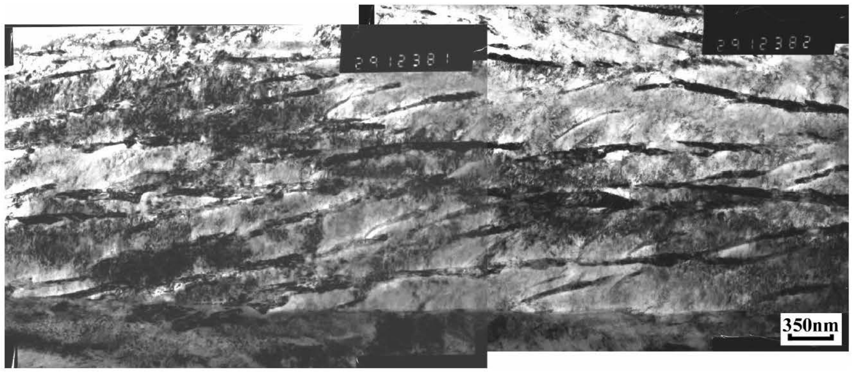
Table 7. The effect of tempering temperature on susceptibility to hydrogen embrittlement E_H (%) under different current density, U20Si.

E_H,% *		Hydrogen charging current density, mA/cm^2		
		0.2	0.5	1
Tempering temperature °C	280	12	53	74
	340	-	48	53
	370	-	27	-

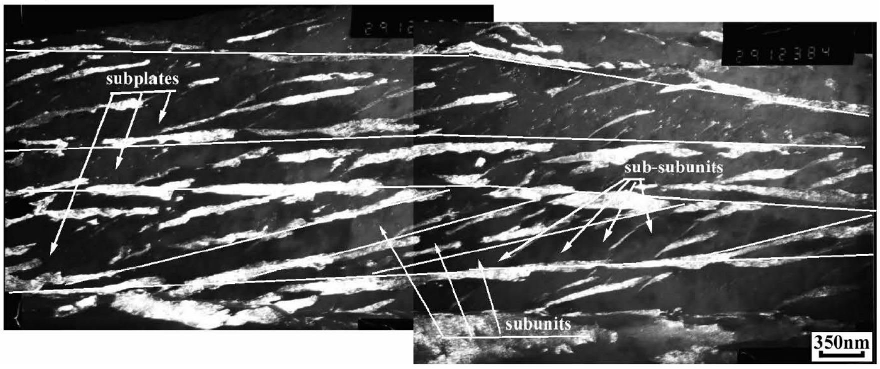
*: EH= (Ψ0-ΨH)/ Ψ0, where Ψ0 and ΨH represent reduction in area before and after charging hydrogen seperately

Table 8. Teat Treatment parameter and K_{ISCC} value.

Steel	Heat treatment	σ_b,MPa	$\sigma_{0.2}$, MPa	K_{ISCC}, MPam$^{1/2}$
30CrMnSiA	Oilquenching, 450°C tempering	1421	1284	38.1
40CrNiMoA	Oil quenching, 470°C tempering 900°Cair-cooling	1401	1303	45.6
U20Si (CFB/M)	340°C tempering	1530	1380	54.5



a)



b)

Fig.11. Bainitic ultra fine structure separated by retained austenite film.

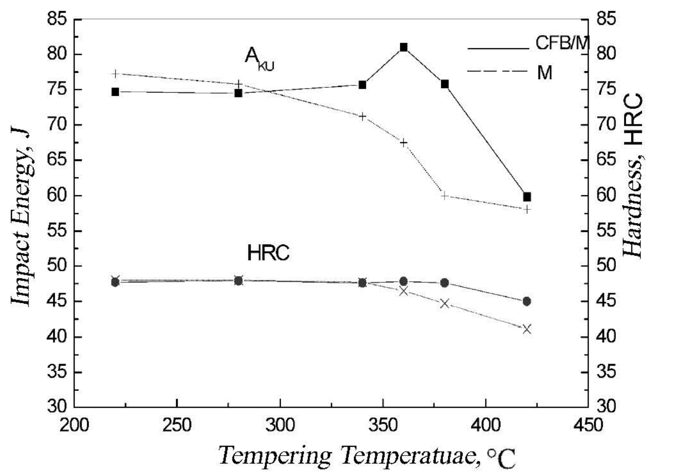


Fig.12. The effect of tempering temperature on the strength and toughness of the steel U20Si with different microstructure.

1. The typical composition and characteristic of ultralow carbon bainitic steel. Table 9 represents examples of the typical composition of ultralow carbon bainitic steel, whose characteristics are as follows: (1) The ultralow carbon bainitic steel is purified with S≤0.006% and P≤0.015% to improve toughness; (2) The content of C is below 0.006% to improve toughness and weldability; (3) The elements of Mn and Mo are added to obtain bainite structure; (4) The elements of Cu, Nb and V are added to obtain second-phase precipitation strengthening; (5) The grains are ultrafined by means of thermomechanical control process (TMCP) to improve strength and toughness; (6) High temperature tempering is employed after TMCP to improve toughness and to precipitate the second-phase for strengthening.

2. TMCP. (1) Example for two-stage control rolling (Figure 13): The first stage: heating-up temperature at 1200°C, finishing rolling temperature at 1000°C, pass reduction≥10%, total reduction≥45%. The second stage concerns mainly out of recrystallization zone: starting rolling temperature at 950°C, finishing

rolling temperature at 780~830°C, pass reduction at 12%, total reduction at 50%.
Water quenching is employed after rolling with cooling velocity of ≥2°C /s.

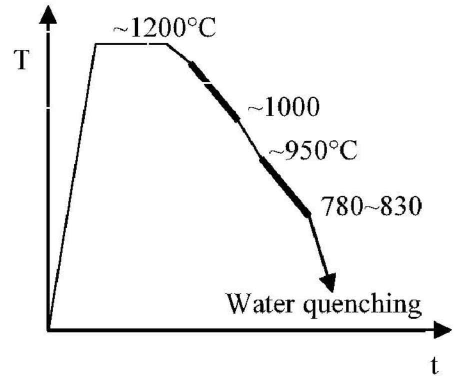


Fig.13. Two-stage control rolling.

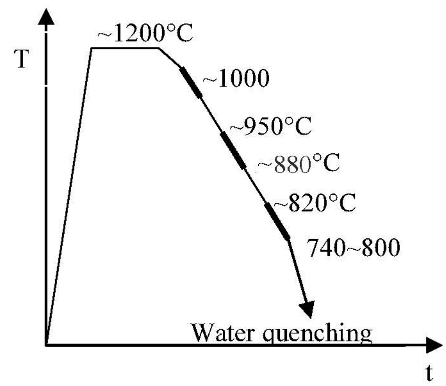


Fig.14.Three-stage control rolling.

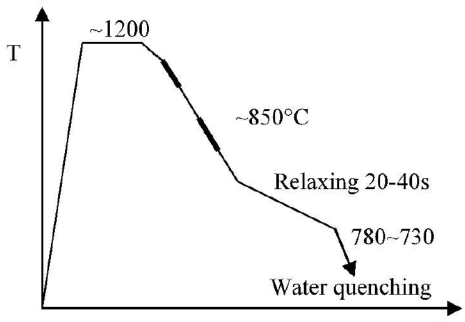


Fig. 15. Two-stage control rolling and relaxation/precipitation/control process.

(2) Example for three-stage control rolling (Figure 14): The first stage: heating-up temperature at 1200°C, finishing rolling temperature at 1000°C, pass reduction≥10%, total reduction>60%. The second stage: starting rolling temperature at 930°C ~950°C, finishing rolling temperature at 880~900°C, pass reduction≥10%, total reduction>60%. The third stage: starting rolling temperature below 820°C, finishing temperature at 760°C ~730°C.

(3) Example for two-stage control rolling and RPC (relaxing/precipitating/control process)[20] (Figure 15): The first stage: starting rolling temperature at 1200°C, and total reduction>60%. The second stage: finishing rolling temperature at about 850°C and total reduction>60%.
Relaxing time is about 20-40 seconds and water quenching temperature at 780°C ~730°C.

3. Tempering and specific examples. (1) Effect of tempering: Tempering treatment after control rolling will significantly increase the toughness. Figure 16 represents the comparison of properties before and after tempering concerning 1# steel (Table 9). With almost the same strength, the toughness after tempering is 200% higher than that of before tempering. (2) Tempering temperature: In steel that contains Nb, V, but not Cu, the spike value of toughness and strength is at about 620°C, as illustrated in Table 10. While in steel that contains Nb, V and Cu, the spike value of toughness and strength is at about 650°C due to the precipitation of ε-Cu (Figures 17, 18).

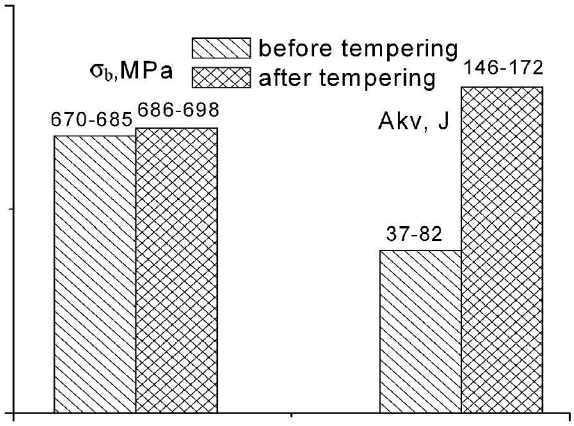


Fig. 16. Comparison of properties before and after 620°C tempering concerning 1# steel in table 9 by two stage control rolling.

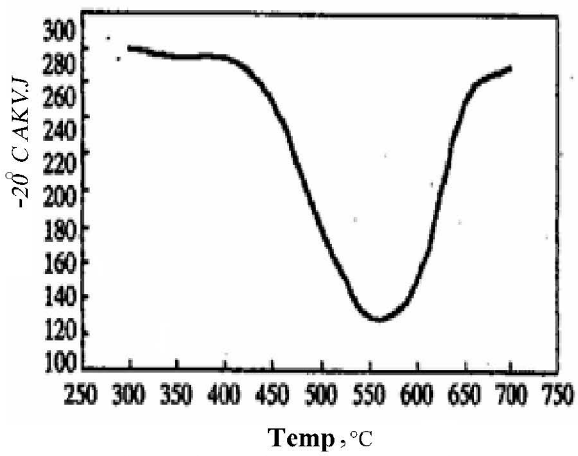


Fig. 17.Relationship between Toughness and Temperature of 3# Steel.

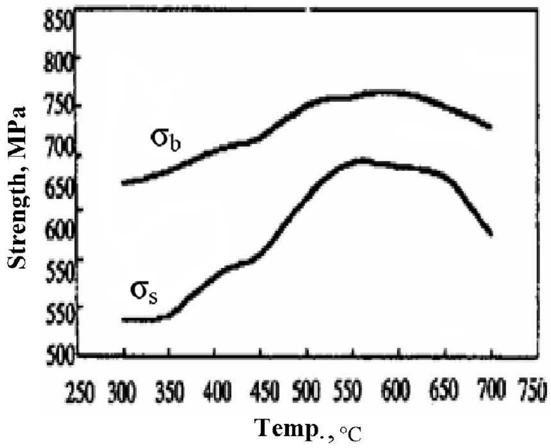


Fig.18. Relationship between Strength and Temperature of 3# Steel.

4. Comparison of tempering properties between two-stage and three-stage control rolling.

Comparing two stage control rolling, the three-stage control rolling bears both higher strength and better toughness (Table 11). Even though the properties will be influenced by ε-Cu phase of 3# steel in Table 11, rolling in the third stage has an important function. The rolling temperature at 820°C ~ (760-730°C), which is out of recrystallization zone, affects properties through three aspects: the first is to increase intracrystalline defects and induce dynamic recovery; the second is to accelerate strain-induction precipitation of second-phase particles which at the same time resist the dynamic recovery of defects; the third is to significantly refine structure with the increased defects and second-phase particles both of which are as nucleating center for bainite.

Concluding Remarks

Air-cooled bainitic steels have the following unique advantages: (1) self-hardening by air cooling after hot working without quenching or quenching-tempering; (2) good combination of strength and toughness; (3) prevention of defects from quenching; (4) production cost saving in a large degree; (5) large saving in energy resources; (6) having solved the contradictions between mechanical properties and processing properties such as strength and toughness, strength and weldability, processing properties and application properties of products, etc. Consequently, there are wide applications and bright prospects for air-cooled bainitic steels in the future.

Table 9.The examples of the typical composition (%) of ultralow carbon bainitic steel.

No	C	Si	Mn	P	S	Nb	Ti	Mo	V	Al	Ni	Cr	Cu	B
1	0.06	0.24	1.54	0.013	0.005	0.037		0.24	0.047	0.029	0.027			0.0004
2	0.04	0.52	1.07	0.016	0.005	0.04		0.24		0.014	0.72	0.54	0.74	
3	≤0.05	0.20~0.45	1.50~1.60	≤0.015	≤0.006	0.05~0.07	0.015~0.020	0.30~0.40	0.04~0.06	0.020~0.045	0.40~0.50		0.60~0.70	
4	0.043	0.33	1.53	0.006	0.0051	0.05	0.048	0.25			0.24		0.29	0.0009

Table 10. Mechanical properties of 1# steel 20mm steel plate after tempering.

Tempering temperature	σ_b, MPa	σ_s, MPa	δ_5, %	-20°C lengthwise Akv, J
550°C	635	505	30	119, 84, 166
620°C	650	555	28	146, 172, 156
770°C	605	445	29	150, 169, 115

Table 11. Comparison of tempering properties between two-stage and three-stage control rolling.

	σ_b, MPa	$\sigma_{0.2}$, MPa	δ_5, %	Akv, J
1# steel of Tab.9, two-stage control rolling, 620°C tempering	650	555	28	146, 172, 156
3# steel of Tab.9, three-stage control rolling, 650°C tempering	715~718	615~ 715	20~ 40	227

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