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## Influence of Cr, Mn and Mo Addition on Structure and Properties of V Microalloyed Medium Carbon Steels

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The effect of austenitizing temperature and Cr, Mo and Mn addition on microstructure and mechanical properties of V microalloyed medium carbon steel has been studied by means of metallography and mechanical testing. The addition of Cr, Mn and Mo leads to a decrease in yield strength (YS) by approximate 100 MPa in comparison to the base steel. It is assumed that Mn and Mo increase hardenability by promoting the formation of bainitic sheaves (BS), *i.e.* by suppressing the formation of ferrite-pearlite and acicular ferrite (FP-AF). Cr at the level used in this work is not that effective. Presence and packet size of bainitic sheaves decrease the Charpy V-notch impact energy at 20 °C (CVN20) in comparison to ferrite-pearlite and acicular ferrite microstructures.

**KEY WORDS:** Medium-carbon steels; Chromium; Molybdenum; Manganese addition; Bainite; Acicular ferrite

### 1. Introduction

The demand for economical steels has increased over past decades. Steels are expected to have a lean chemistry and to be easier to fabricate. At the same time they are expected to have properties at least equal to steels which are being substituted. These demands have been, at least in part, met by V microalloyed medium carbon forging steels in order to substitute traditional quenched and tempered (Q+T) steels; their main advantage is that they save energy by eliminating the heat treatment from the production route, in spite of some lower toughness.

The main alloying element in microalloyed medium carbon forging steels is V. It is assumed that V promotes strengthening by precipitation of V(C,N) particles which precipitate during and/or after austenite-ferrite transformation<sup>[1]</sup>. At the same time, an increase in toughness is provided by intragranular nucleation of acicular ferrite, dominantly on VN particles<sup>[1–3]</sup>. Also, small amount of tita-

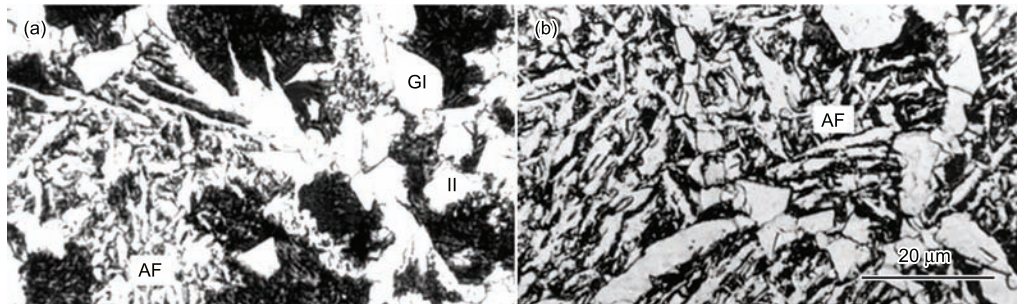
nium is usually added in order to prevent the grain growth at high temperatures<sup>[4]</sup>. Bainite and/or acicular ferrite are frequently encountered structures<sup>[1–4]</sup> in the medium carbon V-microalloyed steel. Both microstructures are formed in the same temperature range; the only difference is the nucleation sites, *i.e.* while bainites nucleates at the austenite grain boundaries (intergranularly), acicular ferrite nucleates on the particles within the grains (intragranularly)<sup>[5,6]</sup>. Therefore, final microstructure is determined by the effectiveness of nucleation sites.

Some of the alloying elements, primarily Cr and Mo are not originally added to the V-microalloyed medium carbon forging steels; their small addition is usually introduced by negligence in recycling process. However, the effect of these elements, including Mn, on the transformation behavior is of the particular interest in this steel grades. They have very strong influence on the formation of proeutectoid ferrite. If the proeutectoid ferrite is formed during transformation, it decorates the prior austenite grains disabling them from their role as nucleation sites for bainite formation. Therefore, in the presence of proeutectoid ferrite, acicular ferrite intragranular nucleation is the

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**Table 1** Chemical compositions of experimental steels (wt%)

Steel	C	Si	Mn	P	S	Cr	Ni	Mo	V	Ti	Al	N
Base-steel	0.26	0.30	1.48	0.0080	0.0080	0.29	0.16	0.03	0.12	0.010	0.02	0.0166
L-7Cr	0.26	0.32	1.57	0.0080	0.0050	0.57	0.16	0.03	0.12	0.010	0.03	0.0159
L-9Mo	0.27	0.32	1.58	0.0080	0.0060	0.29	0.17	0.21	0.10	0.010	0.02	0.0138
L-22Mn	0.26	0.31	1.75	0.0100	0.0100	0.37	0.18	0.04	0.17	0.010	0.03	0.0021

**Fig. 1** Microstructure of high-N steel air-cooled from austenitization temperature of: (a) 950 °C, (b) 1300 °C (GI–grain boundary ferrite idiomorphs; II–intragranular idiomorphs; AF–acicular ferrite)

dominant mechanism for austenite decomposition. Generally, Cr, Mn and Mo raise the hardenability of the steel, defined as their ability to prevent formation of proeutectoid ferrite and pearlite during hardening<sup>[1,5]</sup>. These elements promote the formation of hard phases such as bainite and martensite<sup>[5]</sup>. The influence of V and nitrogen was reported in numerous papers<sup>[1,2,5]</sup>, while the results reporting the influence of Cr, Mo and Mn on the acicular ferrite formation in V microalloyed medium carbon forging steels are limited<sup>[3,7,8]</sup>.

Therefore, the aim of this work is to clarify the influence of Cr, Mo and Mn on the formation of bainite and acicular ferrite during continuous cooling of V microalloyed medium-carbon steels and its influence on mechanical properties.

## 2. Experimental

Four different medium-carbon steels, containing various content of Cr, Mo and Mn, were vacuum melted, casted into ingots, press forged and hot rolled to 22 mm diameter rods. The chemical compositions of tested steels are given in Table 1. The 180 mm long test pieces which were reheated to different austenitizing temperatures, ranging from 950 °C to 1300 °C for 30 min, and cooled in still air. The still air-cooling rate was estimated to be between 1.15 and 1.35 °C/s, depending upon the reheating temperature. The test pieces were then mechanically polished and etched in 2% nital to observe the microstructures by optical microscopy. Tensile test pieces with round shape ( $L_0=40$  mm,  $d_0=8$  mm) and Charpy V-notch impact test pieces, were taken from the center of the bar.

## 3. Results

### 3.1 Microstructure

Four steels (base steel and steels L-7, L-9 and L-

22 with enhanced content of Cr, Mo and Mn, respectively) were prepared to investigate the effect of alloying elements on the transformation behavior of the air cooled medium carbon V-microalloyed steels. Prior austenite grain size was 21–90  $\mu\text{m}$  in the temperature range of 950–1250 °C.

The microstructure of the base steel austenitized at 950–1050 °C consists of polygonal ferrite idiomorphs, nucleated at austenite grain boundaries or within the former austenite grains, surrounded by pearlite and some acicular ferrite, Fig. 1(a). With increasing austenitization temperature to 1150–1300 °C, the fraction of acicular ferrite increases and becomes dominant morphology, Fig. 1(b).

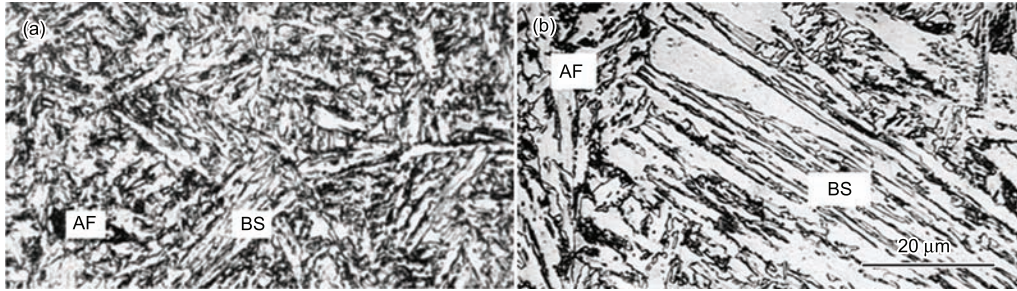
The microstructure of the Mo steel (L-9) reheated to 950–1150 °C is characterized as bainitic sheaves and some acicular ferrite (Fig. 2(a)), and as the absence of primary grain boundary ferrite. Microstructure obtained after cooling from high austenitizing temperature (1250 °C) consists of bainitic sheaves and some acicular ferrite (Fig. 2(b)).

The microstructure of the L-7 (Cr steel) air cooled from 950–1050 °C (Fig. 3(a)) consists of intragranularly nucleated polygonal ferrite, grain boundary idiomorphs and allotriomorphs. With increasing austenitization temperature to 1150–1300 °C, the acicular ferrite becomes dominant morphology, alongside with grain boundary idiomorphs (Fig. 3(b)).

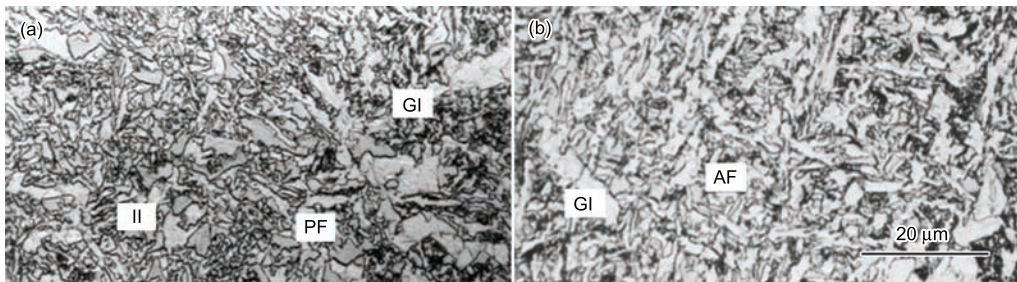
The microstructure obtained in the Mn steel after air cooling from both the low austenitization temperature (950 °C) and the high austenitization temperature (1300 °C) consists of bainitic sheaves. The microstructure is free of grain boundary ferrites (Figs. 4(a) and 4(b)).

The bainitic sheaves, their packet size, in Mo and Mn added steels depend on the reheating temperature. Air cooling from higher reheating temperature

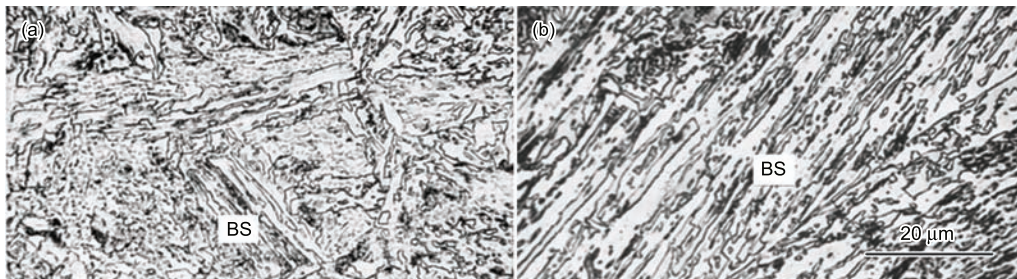




**Fig. 2** Microstructure of Mo steel air-cooled from austenitization temperature of: (a) 1150 °C, (b) 1250 °C (BS–bainitic sheaves, AF–acicular ferrite)



**Fig. 3** Microstructure of Cr steel air-cooled from austenitization temperature of: (a) 1050 °C, (b) 1300 °C (GI–grain boundary idiormorphs; II–intragranular idiormorphs, PF–polygonal ferrite, AF–acicular ferrite)



**Fig. 4** Microstructure of Mn steel air-cooled from austenitization temperature of: (a) 950 °C, (b) 1300 °C (BS–bainitic sheaves)

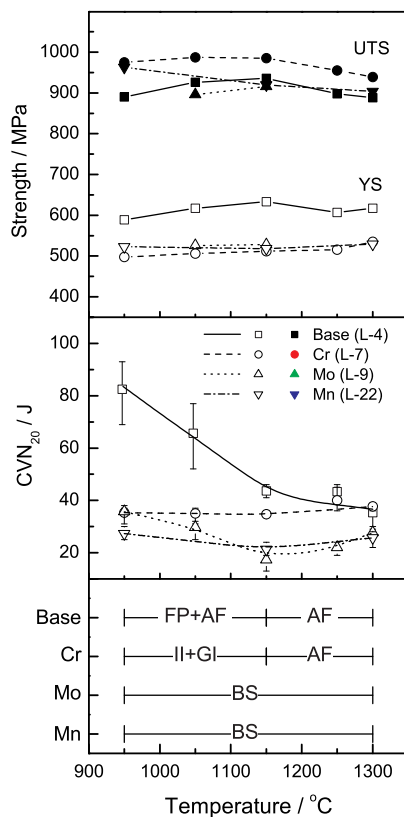
leads to larger packets in comparison to those cooled from lower temperature.

### 3.2 Mechanical properties

The results of the tensile testing and Charpy V-notch impact testing are summarized in Fig. 5, together with respective dominant microstructural features. Fig. 5 shows the relationship between impact energies, tensile properties and structure of four steels (base, L-7, L-9, and L-22) in order to describe the influence of the austenitization temperature. Only the base steel exhibits very strong influence of reheating temperature on toughness; the CVN20 impact toughness steeply decreases to approximate 45 J when reheating temperature increases to 1150 °C, and then levels off at 30–38 J, when austenitization temperature is 1300 °C. The Cr-added steel (L-7) exhibits a very slight increase of the impact toughness in the

range of 31–39 J with an increase of reheating temperature. However the L-9 and L-22 steels with Mo and Mn addition respectively show a similar behavior, *i.e.* decrease in toughness with increasing temperature, in comparison to the base and Cr steels. For L-9 and L-22 steels the decrease in impact toughness ranges from 36 J to 18 J and from 27 J to 21 J respectively with increasing reheating temperature up to 1150 °C. Further increase in reheating temperature leads only to slight increase in toughness (up to 28 J and 27 J for L-9 and L-22 steels respectively).

In regard to the strength, also shown in Fig. 5, the base steel exhibits the yield strength (YS) in the range of 589–633 MPa and ultimate tensile strength (UTS) of 888–936 MPa. The addition of Cr, Mn and Mo lead to a decrease in YS by approx. 100 MPa, while the UTS increases by approx. 50 MPa only in the Cr added steel. The general effect of increasing the reheating temperature was to slightly enhance the yield



**Fig. 5** Effect of austenitization temperature on strength, Charpy V-notch impact energy at 20 °C (CVN20) and dominant microstructures of four experimental steels: (FP–ferritepearlite; AF–acicular ferrite; BS–bainitic sheaves; II–intragranular idiomorphs, GI –grain boundary idiomorphs)

strength level.

## 4. Discussion

### 4.1 Microstructure

The austenite grain size is an important factor in developing the final microstructure in steel<sup>[7,9]</sup>. Prior austenite grain size was 21–90  $\mu\text{m}$  in temperature range of 950–1250 °C used in this work, which is in good agreement with results obtained in similar steels<sup>[7]</sup>. The addition of microalloying elements, especially Ti, acts as grain size inhibitor up to certain temperature (precipitation dissolution temperature). Above this temperature the grains coarsen rapidly and this increases the amount of intragranularly nucleated acicular ferrite, because the austenite grain boundaries are preferred sites for nucleation of ferrite, pearlite and bainite. Therefore, with larger austenite grains fewer nucleation sites will be available for the above phases to form; as a result, intragranular nucleation on particles will be promoted at the expense of grain boundary transformation products<sup>[8]</sup>. The process of nucleation on inclusions, together with the autocatalytic nucleation, leads to a chaotic

arrangement of plates and fine-grained interlocking microstructure characteristic of acicular ferrite. The formation of bainites or acicular ferrite plays dominant role in the transformation behavior of the air cooled medium carbon V-microalloyed steels tested in this work. In order to describe the influence of alloying elements on the transformation behavior,  $A_{r3}$  temperature, and bainitic starting formation temperature,  $B_s$ , are predicted using Eqs. (1)<sup>[10]</sup> and (2)<sup>[11]</sup>. The results are given in Table 2.

$$A_{r3} (\text{°C}) = 910 - 310(\%C) - 80(\%Mn) - 20(\%Cu) - 15(\%Cr) - 55(\%Ni) - 80(\%Mo) + 0.35(t-8) \quad (1)$$

$$B_s (\text{°C}) = 830 - 270(\%C) - 90(\%Mn) - 70(\%Cr) - 37(\%Ni) - 83(\%Mo) \quad (2)$$

**Table 2** Calculated  $A_{r3}$  and  $B_s$  temperatures

Steel	$A_{r3}/\text{°C}$	$B_s/\text{°C}$
Base-steel	695	598
Cr-steel	684	570
Mo-steel	670	571
Mn-steel	671	566

The equilibrium temperatures for complete dissolution of VN in austenite were calculated according to Eq. (3)<sup>[12]</sup>, and the corresponding results are given in Table 3. Due to preferable formation of TiN at high temperatures, the total nitrogen content for calculation of dissolution temperature is reduced for  $29 \times 10^{-6}$ .

**Table 3** Calculated temperature for complete dissolution of VN

Steel	$T_{VN}/\text{°C}$
Base steel	1078
Cr steel	1072
Mo steel	1037
Mn steel	*

$$\log[V] \cdot [N] = -\frac{7840}{T_{VN}} + 3.02 \quad (3)$$

In the lower austenitization temperature range (950–1050 °C) the great deal of vanadium is present as VN since its complete dissolution occurs at temperatures higher than 1078 °C (Table 3). Therefore, less V is available to segregate at grain boundaries, resulting in favoring formation of grain boundary ferrite in comparison to the grain boundary bainite while intragranular nucleation of acicular ferrite is promoted (Fig. 1(a)). For high austenitization temperatures (1150–1300 °C), the microstructure of the base steel consists predominantly of acicular ferrite with some grain boundary ferrites (Fig. 1(b)). It is assumed that a coarse austenite grain size suppresses the formation of grain boundary bainite and promotes the formation of acicular ferrite<sup>[8,13–15]</sup>. According to Table 3 and the results of Roberts *et al.*<sup>[12]</sup> all of the V

is assumed to be in solid solution. However, due to the thermal dispersion V is more evenly distributed within the austenite grains<sup>[16,17]</sup>, causing a dilution of its concentration at grain boundaries and an inhibiting effect on grain boundary ferrite nucleation is precluded. Therefore, intragranular nucleation of acicular ferrite follows the formation of the grain boundary ferrites<sup>[6]</sup>.

It is assumed that the formation of an allotriomorphic ferrite layer on the prior austenite grain boundaries inhibits the formation of bainite and contributes indirectly to the intragranular nucleation of acicular ferrite<sup>[13,14,18–20]</sup>. However, this ferrite must be inserted in the sense that it should not develop into Widmanstätten ferrite or bainite at lower transformation temperature. This can be obtained by the partitioning of carbon into the austenite at the austenite/ferrite interface, providing the local increase in concentration of carbon large enough to depress the local Widmanstätten ferrite or bainite start temperature below the heat-treatment temperature<sup>[14]</sup>. Therefore, promotion of grain boundary ferrite will encourage intragranular acicular ferrite nucleation<sup>[21]</sup>. The addition of Cr, Mo and Mn in quenched and tempered steels suppresses the formation of allotriomorphic ferrites and pearlite, enhancing the formation of martensites and/or bainites<sup>[15]</sup>. In the present steels, Mn and Mo effectively suppress the formation of grain boundary allotriomorphic ferrite and promote the formation of bainite (Figs. 2 and 4). This effect is slightly more pronounced in Mn steel due to low content of N and somehow higher content of V who is very well known for its hardenability effect. In the case of Cr steel, resulting microstructure obtained after continuous cooling from austenitizing temperatures does not reveal bainites, but ferrite idiomorphs and allotriomorphic and acicular ferrite. It seems that the Cr content used in this work is too low to suppress the formation of grain boundary ferrite and produce typical hardening effect, *i.e.* the presence of bainite or martensite (Fig. 3).

The data of Table 2 indicate that the addition of Mn, Cr and Mo decreases the  $B_s$  temperature in medium carbon V microalloyed steels. The acicular ferrite formation start temperature (base steel) is apparently higher than the bainitic ferrite transformation start temperature (Mn and Mo added steels). The Cr added steel does not seem to follow this pattern. In Mn steel, an additional phenomenon is important. All nitrogen is present as TiN, due to low content of nitrogen (Table 1), resulting in practically nitrogen free steel. Therefore, the formation of VN during cooling and further nucleation of acicular ferrite on VN particles are not occurring.

#### 4.2 Strength

In all four steels, the pronounced yield point was not observed. Since the bainites are characterized by

a high density of mobile dislocations<sup>[21]</sup>, only 0.2% offset stress was possible to be determined. A higher yield stress of the base steel (which exhibits a higher  $B_s$  temperature) in comparison to the Mn, Cr and Mo added steels is assumed to be due to more pronounced precipitation strengthening by VN second phase particles<sup>[22,23]</sup>. Since the  $B_s$  temperatures at which bainite (Mn and Mo added steels) or acicular ferrite (Cr added steel) form are lower, the precipitation of VN will not be pronounced due to reduced diffusivity<sup>[24]</sup>.

The strain hardening rate of bainitic sheaves is very high<sup>[25]</sup> in comparison to the ferritic/pearlitic microstructure, resulting in a higher ultimate tensile strength. In the Mn and Mo steels, this effect leads to a larger difference between yield and ultimate tensile strength in comparison to the base steel. On the other hand, this cannot fully explain the highest UTS obtained in steel with Cr addition.

#### 4.3 Toughness

The change of CVN20 energy in Fig. 5 reflects microstructural changes, confirming a strong structure sensitivity of toughness. The fine ferrite-pearlite structure which is present alongside with acicular ferrite in base steel reheated in the low temperature range exhibits the highest toughness. The CVN20 energy decreases with increasing austenitization temperature reflecting a decrease of fraction of ferrite-pearlite in microstructure in favor of acicular ferrite. However, acicular ferrite steels (base and Cr steel) exhibit a better toughness than bainitic steels (Mn and Mo steels). These low values of toughness in Mo and Mn added steels are attributed to contribution of both: (i) dominant presence of bainitic sheaves and (ii) the large packet size of bainitic sheaves. Bainitic sheaves have low capacity of stopping propagation of brittle crack; this behavior is more pronounced when bainitic sheaves form larger packets<sup>[26]</sup>.

The process of nucleation on inclusions, together with the autocatalytic nucleation, leads to a chaotic arrangement of plates and fine-grained interlocking microstructure characteristic of acicular ferrite. Such microstructures are better suited to deflect propagation of cleavage cracks and therefore more desirable from toughness point of view in comparison to bainitic sheaves<sup>[3,8,18]</sup>.

### 5. Conclusions

The effects of austenitizing temperature and small additions of Cr, Mo and Mn on transformation behavior and final microstructure and mechanical properties of V microalloyed medium carbon steel have been studied by means of optical metallography and mechanical testing

(1) The addition or enrichment of Mn and Mo suppresses the formation of grain boundary ferrite,

pearlite and acicular ferrite and promotes the formation of bainite in medium carbon V-microalloyed steel, while the level of Cr used in this work leads to ferrite-pearlite-acicular ferrite structure.

(2) The Cr, Mn and Mo added steels exhibit a lower yield strength in comparison to the base steel principally due to less effective strengthening by V(C,N) particles.

(3) The impact toughness increases as microstructure change in the following sequence: bainitic sheaves, acicular ferrite and fine ferrite-pearlite.

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