Characterization of Precipitates in Vanadium and Titanium Microalloyed Steels

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Transmission electron microscopic observations were carried out on carbon extraction replicas prepared from two commercial V-microalloyed steels and one commercial Ti-microalloyed steel hot rolled to 10 mm diameter bars at different rolling conditions.

The presence of about 0.13% Cu in V- or Ti-microalloyed steels led to the formation of copper sulphides preferentially rather than manganese sulphides although the steels containing more than 1% Mn. In Ti-microalloyed steel, globular titanium carbosulphides of the type $Ti_4C_2S_2$ are observed in addition to copper sulphide.

In V-steels, transmission electron microscopy revealed very fine precipitates in the pro-eutectoid ferrite (≈ 5 nm) which are identified as carbides or carbonitrides of the type $M(C,N)$ ($M=V$ and Cr , where $V/Cr \approx 5$). Some relatively coarse particles ($\approx 0.1 \mu m$) were also observed (with $V/Cr > 15$) which are suggested to be V-nitrides or carbonitrides formed at relatively high temperatures in austenite.

In Ti-steel, coarse titanium nitride particles ($> 5 \mu m$) were observed together with precipitates of the type MC ($M=Ti$ and Cr) in the form of very fine precipitates (≈ 5 nm, $Ti/Cr \approx 9$) or relatively coarse carbide particles ($\approx 0.1 \mu m$, $Ti/Cr > 30$).

KEY WORDS: vanadium microalloyed steel; titanium microalloyed steel; transmission electron microscopy; precipitates; electrolytic chemical analysis.

1. Introduction

In recent years, successful improvement in the mechanical properties of low-carbon steels has been achieved by microadditions of strong carbide-forming elements such as niobium, vanadium or titanium. Such microalloyed steels have higher strength levels as a result of grain refinement of ferrite. The resulting fine-grained structure is often further strengthened by fine precipitates of particular alloy carbide. For strengthening ferrite, the precipitate must be fine and for niobium steel, it has been estimated that for maximum strength the particle diameter should be about 3 nm.¹⁾

Precipitation strengthening has been examined in high

purity steels.^{2,3)} However, no attention has been given to the effects of element present in the commercial steels such as copper and chromium on the precipitation behaviour of V- or Ti-microalloyed steels. The present study presents the transmission electron microscopic observations carried out on commercial V- and Ti-microalloyed steels in the hot rolling condition.

2. Experimental

Transmission electron microscopic observations were carried out on carbon extraction replicas prepared from two V-steels and one Ti-steel, melted in electric arc furnace from commercial steel scrap and hot rolled to

Table 1. The chemical analysis and rolling condition of V- and Ti-microalloyed steels.

	Steel No.	Chemical composition (wt%)										Rolling condition (°C)	
		C	Mn	Si	P	S	Al	Cr	Cu	V	Ti	T_R	$T_{F,R}$
V-steels	V1	0.166	1.161	0.405	0.048	0.027	0.056	0.113	0.097	0.120	0.003	1 250	1 000
	V2	0.287	1.185	0.579	0.046	0.019	0.026	0.205	0.175	0.152	0.003	1 250	800
Ti-steel	Ti1	0.204	1.395	0.332	0.049	0.034	0.035	0.103	0.134	0.003	0.118	1 250	800

T_R : reheating temperature, $T_{F,R}$: finish-rolling temperature.

Table 2. Electrolytic chemical analysis of V- and Ti-microalloyed steels.

(a) V-steels

Steel No.	Temp. (°C)	V_p (wt%)	V_s (wt%)	N (wt%)				
				N_t	$N_{(nit)}$	$N_{(AlN)}$	$N_{(VN)}$	N_s
V1	1 250	—	0.1200	0.0114	0.0010	0.0010	—	0.0104
	1 000	—	0.1200	0.0114	0.0010	0.0010	—	0.0104
V2	1 250	0.0005	0.1515	0.0124	0.0005	0.0003	0.0002	0.0119
	800	0.0036	0.1484	0.0124	0.0024	0.0012	0.0012	0.0100

(b) Ti-steel

Steel No.	Temp. (°C)	Ti_p (wt%)	Ti_s (wt%)	N (wt%)				
				N_t	$N_{(nit)}$	$N_{(AlN)}$	$N_{(TiN)}$	N_s
Ti1	1 250	0.0915	0.0265	0.0137	0.0133	0.0003	0.0130	0.0004
	800	0.0997	0.0183	0.0137	0.0137	0.0003	0.0134	—

 V_p, Ti_p : insoluble V and Ti, respectively,

 V_s, Ti_s : soluble V and Ti, respectively,

 N_t : total nitrogen,

 $N_{(nit)}$: nitrogen combined as nitrides,

 $N_{(AlN)}$: nitrogen bound with Al,

 $N_{(VN)}$: nitrogen bound with V,

 $N_{(TiN)}$: nitrogen bound with Ti,

 N_s : free nitrogen.

 N_t = Total nitrogen (is determined)

 $N_{(nit)}$ = Nitrogen combined as nitrides (is determined)

 N_s = Free nitrogen = $N_t - N_{(nit)}$
 $N_{(AlN)}$ = Nitrogen bound with Al (is determined)

 $N_{(VN)}$ = Nitrogen bound with V = $[N_{(nit)} - N_{(AlN)}]$ in V-steels

 $N_{(TiN)}$ = Nitrogen bound with Ti = $[N_{(nit)} - N_{(AlN)}]$ in Ti-steels

Fig. 1. Schematic presentation of analytical steps used to determine the fraction of nitrogen as vanadium nitride and aluminium nitride in V-microalloyed steels, and as titanium nitride and aluminium nitride in Ti-microalloyed steels.

 ϕ 10 mm bars at different rolling conditions.

 The rolling condition and chemical analysis of steels used in these observations are given in **Table 1**.

Transmission electron microscopy was carried out on a Philips EM400 electron microscope equipped with energy dispersive X-ray facilities. Carbon extraction replicas for transmission electron microscopy were prepared as following:

- polishing using diamond paste of 2 μ m,
- etching in 3% nital solution (containing 3 vol% HNO_3),
- carbon deposition, and
- ungluing in 10% nital solution (containing 10 vol%

Fig.2. Copper sulphides observed on carbon replica from V-steel (Steel VI).

- Transmission electron micrograph showing the two types of CuS observed (globular and elongated)
- Electron diffraction pattern obtained from CuS (hexagonal CuS-Zone axis [001] of type $\langle 001 \rangle$)
- X-ray microanalysis of particle 1 in (a)

 HNO_3).

The particle size was measured from magnified TEM images.

Some specimens were water-quenched immediately after austenitizing for 20 min at 1 250°C. Others

water-quenched from finish-rolling temperatures. Water-quenched specimens (from austenitizing temperature or finish-rolling temperature) were subjected to electrolytic chemical analysis to determine the amount of undissolved vanadium or titanium, and consequently the wt% of vanadium or titanium in solution. The nitrogen combined as total nitrides and as aluminum nitride were determined by the Beeghly method.⁴⁾ By subtracting the amount of nitrogen in aluminum nitride, $N_{(AlN)}$, from total nitride the amounts of nitrogen bound with vanadium, $N_{(VN)}$, or that bound with titanium, $N_{(TiN)}$, were calculated in V- or Ti-microalloyed steels. The methodology for analytical determination of the form of nitrogen is shown in Fig. 1. The results of these analysis are given in Table 2.

Light microscopic observations carried on specimens of hot rolled and normal air cooled bars, after polishing and etching in 2% nital solution showed ferrite-pearlite structure in the three V- and Ti-microalloyed steels.

3. Results

3.1. Vanadium Steels

An appreciable amount of copper sulphides in the form of globular (0.2–1.0 μm diameter) or elongated (up to 10 μm long) were observed and identified as hexagonal CuS by electron diffraction, Figs. 2(a) to 2(c). The results of X-ray microanalysis gave the following composition: 67% Cu and 33% S, which corresponds to the stoichiometric composition of CuS.

The precipitates observed in the V-steels were essentially constitutions of vanadium-rich particles with

face centered cubic (FCC) crystal structure, Figs. 3 and 4. Because of the similarity between the crystal structure and lattice parameters of vanadium carbide and vanadium nitride,⁵⁾ it was difficult to differentiate VC and VN by transmission electron microscopy. Furthermore, the carbon and nitrogen are not detectable by the X-ray microanalysis system used.

Three sizes of vanadium-rich particles were classified:

- coarse particles with diameter of about 0.1 μm (with $V/Cr > 15$), Fig. 4(a),
- globular particles of about 20 nm, and
- very fine participates of about 5 nm (with $V/Cr \approx 5$), Fig. 3 and 4(b).

To be noted are the absence of carbide (or carbonitride) precipitation in the pearlitic ferrite (as shown in Fig. 3(c)) and the enrichment in Cr of the very fine precipitates ($\approx 15\%$ Cr), Fig. 4(b). Some mixed carbides of vanadium and titanium were also found in V-steel (steel V2) although the presence of titanium is only as traces (0.003% Ti), Fig. 4(c).

3.2. Titanium Steel

Titanium steel showed several types of non-metallic inclusions and precipitates. The observed non-metallic inclusions are classified into three categories:

- some coarse cuboidal titanium nitride particles (5–10 μm side length), Figs. 5(a) and 5(b),
- several globular (1 μm of diameter) or elongated (up

Fig. 3. Precipitation in V-steels.

- (a) Transmission electron micrograph-precipitates of $V(C, N)$
- (b) Electron diffraction (FCC structure compatible with VC and VN)
- (c), (d) Transmission electron micrographs illustrate the absence of precipitation in pearlitic ferrite and the fine precipitation of $V(C, N)$ in ferrite

Fig. 4. X-ray microanalysis on V-rich particles in V-steels (steels V1 and V2).

- (a) Coarse V-carbonitride particle ($\approx 0.1 \mu\text{m}$)
- (b) X-ray microanalysis of very fine precipitates ($\approx 5 \text{ nm}$). The enrichment in Cr is noted in these precipitates ($\approx 15\%$ Cr).
- (c) Mixed carbide $(V + Ti)C$ —(Steel V2)

Fig. 5.

Titanium nitrides, titanium carbosulphides and copper sulphides observed in Ti-steel (Steel Ti1).

- (a), (b) Coarse TiN
- (c) Transmission electron micrograph showing elongated copper sulphide (1) and globular titanium carbosulphide (2)
- (d) Electron diffraction pattern obtained from particle 2 in (c) (hexagonal $Ti_4C_2S_2$, Zone axis $[210]$ of type $\langle 10\bar{1}0 \rangle$)
- (e) X-ray microanalysis of copper sulphide (1 in (c))
- (f) X-ray microanalysis of Ti-carbosulphide (2 in (c))

to 10 μm long) copper sulphide, **Figs. 5(c) and 5(e)**, and

- several globular titanium sulphide or carbosulphide (0.2–0.5 μm of diameter), occasionally associated with copper sulphide, **Figs. 5(c) to 5(f)**.

No attempt was made to identify the copper sulphides observed in Ti-steel, but their composition obtained from X-ray microanalysis was slightly different from those observed in V-steels (78 % Cu and 22 % S which is closer to Cu_2S than CuS).

Titanium sulphide was identified by electron diffraction as hexagonal titanium carbosulphide $Ti_4C_2S_2$, **Fig. 5(d)**. Titanium to sulphur ratio in these particles obtained from X-ray microanalysis was found to be 3 to 1 which corresponds to 2 atoms of titanium for 1 atom of sulphur.

The fine precipitates found in Ti-steel were Ti-rich particles and were observed in two forms:

- plates of square geometry with varying sizes from 0.05 to 0.1 μm in side length, identified by electron diffraction as TiC with FCC crystal structure, **Figs. 6(a) and 6(b)**, and
- very fine TiC precipitates in ferrite (about 5 nm in diameter), **Figs. 7(a) and 7(b)**.

X-ray microanalysis carried out on these two types of

precipitates showed that the coarse plates contain only titanium and that Cr is present in the very fine particles (90 % Ti and 10 % Cr), **Figs. 6(c) and 7(c)**. In Ti-steel, similarly with V-steels, the absence of precipitation in pearlitic ferrite was noted, **Fig. 7(a)**.

4. Discussion of Results

In V-steels, transmission electron microscopy revealed a fine dispersion of precipitates in the pro-eutectoid ferrite (≈ 5 nm) which are identified as carbides or carbonitrides of the type $M(C, N)$ ($M = V$ and Cr , where $V/Cr \approx 5$). Some coarse particles ($\approx 0.1 \mu m$) were also observed (with $V/Cr > 15$) which are suggested to be V-nitrides or carbonitrides formed at relatively high temperatures (in austenite) due to the low solubility of vanadium nitride comparing with vanadium carbide.⁶⁾

In Ti-steel, coarse titanium nitride particles ($> 5 \mu m$) were observed together with precipitates of the type MC ($M = Ti$ and Cr) in the form of very fine precipitates (≈ 5 nm, $Ti/Cr \approx 9$) or relatively coarse carbide particles ($\approx 0.1 \mu m$, $Ti/Cr > 30$).

Electrolytic chemical analysis and wet chemical analysis (Table 2) showed that all nitrogen was consumed

Fig. 6. Coarse TiC observed in Ti-steel (Steel Ti1).
 (a) Transmission electron micrograph
 (b) Electron diffraction pattern obtained from particle 1 in (a) (TiC, Zone axis [100])
 (c) X-ray microanalysis of the particle 1 in (a)

Fig. 7. Very fine TiC observed in Ti-steel (steel Ti1).
 (a), (b) Transmission electron micrographs showing the very fine TiC precipitates in ferrite and the absence of precipitation in pearlitic ferrite
 (c) X-ray microanalysis of fine TiC precipitates

as TiN which remained undissolved even at 1250°C. Due to the high stability of TiN, it precipitates at very high temperatures, most likely in the liquid state^{7,8)} as coarse particles.

The relatively coarse titanium carbide particles (0.05–0.1 μm) seem to be those which were undissolved

at reheating or formed at relatively high temperatures (in austenite) during rolling.

The very fine precipitates ($\approx 5\text{ nm}$) are likely to be formed during the austenite to ferrite transformation. The enrichment in Cr of the very fine precipitates of V-carbonitride (with $\text{V/Cr} \approx 5$) and titanium carbide (with $\text{Ti/Cr} \approx 9$) comparing with the relatively coarse precipitates of V-rich particles (with $\text{V/Cr} > 15$) and Ti-rich particles (with $\text{Ti/Cr} > 30$) may confirm this explanation because of the high solubility of chromium carbides in austenite.⁹⁾

The presence of about 0.13% Cu in steels led to the formation of copper sulphides preferentially rather than manganese sulphide although the steels containing more than 1.0% Mn.

In Ti-steel, globular titanium carbo-sulphides of the type $\text{Ti}_4\text{C}_2\text{S}_2$ are present in addition to copper sulphide. In his study on Ti-microalloyed steels, Williams¹⁰⁾ has considered that MnS should be the only sulphide present in Ti-microalloyed steels with high manganese contents above 1%. The present study shows the high affinity of titanium to sulphur even in the presence of high manganese contents.

The coarse titanium-nitrides and carbo-sulphides reduce the amount of dissolved titanium in austenite available to precipitate as titanium carbide during the austenite to ferrite transformation and so detract from the precipitation strengthening.

5. Conclusions

In hot rolled V- and Ti-microalloyed steels, transmission electron microscopy revealed several types of non-metallic inclusions and precipitates:

(1) Globular (0.2–1.0 μm diameter) and elongated (up to 10 μm long) copper sulphides identified as CuS and Cu_2S in vanadium and titanium microalloyed steels, respectively.

(2) Globular titanium carbo-sulphide $\text{Ti}_4\text{C}_2\text{S}_2$ (0.2–0.5 μm of diameter) and coarse cuboidal titanium nitride particles (5–10 μm side length) in Ti-microalloyed steel.

(3) Very fine precipitates in the pro-eutectoid ferrite ($\approx 5\text{ nm}$) identified as carbides or carbonitrides of the type $M(\text{C}, \text{N})$ ($M = \text{V}$ and Cr , where $\text{V/Cr} \approx 5$) in V-steels and carbides of the type MC ($M = \text{Ti}$ and Cr , where $\text{Ti/Cr} \approx 9$) in Ti-steel.

(4) Relatively coarse ($\approx 0.1\text{ }\mu\text{m}$) particles of V-nitrides or carbonitrides (with $\text{V/Cr} > 15$) in V-microalloyed steels, and Ti-carbides (with $\text{Ti/Cr} > 30$) in Ti-microalloyed steel.

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