8306-026

PROCESSING CHARACTERISTICS AND PROPERTIES OF Ti-V-N STEELS

Tadeusz Siwecki
Institutet för Metallforskning
S-114 28 Stockholm, Sweden

Alf Sandberg
Institutet för Metallforskning
S-114 28 Stockholm, Sweden

William Roberts
Institutet för Metallforskning
S-114 28 Stockholm, Sweden

ABSTRACT

The incentive to develop Ti-V microalloyed steels stems from the desire to combine the excellent grain-coarsening characteristics of Ti-grades with the effective precipitation strengthening derived from vanadium, especially when the latter is combined with nitrogen. The present study has been undertaken to establish the degree to which V and excess N detract from the grain-coarsening resistance of a Ti-steel, and to determine whether or not the presence of Ti modifies the precipitation-strengthening from V(C,N).

It is found that Ti-V-N alloys are, in the as-cast condition (strand), characterized by GCT's only marginally lower than steels based on Ti-only. However, in hot-rolled material, the presence of fine V(C,N) in addition to (Ti,V)N can result in a deterioration of the grain-growth inhibition. The effective elimination of grain growth of austenite both during and following hot rolling renders Ti-V-N grades especially suitable for recrystallization rolling, whereby relatively fine as-rolled ferrite grain sizes can be achieved via conventional schedules with finishing temperatures in the range 900-1000°C. The precipitation-strengthening potential of vanadium and nitrogen is diminished somewhat when, in addition, Ti is present. The reason for this is partly that vanadium is combined as stable (Ti,V)N-particles which are responsible for the limitation of grain growth at high temperatures, and partly that V(C,N) deposits epitaxially on pre-existing (Ti,V)N-particles in austenite following the termination of rolling. Both these effects reduce the amount of vanadium and nitrogen available for strengthening via precipitation in ferrite.

THE USEFULNESS OF SMALL ADDITIONS of Ti (<0,02%) in microalloyed steels stems from the extreme stability of titanium nitride (TiN) precipitates. Particles of pure TiN are resistant to both coarsening and dissolution during reheating and hot rolling, and in association with welding (HAZ). With continuous-casting technology, it is feasible to produce fine TiN-precipitates even in the as-cast condition (average size of particles, 5-20 nm); these remain comparatively stable throughout subsequent processing. Microstructurally, the principal benefit derived from the presence of such a dispersion is an enhanced resistance against austenite grain growth. Hence, Ti-steels can be processed to give relatively fine as-hot-rolled ferrite grain sizes even when the finish-rolling temperature (FRT) is quite high. The reason for this is that a fine austenite grain size is attained via static recrystallization when rolling is finished in the temperature range 900-1000°C, and, most important, that such a fine microstructure can be retained during cooling down to Ar_3 because of the grain-growth inhibition via TiN; furthermore, the latter is effective in limiting grain growth between the individual rolling passes. This type of high-FRT thermomechanical processing is called *recrystallization rolling* and is a realistic alternative only with Ti-microalloyed grades (1).

Another useful effect of the grain-growth inhibition derived from a fine TiN-dispersion is the very pronounced limitation of HAZ-grain coarsening during welding of Ti-microalloyed steels. For a given welding cycle, the resulting austenite grain size is smaller in Ti-steels than for other microalloyed grades and the HAZ-hardness, after transformation, is therefore lower (greater volume fraction of polygonal ferrite as opposed to plate-ferrite products). The low hardness and high proportion of polygonal ferrite in the HAZ confer good impact toughness and superior resistance to hydrogen embrittlement irrespective of whether hydrogen is introduced during welding or in subsequent service (e.g.H_2S-environment).

At the alloying levels which have been found to confer optimum grain-growth inhibition characteristics (<0,02%), titanium does not engender any pronounced strengthening in microalloyed steels. Hence, for HSLA grades, it is necessary that Ti be combined with some other microaddition. Vanadium would seem to be a suitable candidate for two reasons:

i) the element is comparatively soluble in austenite and the formation of compounds, type (Ti,V)(C,N), during reheating and hot rolling are less likely to detract too seriously from its precipitation-hardening potential; and
ii) the rather weak effect of vanadium on the kinetics of static recrystallization above 900°C is desirable from the point of view of effective grain refinement via recrystallization hot rolling (i.e. recrystallization can proceed to completion at a sufficiently low temperature, which will not always be the case for, say, Ti-Nb austenite).

The present paper is therefore concerned with the possibility to combine vanadium and titanium additions in microalloyed steels. Such an endeavour is motivated by a general interest to produce fine-grained HSLA-steels with moderate to high strengths via straightforward rolling schemes involving high finishing temperatures (>900°C). Apart from yielding an attractive product, such rolling procedures carry the additional advantages of high throughput potential combined with rolling loads with are manageable for most mills. Attention is focussed on steels having (wt.%) 0,13C-1,5Mn-0,01Ti base with vanadium and nitrogen levels in the range 0,03-0,13 and 0,01-0,02 respectively. Questions of particular concern have been:

i) if and to what degree the grain-coarsening inhibition derived from TiN is impaired by a Ti:N ratio less than the stoichiometric one (excess nitrogen being required for effective precipitation hardening from V);
ii) whether effective grain refinement via recrystallization rolling is feasible in Ti-V-N steels over the entire range of vanadium and nitrogen contents studied; and
iii) to what extent the presence of Ti detracts from the precipitation-hardening potential of vanadium.

MATERIALS AND EXPERIMENTS

STEELS EXAMINED — The results reported in this paper pertain to four Ti-V-N microalloyed steels, with various levels of vanadium and nitrogen, which originated from Svenskt Stål AB, Oxelösund. The analyses (wt.%) are tabulated below:

TABLE 1

Designation	C	Mn	Si	P	S	Al	V	Ti	N
A	0,14	1,59	0,44	0,012	0,013	0,029	0,029	0,009	0,011
B	0,14	1,51	0,45	0,014	0,011	0,025	0,036	0,013	0,011
C	0,14	1,22	0,35	0,021	0,019	0,027	0,061	0,010	0,013
D	0,13	1,47	0,42	0,014	0,019	0,023	0,130	0,011	0,023

Steels A-C were full-scale BOF-charges and, in each case, material was provided in both as-strand-cast and as-hot-rolled (16 mm plate) conditions. Variant D was prepared as a 50 kg laboratory ingot and was tested for the most part in the as-cast condition. The conditions during solidification and cooling of the ingot were such as to closely approximate those prevailing during strand casting. The as-received material was formed into suitable specimens for determination of the grain-coarsening resistance (10x10x10 mm cubes) and for hot-compression testing (cylinders, $H_{o}\mathrm{x}\emptyset_{o}$ =15x10 mm).

THERMOMECHANICAL TREATMENT — The hot-compression equipment used in the present study is built up around a 100 kN MTS servo-hydraulic testing machine. A detailed description of the apparatus has been given previously, e.g. (2). Quenching of the specimen can be effected at any particular point in a thermomechanical treatment by rapidly withdrawing the lower compression tool into a water spray located beneath the furnace.

For the rolling simulations, the specimens were first austenitized for 5 min. at 1200°C. The reduction scheme adopted comprised four steps each involving a 20% height reduction; the first three were performed at 1150, 1075 and 1000°C while the temperature for the final deformation step was varied between 800 and 950°C. Cooling during the deformation phase of the thermomechanical schedule and during the subsequent $\gamma \to \alpha$ transformation was such as to simulate rolling and air cooling of 40 mm and 12 mm plate (average rate of temperature fall between 750 and 550°C = 0,25 and 0,9°C/s respectively). In some cases, the application of accelerated cooling between the FRT and a 'water-end temperature' in the range 600-700°C was simulated; the cooling rate subsequent to the forced cooling was reverted to the rate characteristic for the plate thickness under consideration. The strain rate during compression was nominally $2s^{-1}$ which is within the range typical for hot rolling of plate. For each combination of steel and deformation scheme, a specimen was 'quenched out' immediately prior to the start of transformation in order to characterize the prior austenite microstructure.

METALLOGRAPHIC EXAMINATION — Grain-size determination (linear intercept) was effected via standard methods on samples etched in 1%-nital (ferrite-pearlite) or saturated aqueous picric acid containing a wetting agent (prior austenite grain boundaries). Characterization of precipitates with electron microscopy was carried out on extraction replicas and foils; the general examination relied on a JEOL 1000D HVEM while a Vacuum Generators HB 501 STEM instrument was used for high-resolution analytical microscopy.

YIELD-STRENGTH DETERMINATION— Small compression specimens (H_o= 5 mm, $\emptyset_o$=5 mm) were machined from previously thermomechanically-processed samples and used for evaluation of the 'as-rolled' lower-yield strength (R_{eL}). Compression tests were performed in a 250 kN Schenk-Trebel machine at 20°C and $\dot{\varepsilon}= 5.10^{-4}s^{-1}$; the R_{eL}, values given are mean values from four separate determinations.

GRAIN-COARSENING BEHAVIOUR

EFFECT OF DIFFERENT VANADIUM AND NITROGEN CONTENTS — The grain-coarsening temperature (GCT) of Ti-microalloyed steels in the as-continuously-cast condition is very high, usually 1200-1300°C, so it is pertinent to inquire to what extent the resistance to abnormal grain growth is impaired when, in addition, vanadium and excess nitrogen (w.r.t. stoichiometry with Ti) are present. The GCT's characterizing the various steels in the *as-cast condition* are listed in the table below (heating rate to temperature = 4°C/s; time at temperature = 30 min.):

TABLE 2

Steel$^{x)}$	GCT (°C)	D^{γ} at GCT (µm)
A (0,029V; 0,011N)	1210	17,4
B (0,036V; 0,011N)	1190	17,2
C (0,061V; 0,013N)	1170	16,8
D (0,130V; 0,023N)	1210	16,7

x) 0,009-0,013 Ti

The above values for GCT are probably somewhat lower than might be expected for steels with 0,01-0,015 Ti and a near-stoichiometric amount of nitrogen (∿0,005 N), for which 1220-1250°C is typical (3-7). Increasing the vanadium and nitrogen contents to high levels does not seem to affect the GCT adversely. The probable reason why the GCT is reduced in steels with Ti:N< stoichiometric can be gleaned from standard solubility arguments (Fig.1). An austenite with excess nitrogen will start to form TiN, after solidification, at a higher temperature than if Ti:N were equal to the stoichiometric value; hence, the amount of Ti present as *small* TiN-particles, formed at, say, 1400°C or lower, is less in the former case.

The usual impression conveyed in the literature is that abnormal grain growth is invariably associated with ripening and dissolution of the restraining particles. However, this is not true for Ti or Ti-V austenite since the TiN-dispersion is virtually unaltered during holding at <1250°C. The crux of the matter lies in the *distribution of grain sizes* under the relevant conditions of holding. Following Hellman and Hillert (8), the growth rate of spherical grains with radius R is given by

$$\frac{dR}{dt} = \alpha\sigma.m.(1/R_{cr} - 1/R \pm Z) \qquad (1)$$

where α is a constant (∿1 for a three-dimensional grain array), σ is the grain-boundary energy, m the grain-boundary mobility and R_{cr} is the size of a grain which is neither growing nor shrinking. $Z\sigma$ is the Zener drag which for spherical inclusions (radius, r, volume fraction, f) is $3\beta f/4r$ where β corrects for the fact that particle-boundary contact is possible over a larger distance as the boundary curvature decreases (8). From Eq.(1), normal grain growth stops when all grain sizes satisfy the inequality:

$$R_{cr}/(1+ZR_{cr}) \leq R \leq R_{cr}/(1-ZR_{cr}). \qquad (2)$$

Making the rather arbitrary assumption that the mean grain size when Eq.(2) is satisfied is the same in two- and three-dimensional systems, then the grain-size limit defined by the particle dispersion is

$$\bar{R}\ (\mathrm{limit}) = 1/3Z = 4r/9\beta f. \qquad (3)$$

When further grain growth is inhibited by particles R_{cr} can be approximated to $\bar{R}$ (limit)(8).

It is clear from Eqs.(1) and (2) that when grains of size R_i exist in an assembly with average size $\bar{R}(\mathrm{limit}) \equiv \bar{R}$, then growth of such grains can continue if $R_i/\bar{R} > 1/(1-\bar{R}Z)$ i.e. if $R_i > 1{,}5\bar{R}$. Furthermore, the form of Eq.(1) is such that the growth rate of such grains is initially very slow but increases markedly as the relative size, $R/\bar{R}$, increases. Hence, abnormal grain growth can proceed even in a situation where the majority of grains are pinned by stable precipitates; the prerequisite that the particles are in the process of ripening or dissolving is no longer a necessary one. From Eq.(1), it is also evident that the growth rate of abnormal grains will be faster if $\bar{R}$(limit) is decreased or m increased (higher temperature). The GCT is the temperature at which the integrated $\frac{dR}{dt}$ during the relevant holding time is sufficient to engender a noticeable difference between the size of the abnormal grains and that in the 'matrix' of average grains.

At first sight, the above arguments are at variance with the experimental observations discussed earlier that excess nitrogen, and a concomitantly reduced volume fraction of small TiN particles, is consistent with a lower GCT. Theoretically, a decrease in f should give a greater limiting grain size and thereby an *augmented* resistance to abnormal grain growth (Eqs.(1) and (3)). However, in low-carbon steels, the likely situation is that the austenite grain

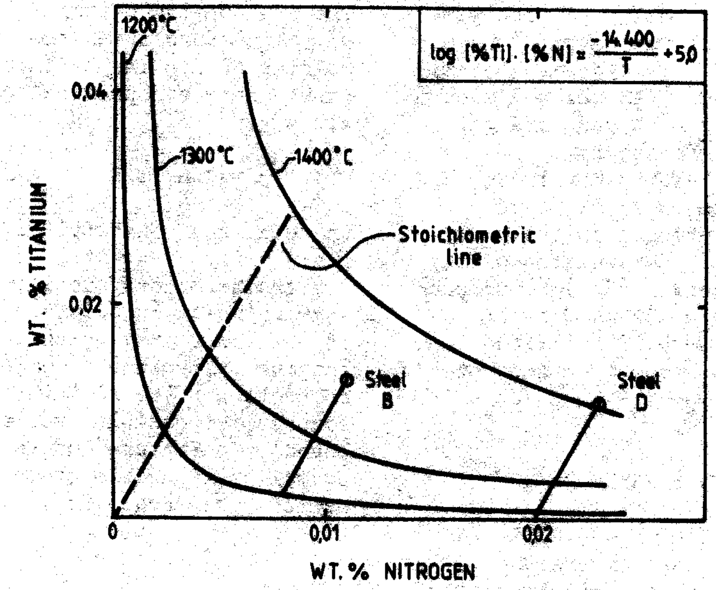


Fig. 1 Solubility curves illustrating the effect of a nitrogen level exceeding the stoichiometric value w.r.t. Ti on the volume fraction and temperature of formation of TiN (solubility data from Matsuda and Okumura (3)).

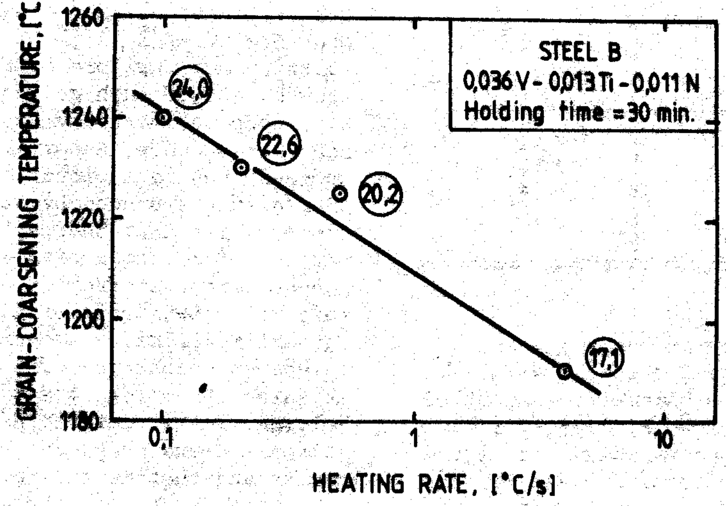


Fig. 2 Effect of heating rate on GCT for steel B. Encircled numbers refer to the size of small austenite grains at the GCT.

size engendered by transformation from ferrite + pearlite is usually greater than $\bar{R}$(limit) and there is no normal grain growth up to a size prescribed by the particle dispersion. This is supported by the data in Table 2 where $\bar{R}$ is about the same for all steels in spite of quite large differences in the amount of nitrogen present (i.e. different volume fractions of small TiN particles). In this instance, i.e. $\bar{R}$ is *independent* of Z, Eq.(1) predicts that the GCT is increased if the volume fraction of TiN, and thereby Z, is raised, which is in agreement with observation.

A corollary of the above argument is that the the GCT of Ti and Ti-V microalloyed steels should be a function of heating rate; $\bar{R}(\alpha\rightarrow\gamma)$ will increase with decreasing heating rate and the GCT should be raised accordingly. Data for steel B (0,036V-0,013Ti-0,011N) which support this contention are presented in Fig.2. If $\bar{R}(\alpha\rightarrow\gamma)$ were less than $\bar{R}$(limit), then one would expect that normal grain growth up to a limiting value should proceed after transformation, leading to a GCT which is independent of heating rate. The data in Fig.2 demonstrate that for heating rates typical for reheating of slabs, the GCT's of Ti-V steels are about 50°C higher than the values given in Table 2.

One additional consideration relevant to Ti-V-N steels is the possibility that 'TiN'-particles may contain vanadium and therefore be less soluble than pure TiN. STEM microanalysis of specimens held for 30 min. at the GCT and then quenched gives the following results (for a more detailed presentation see ref.(9)):

TABLE 3

Steel	Particle size	Approximate composition of 'TiN'
B(0,036V;0,011N)	5-40 nm	$(Ti_{0,9}V_{0,1})N$
D(0,130V;0,023N)	10 nm	$(Ti_{0,25}V_{0,75})N$
"	40 nm	$(Ti_{0,4}V_{0,6})N$
"	80 nm	$(Ti_{0,45}V_{0,55})N$

For the low-V variant, the composition of the particles is sufficiently close to TiN that their solubility can to a first approximation be regarded as the same as that of the latter. Similar studies on 0,01Ti-0,05Nb steels (10) indicate that the particles inhibiting grain growth at high temperatures have the approximate composition $Ti_{0,6}Nb_{0,4}N$. Since the solubility of NbN in austenite is less than that of VN, it is perhaps reasonable that x in $Ti_{1-x}Q_xN$ is greater when Q≡Nb than when Q≡V. The particles in the high-vanadium steel, D, are considerably more vanadium-rich than in steel B, as might be expected. In addition, a clear dependence of Ti:V ratio on particle size was found; hence, for the larger inclusions, which are formed at higher temperatures, the equilibrium Ti:V ratio is greater than for those particles nucleated later on during cooling (small). Naturally, the volume fraction of (Ti,V)N-particles in steel D is considerably greater than in the low-V alloy; however, the GCT's are not much different (Table 2). In addition, the average particle size is greater for steel D suggesting that the (Ti,V)N-particles with low Ti:V ratio are characterized by a faster rate of coarsening than 'pure' TiN, presumably because of their greater solubility. Hence, our earlier statement, that the 'TiN'-dispersion is completely stable during reheating at the GCT, may not be justified in the case of Ti-V-N steels with high levels of vanadium and nitrogen.

GRAIN COARSENING AFTER HOT ROLLING — From early work on Ti-microalloyed steels (e.g.refs. (6,7)), it is known that the GCT of hot-rolled material is lower than in the cast condition, i.e. reheating more than once impairs the grain-coarsening resistance. This behaviour can readily be understood in terms of the refinement of the average austenite grain size engendered by multiple reheating, i.e. $\bar{R}(\alpha\rightarrow\gamma)$ is reduced and thereby the GCT (Eq.(1)).

The GCT of steels A and B (0,029 and 0,036V respectively) in the as-hot-rolled condition were determined as 1080 and 1060°C for heating at 4°C/s; the corresponding austenite grain sizes were 13,6 and 14,1 µm. Hence, hot rolling causes a reduction in GCT by up to 150°C (compare with Table 2). This decrease in the resistance to abnormal grain growth is too great to be completely accounted for in terms of the reduced size of the small matrix grains (17→14 µm).

Some effort has been expended in trying to account for the reduction in GCT of Ti-V austenite which is brought about by hot-roll processing. The following observations are pertinent:

i) The size distributions of (Ti,V)N-particles in the as-cast and hot-rolled conditions are only marginally different (Fig.3). As-cast steel is characterized by a greater number of fine particles (cube edge <8 nm) and a somewhat larger spread in the distribution, althought the average size is very nearly the same in both instances.
ii) The GCT of as-cast material can be altered quite dramatically by performing a prior austenitization treatment and cooling at varying rates. Results from a series of experiments, involving heating cast material to 1150°C, 30 min. and cooling at different rates followed by a GCT-determination in the normal way, are shown in Fig.4. Corresponding austenite grain sizes at the GCT are also given. The grain-coarsening resistance is augmented very markedly as the cooling rate in association with prior processing is reduced, i.e. the GCT is highest for a cooling rate appropriate to 220 mm strand.
iii) The GCT of steel B in the as-hot-rolled condition can be restored more or less completely, 1060 to 1190°C, via annealing in the α+γ region (750°C, 2h). However, this effect seems to be coupled with a considerable coarsening of the austenite grain size, which was 25 µm after such an intercritical-annealing treatment.

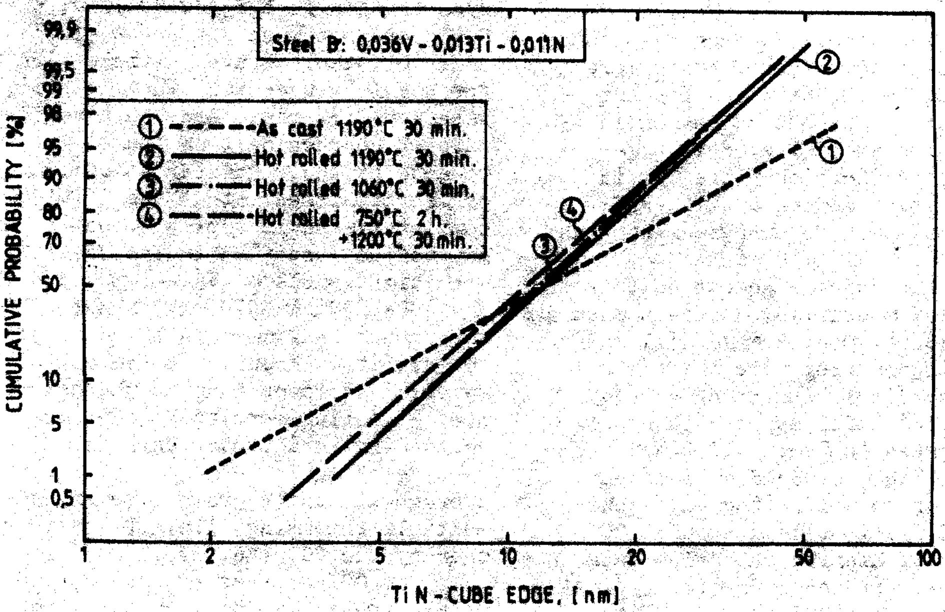


Fig.3 Cumulative TiN-particle-size distributions for steel B in various conditions.

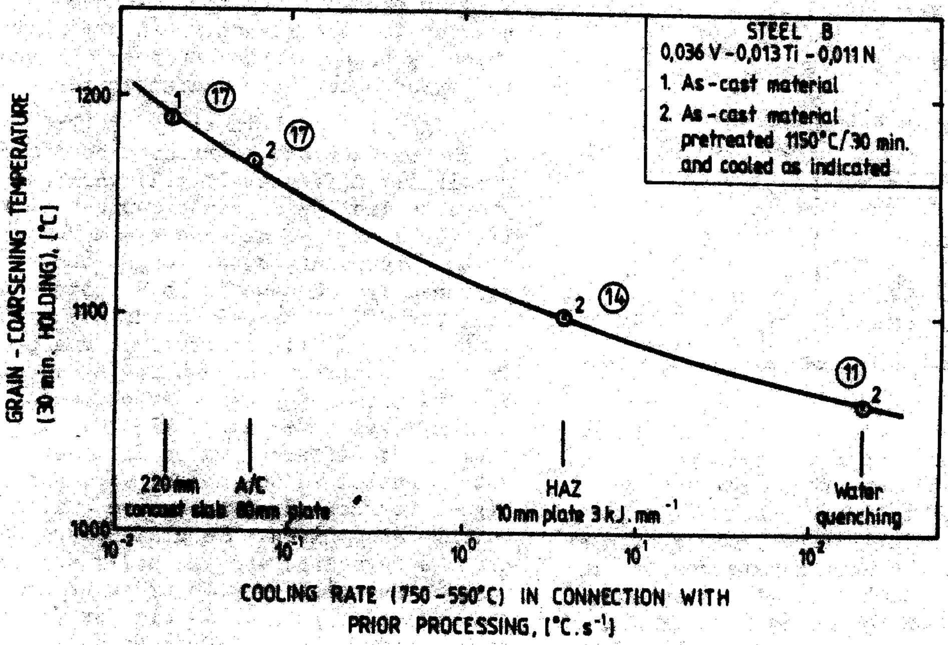


Fig.4 Illustrating the effect of cooling rate during previous processing on the GCT of steel B. Encircled numbers are average diameters of the 'matrix' austenite grains at the GCT.

The above findings suggest that the marked decrease in grain-coarsening resistance of hot-rolled Ti-V austenite owes its origin to the bimodal precipitate dispersion ('TiN' + V(C,N)) which is present on reheating from ferrite. The typical appearance of precipitates in as-hot-rolled steel B is shown in Fig.5; the number of V(C,N)-particles greatly exceeds that of TiN. On reheating, the austenite grains formed after transformation are pinned mainly by V(C,N). The latter ripen and dissolve successively during holding at >1000°C (solution temperature for VN in steel B assuming all Ti is combined as TiN is ca. 940°C). When V(C,N) disappears, a number of grain-boundary segments which are not in contact with any TiN-particles, are released and some limited grain growth can proceed. This will have the effect of widening the grain-size distribution (many segments remain immobile, pinned by TiN) and increasing the risk for abnormal grain growth (i.e. $R_i/\bar{R}$ for the critical grains is initially greater and the GCT is lowered accordingly). Such behaviour will be characteristic for a situation where the V(C,N)-particles are smaller and more prolific than TiN; the effect will be much less noticable if V(C,N) and TiN exist as equally-sized inclusions or if the former are larger (the probability that segments are pinned by V(C,N) only is then reduced). This reasoning is in agreement with the observations on the effect of cooling rate after prior processing on GCT, which are summarized in Fig.4, because the average size of V(C,N)-inclusions is expected to increase with decreasing cooling rate. Moreover, the improvement in GCT of as-hot-rolled material engendered by intercritical annealing is, on this basis, a combined effect of the increase in austenite grain size (pre-existing γ nuclei) and coarsening of V(C,N)-particles which is likely to be appreciable after 2h at 750°C.

In further support of the above rationale, it is noteworthy that pretreatment of steel B in the as-hot-rolled condition (i.e. after reheating once) at 1050°C,30 min followed by cooling at 0,06°C/s (≡80 mm plate, 750→550°C), causes the GCT to increase to 1130°C (as-hot-rolled GCT = 1060°C; 16 mm plate). Clearly, for Ti-V austenite, the cooling rate after prior processing has a greater bearing on the GCT than the number of times the steel is reheated.

One might suspect that the diminished grain-coarsening resistance of Ti-V steels after hot rolling will be of some significance when it comes to welding. In practice, however, the thermal cycle during welding is sufficiently rapid that abnormal grain growth does not proceed to any great extent. For example, after a weld cycle involving heating at 300°C/s to 1350°C, holding 6s and then cooling at 10°C/s to 800°C before quenching, the austenite grain size in steel B (as rolled) is only 45 µm compared with ca. 200µm for a correspondingly-treated 0,03%Nb -microalloyed steel (9). The fact that the Zener drag from TiN is present throughout the welding cycle means that the integrated dR/dt (Eq.(1)) is in no case excessive, in spite of the fact that the grain-size distribution, in itself, might well be conducive to abnormal grain coarsening.

MICROSTRUCTURE EVOLUTION DURING HOT ROLLING

The behaviour of Ti-V steels during hot rolling is discussed in detail in a companion paper in these proceedings (1). The principal effect derived from the presence of TiN-particles is the virtual elimination of grain growth both between rolling passes and, more importantly, during cooling between the FRT and Ar_3. The Zener drag from TiN-inclusions also engenders a significant decrease in the rate of static recrystallization especially following small prestrains.

STATIC RECRYSTALLIZATION – The recrystallization characteristics of 0,01Ti-0,04V-0,01N austenite (i.e. steels A and B) in association with hot deformation are discussed in detail in (1). The empirical dependences of time to 50% recrystallization ($t_{0,5}$) and recrystallized grain size (D_{rex}) on pre-existing grain size (D_o), strain (ε) and temperature (T°K) are ($t_{0,5}$ in s, D_{rex} in µm):

$$t_{0,5}=5.10^{-18}.(\varepsilon-0{,}058)^{-3{,}5}\ D_o^2\ \exp\left(\frac{280.000}{RT}\right) \quad (4)$$

and

$$D_{rex}=4{,}3+195{,}7.D_o^{0{,}15}\ \varepsilon^{-0{,}57}\left[\exp\left(\frac{350.000}{RT}\right)\right]^{-0{,}11} \quad (5)$$

respectively. These relationships have been established via single-step, strain/hold experiments using the hot-compression equipment described earlier.

In order to establish the effect of raised vanadium and nitrogen contents on the static-recrystallization behaviour, a number of hot-compression tests were run on steel D (0,13V-0,023N). Some grain-size data from experiments involving holding for 10s after prior deformation to various strains at different temperatures are given in Fig.6. For 7% height reduction at all temperatures and for 15% reduction at 1000°C or less, recrystallization is incomplete after 10s and the grain size is not much different from the pre-existing one (12,6 µm). However, following a 30% reduction, the reaction does go to completion within 10s at all temperatures, D_{rex} being coarser than D_o at 1100°C but somewhat refined at 900°C.

Results for D_{rex} from a considerable number of deformation/hold experiments with different holding times conform to the following empirical relationship,

$$D_{rex}=1{,}1+170{,}0.D_o^{\ 0{,}15}\ \varepsilon^{-0{,}57}\left[\exp\left(\frac{350.000}{RT}\right)\right]^{-0{,}11} \quad (6)$$

which is valid for Ti-V-N steels with 0,08<%V <0,13 and ∿0,02%N. Eqs.(5) and (6) together with all relevant data points are plotted in Fig.7, from which it is clear that increasing the vanadium and nitrogen levels in a Ti-V-N austenite

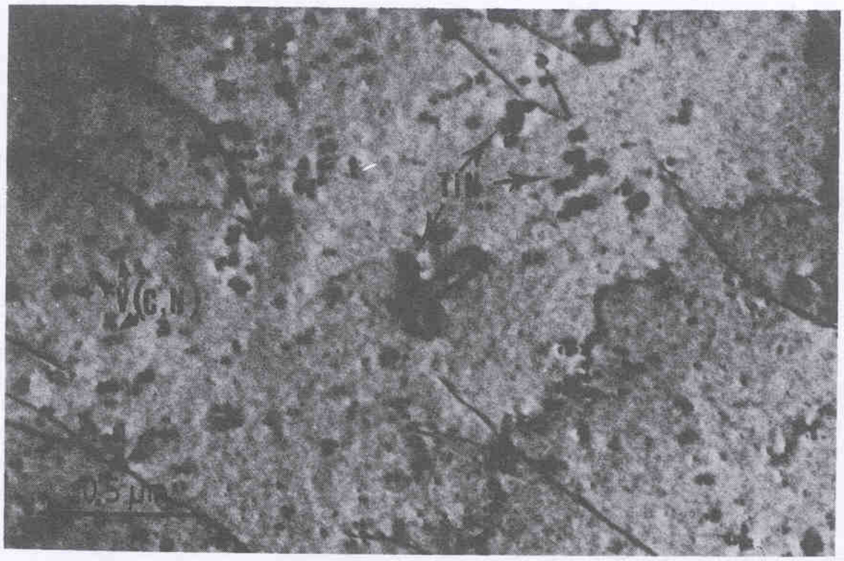


Fig.5 Particles in steel B in the as-rolled condition (16 mm plate); thin foil, HVEM.

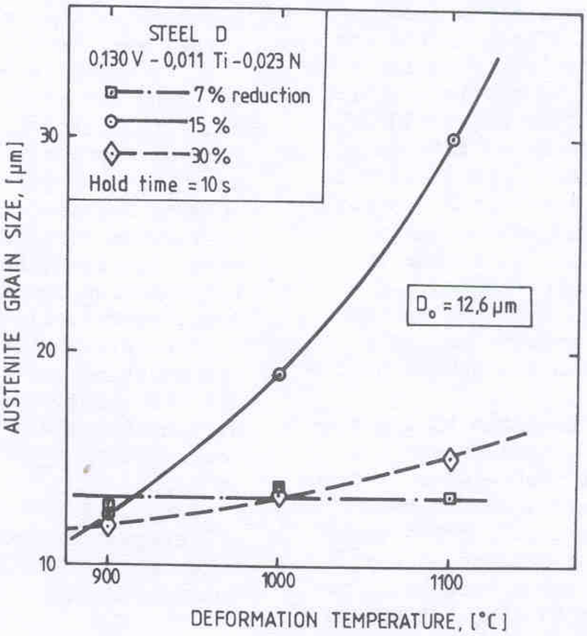


Fig.6 Average grain size as a function of height reduction and temperature for the high-V, high-N variant, steel D. Hot compression, holding time =10s.

is concomitant with a reduced recrystallized grain size, all other things being equal (ε, D_o, T). Similar observations have been reported earlier for V-N steels (11). The recrystallization kinetics of Ti-V-N austenite are evidently not particularly affected if the vanadium and nitrogen levels are increased and the experimental observations on steel D conform tolerably well to Eq.(4).

PREDICTION OF MICROSTRUCTURE EVOLUTION —Optimization of rolling schedules for processing of Ti-V-N steels by recrystallization hot rolling requires detailed knowledge pertaining to the coupling between rolling schedule (temperatures, reductions, inter-pass times) and the development of microstructure (static recrystallization and recovery, grain growth, austenite to ferrite transformation). In the companion paper mentioned above (1), the essence of a computer model for predicting microstructure evolution during hot rolling is presented. For Ti-V steels with 0,01%Ti, 0,03-0,04%V and 0,01%N (i.e. steels A and B in the present work), the predictions of the model, with regard to the relationship between deformation scheme and the concomitant microstructural alterations, is well confirmed in both laboratory hot-compression experiments and full-scale rolling.

This computational routine has even been applied to Ti-V-N austenites with augmented levels of V and N. Hence, Eq.(6) has been used to define the dependence of recrystallized grain size on D_o, ε and T; as regards the recrystallization kinetics and the rate of static recovery, the same behaviour as in Ti-0,04%V-0,01%N austenite has been assumed (1). Furthermore, it is presumed that the rate of grain growth is negligible. The predictions of the microstructure-evolution model have been compared with data from laboratory hot-compression testing of steel D. Samples of as-cast material which had previously been reheated for 5min. at 1200°C, were subjected to the following deformation schemes.

TABLE 4

T,(°C)	Height reduction,(%)		
	Scheme 1	Scheme 2	Scheme 3
1150	18	17	17
1075	10	17	17
1000	10	17	17
950		17	25

The first specimen in a particular series was quenched after having undergone the initial reduction plus cooling to the temperature of the second deformation. The second sample was deformed at the first two temperatures before cooling to the third, and so forth. Hence, the development of the austenite microstructure in association with the above deformation schedules could be monitored step by step. Two specimens were subjected to all deformation steps, one being quenched from Ar_3 (∼800°C) while the other was allowed to transform to ferrite. The cooling rate during the experiments was maintained at either 0,25°C/s (scheme 1) or 0,9°C/s (schemes 2 and 3); between 750 and 550°C, these values correspond to air cooling of 40 and 12 mm plate respectively. After reheating, the austenite grain size was 13 µm. The austenite grain sizes found in the experiments outlined above are compared in Fig.8 with those predicted via the microstructure model. The measure of agreement is clearly acceptable. The experimental ferrite grain sizes for schemes 1-3 were 11,3, 7,8 and 7,1 µm respectively which compare with 11,3 8,8 and 7,2 µm evaluated theoretically (see ref. (1)).

In the companion article (1), the effect of the principal rolling variables on the degree of microstructural refinement obtainable via recrystallization hot rolling of 0,01Ti-0,04V-0,01N steel is investigated theoretically in a systematic way. It is instructive to compare the microstructural changes which are predicted for Ti-V-N steels with different levels of vanadium and nitrogen, when these are subjected to the same rolling schedule. To this end, the following reduction scheme was adopted (25 mm plate, 11 passes): 220(mm)-200-170-150-130-112-94-77-60-45-33-25. This has been combined with various rolling temperature ranges partly by altering the start temperature (1200,1100,1050°C) and partly by introducing a 60s hold between passes 6 and 7 (normal inter-pass period =10s); this gives six FRT's in all lying between 900 and 1070°C. The microstructure model has been used to evaluate the austenite grain size at Ar_3 (∼800°C); this is converted to a ferrite grain size via the correlation between D^{α} and D^{γ} given in ref.(1). Figure 9 presents a summary of the results of the calculation in the form of a plot of D^{α} versus finish-rolling temperature; the corresponding austenite grain sizes immediately prior to transformation are also indicated. A more detailed discussion of the form of such plots is given in ref.(1). For the present purposes it is sufficient to note that the microstructural refinement engendered by a given rolling scheme and cooling procedure is greater for the high-V, high-N steel. This is to be expected since we have already noted that the statically-recrystallized grain size, under otherwise identical conditions, is smaller for Ti-V-N austenite with high vanadium and nitrogen contents than for the variants with 0,04%V and 0,01%N (Fig.7).

Fig.10 compares theoretical forecasts regarding microstructural evolution for C-Mn and Ti-V-N austenite, the latter having different levels of vanadium and nitrogen, which are subjected to the same rolling schedule. These data refer to rolling of 25 mm plate in 11 passes starting from 1100°C; the initial grain size after reheating was taken to be 20 µm for the Ti-V-N steels and 300 µm in the case of C-Mn austenite. Again, the high-V, high-N steel is characterized by the most effective microstructural refinement. It is interesting to note, however, that the *recrystallized* grain

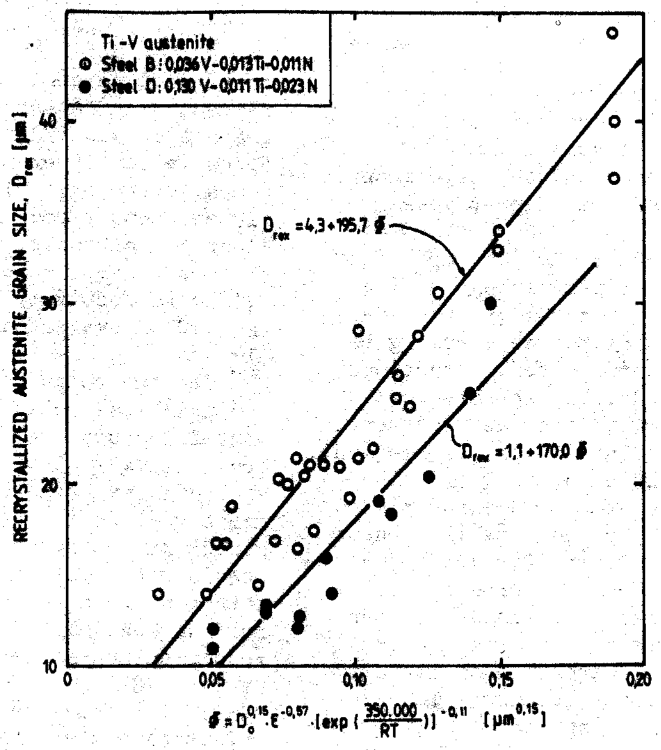


Fig.7 Correlation between statically-recrystallized grain size and strain, pre-existing grain size and temperature for Ti-V-N austenites with different levels of vanadium and nitrogen.

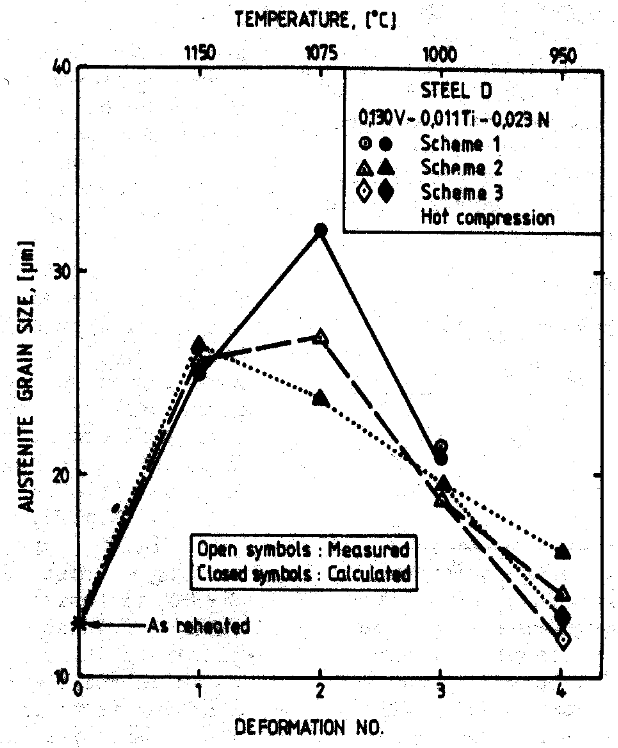


Fig.8 Comparison of observed D^{γ} with that predicted theoretically for hot-compression testing (3 or 4 steps) of Ti-V-N austenite with high-V, high-N. For further details, see Table 4 and text.

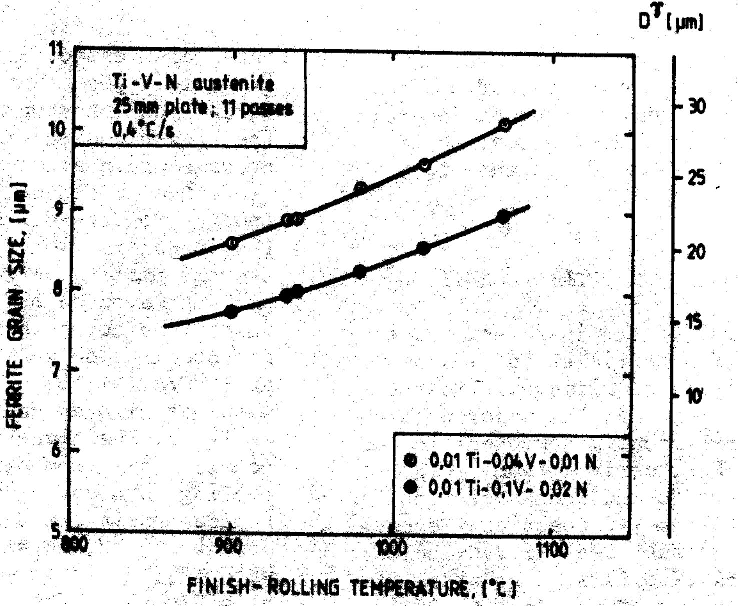


Fig. 9 Computed dependence of D^α on finish-rolling temperature for rolling 25 mm plate of Ti-V-N steels with various levels of vanadium and nitrogen (for further details, see text).

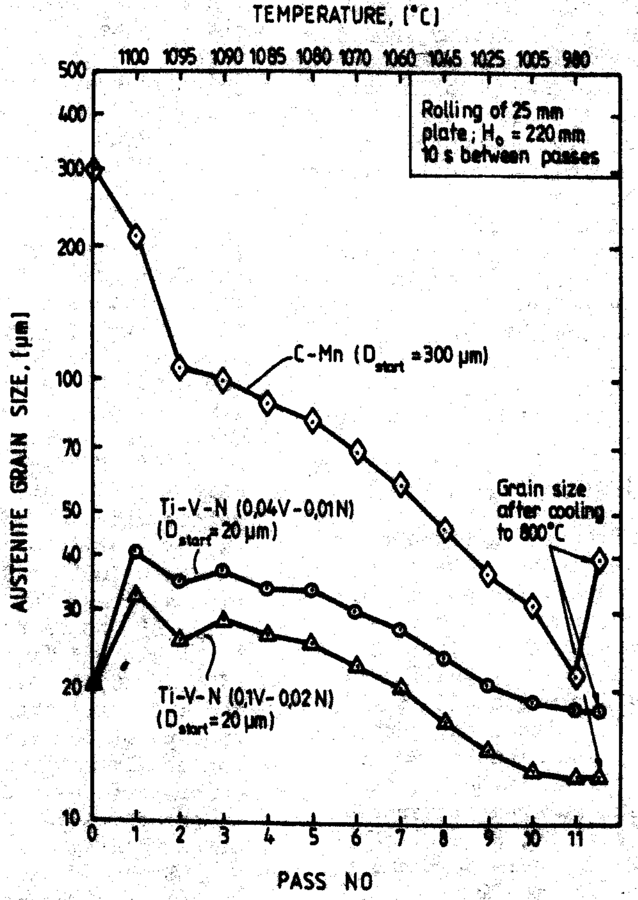


Fig. 10 Comparison of microstructure evolution in C-Mn and Ti-V austenites subjected to the same rolling schedule (for further details, see text).

size of the C-Mn steel following the final pass is actually not much larger than for the Ti-V-N austenites. However, the former is, of course, subject to grain growth and the austenite grain size increases appreciably during cooling between the FRT (in this case 980°C) and 800°C ($\sim Ar_3$).

YIELD STRENGTH IN HOT-ROLLED CONDITION

As was made clear in the introductory section, the stable (Ti,V)N-particles in Ti-V-N steels do not contribute significantly to the as-hot-rolled strength; instead, the major portion of the precipitation-hardening component in the lower-yield stress, R_{eL}, derives from V(C,N)-precipitates which are formed in association with or subsequent to the $\gamma \rightarrow \alpha$ reaction. We have already seen (Table 3) that the (Ti,V)N-inclusions in high-V,high-N materials, e.g. steel D, can contain large amounts of vanadium (>60%); this is especially true in the case of particles which have formed at relatively low temperatures during cooling of the strand. The vanadium combined with Ti as compound particles is not available for precipitation hardening. Hence, it is reasonable to expect that, for given processing, the strength level of Ti-V-N grades should be somewhat lower than for equivalent V-N steels.

Simplified simulations of recrystallization rolling have been carried out on steels A (0,029V-0,011N) and D(0,13V-0,023N) via hot compression. The deformation scheme and cooling conditions were as described earlier in the chapter on experimental methods. The ferrite grain size and lower yield stress were determined for every combination of steel, deformation scheme and cooling conditions. Fig.11 gives data for R_{eL}, D^α and the precipitation-strengthening contribution to the lower yield stress, ΔRp, as a function of finish-rolling temperature. The latter is evaluated from the regression formula for C-Mn steels recommended Gladman et al.(12):

$$\Delta R_p(\text{MPa}) = R_{eL} - \left[88 + 37\%\text{Mn} + 83\%\text{Si} + 2920\%\text{N}_f + 15{,}1(D^\alpha)^{-1/2}\right]$$

where the amount of free nitrogen is taken to be zero. Noteworthy from Fig.11 is that the increase in R_{eL} associated with a reduced finishing temperature is derived for the most part from grain refinement; furthermore, the grain size of the high-V,high-N variant (steel D) is significantly smaller than that of steel A processed in the same manner. Moreover, it is quite clear that the precipitation-strengthening contribution due to vanadium is impaired when, in addition, Ti is present. For a material with somewhat lower levels of V and N than in steel D, Siwecki et al.(11) observed $\Delta R_p \doteq 210$MPa for FRT=950°C and cooling at a rate corresponding to 12 mm plate A/C; this is twice the value for variant D found in this study (Fig.11).

The effect of accelerated cooling between 950°C and 'water-end temperatures' (T_{end}) between 600 and 700°C on R_{eL}, D^α and ΔR_p is summarized in Fig.12. Fast cooling is clearly beneficial especially when T_{end} is as low as 600°C. It would appear that for higher water-end temperatures, the transformation is not complete when the slower cooling is resumed, with coarser average grain sizes as a result. Furthermore, since the strengthening V(C,N)-precipitates are thought to form during or immediately following the transformation to ferrite, then a small average particle size, and thereby a high ΔR_p, will be favoured by fast cooling and a low T_{end}, which is exactly what is found (Fig.12). In fact, for steel A, ΔR_p=82MPa with accelerated cooling at 12°C/s ($\sim$12 mm plate) and T_{end}=600°C; this is about as high as can be expected for such a lean analysis. The high-V,high-N alloy (D) benefits considerably from being subjected to accelerated cooling both as regards increased strength and reduced grain size. For fast cooling at 10°C/s down to 650°C, ΔR_p=170MPa, which can be compared with $\sim$255MPa in an equivalent V-N steel cooled at 5°C/s (11). Thus, the addition of Ti to a high-V,high-N microalloyed steel evidently detracts from the precipitation-hardening potential even when accelerated cooling is applied, although the reduction in ΔR_p is proportionally somewhat smaller than with air cooling (see above). It is worth noting that ferrite grain sizes in the region of 6 µm are achieved in the more highly-alloyed steel via application of quite moderate accelerated cooling and this with a finish-deformation temperature of 950°C!

CORRELATION BETWEEN YIELD STRENGTH AND PRECIPITATE STRUCTURE – For steel D with 0,13%V and 0,023%N, the stable (Ti-V)N-particles which limit grain growth at high reheating temperatures contain more than 50% V. Since this vanadium is not then able to contribute to precipitation hardening, a plausible argument is that Ti-V-N grades are characterized by lower strength than equivalent V-N variants because the *available* vanadium content is reduced via its incorporation into high-temperature particles. However, even assuming an average analysis of $(Ti_{0,3}V_{0,7})N$ in steel D (Table 3), only $\sim$0,025%V will be combined in this way together with $\sim$0,01% nitrogen (if all Ti, 0,011%, is considered to be in the particles). This leaves 0,105%V and 0,013%N available for precipitation as V(C,N). According to Siwecki et al. (11), ΔR_p for a steel with these levels of V and N but without Ti is 180MPa and 220MPa for cooling (750→550°C) at 0,9 and 5°C/s respectively. The conclusion is that the smaller contribution from precipitation hardening in steel D cannot be completely rationalized on the basis of vanadium combined in particles which are stable at high temperatures and which do not contribute to strengthening.

Since VN and TiN have identical crystal structures (face-centred cubic) and very similar lattice parameters, 0,413 nm and 0,424 nm respectively, it is feasible that stable (Ti,V)N-particles can function as nucleation centres for V(C,N)-precipitation *in austenite* during cooling after the termination of rolling. In V-N steels,

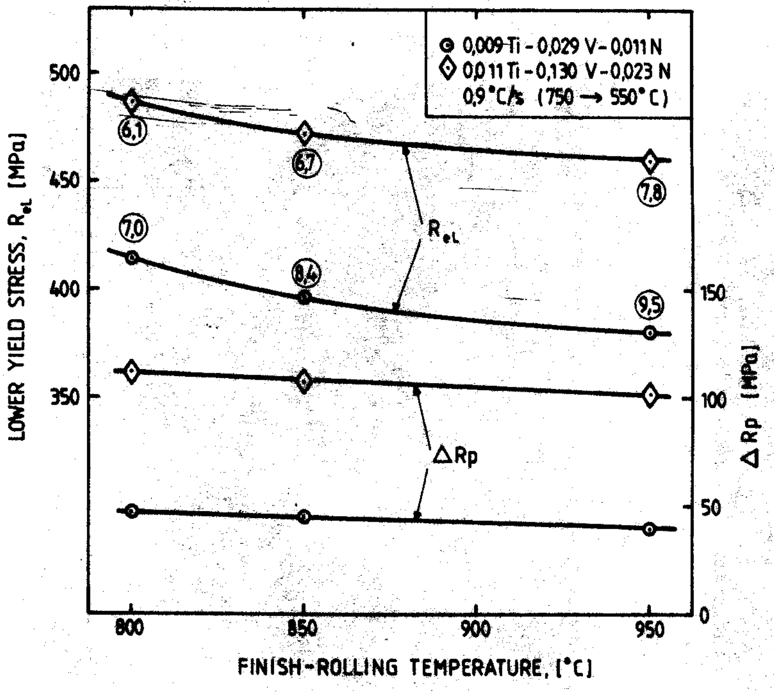
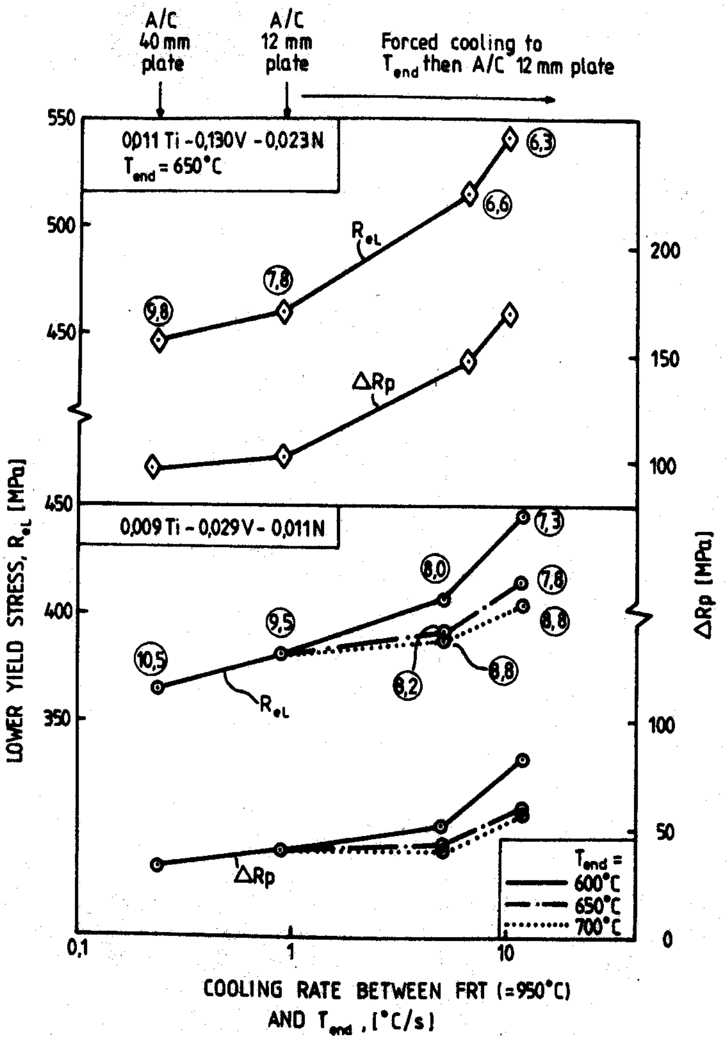


Fig.11 Lower yield stress and precipitation-hardening contribution to yield stress for Ti-V-N steels subjected to hot-rolling simulation with natural cooling (see text for details). Encircled numbers refer to D^{α}.

Fig.12 Lower yield stress and precipitation-hardening contribution to yield stress for Ti-V-N steels subjected to hot-rolling simulation combined with accelerated cooling (see text for details). Encircled numbers refer to D^{α}.



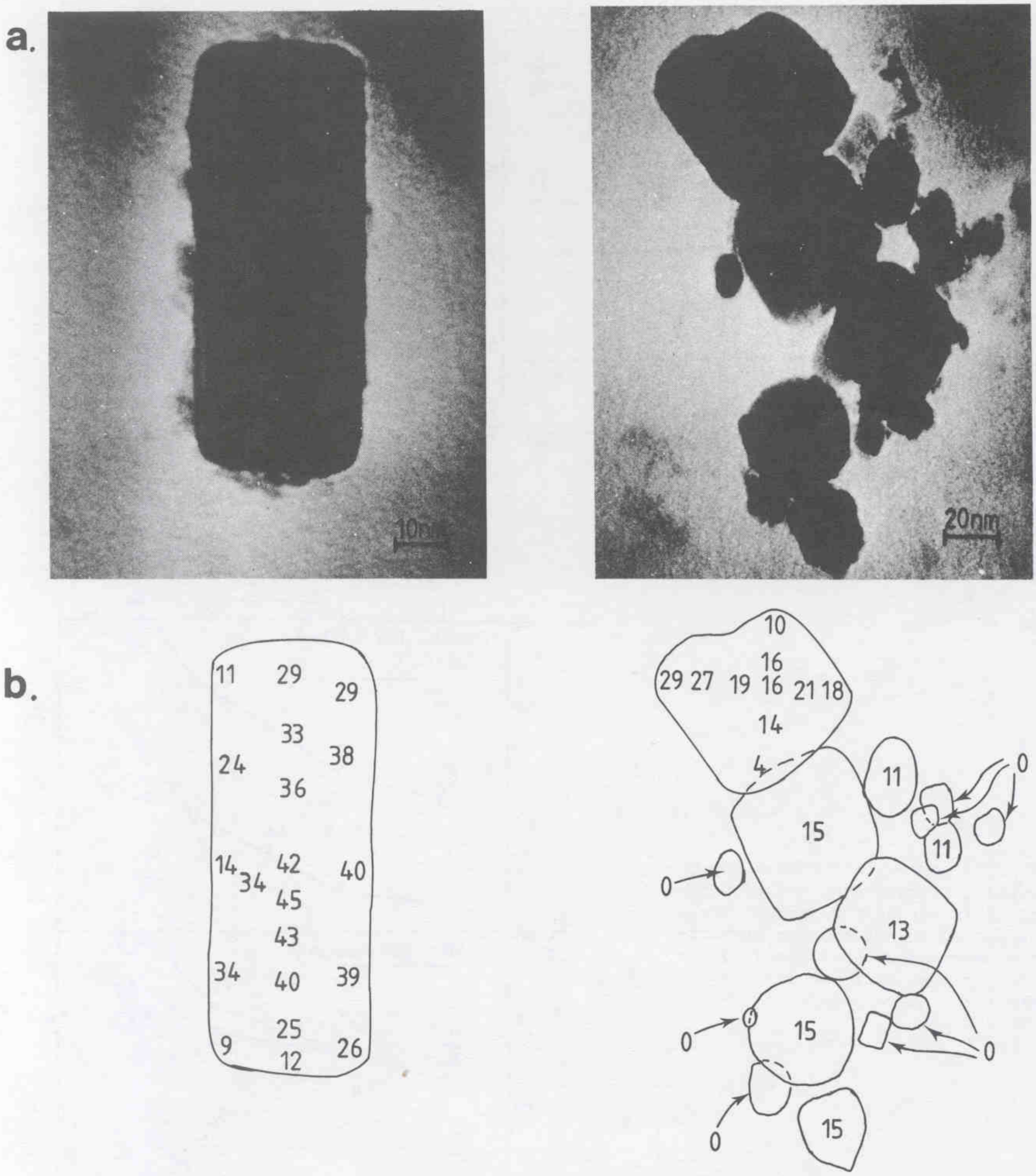


Fig.13 a) Precipitates in steel D subjected to hot-rolling simulation and cooling (750→550°C) at 0,9°C/s (STEM; carbon-extraction replica).
b) Ti-content (% of metal atoms) at various points within the particles (EDS).

it is generally accepted that particles are not formed in austenite if the FRT is high (>900°C), the rate of precipitation being low in undeformed austenite because of the difficulty of nucleation. However, the rate of precipitation of V(C,N) may well be considerably higher for Ti-V-N steels, if the reaction proceeds via continued growth of existing (Ti,V)N-particles, because of the elimination of the nucleation step. This being the case, the levels of vanadium and nitrogen available for useful precipitation in ferrite will be limited further.

In order to test the above rationale, a number of specimens of steel D (high-V,high-N) in the as-hot-deformed condition (cooling at 0,9°C/s) were subjected to very careful STEM-microanalysis.Two typical examples of the observed precipitate structures are presented in Fig.13 together with keys showing Ti-concentrations both in different individual particles and at different points within one and the same particle. The single (Ti,V)N-particle shown on the left is relatively large (70x25 nm) and has a composition in its central portions which corresponds to approximately $(Ti_{0,4}V_{0,6})N$; the composition is similar at its right-hand edge. The bottom of the particle and the left-hand edge, on the other hand, correspond more closely to $(Ti_{0,1}V_{0,9})N$. These results constitute evidence, in the most concrete way possible, for continued growth of pre-existing (Ti,V)N-particles via a fully epitaxial deposition of V(C,N) at their peripheries. The reason why such growth has apparently proceeded preferentially in two directions is not clear. It would also appear that some interdiffusion of V and Ti takes place within the particle during growth since the latter element is always registered even in areas where the particle has apparently grown via incorporation of V(C,N). In the right-hand plate showing the collection of particles in Fig.13, the larger precipitates (10-50 nm) contain Ti, albeit rather modest amounts (10-30% of the metal atoms); all smaller particles (5-10 nm) are 'pure' V(C,N) and have almost certainly been formed in association with the transformation to ferrite. The interpretation of the r.h. plate in Fig.13 is that the larger particles are originally (Ti,V)N, with approximate composition $(Ti_{0,5}V_{0,5})N$, after the termination of rolling. These then develop further,during cooling from the FRT down to Ar_3, via deposition of V(C,N) combined with interdiffusion of V and Ti such that the average vanadium level is increased throughout the inclusions. Following transformation to ferrite, the driving force for V(C,N)-precipitation is now so great that interphase or homogeneous nucleation of this compound can occur separately, independent of the pre-existing Ti-bearing particles.

The average composition of the compound particles in steel D is about $(Ti_{0,2}V_{0,8})N$ which will tie up ∿0,05%V and ∿0,016%N (on the assumption that all Ti is combined), leaving 0,08%V and 0,007%N for V(C,N)-formation. For these V and N levels, Siwecki et al.(11) report ΔR_p=130 and 180MPa for cooling at 0,9 and 5°C/s respectively (steel without Ti); these values are in the vicinity of the ΔR_p's found for alloy D in this study (Fig.12). The conclusion is, therefore, that the diminished ΔR_p in Ti-V-N steels as compared with equivalent Ti-free grades, stems from a reduction in the level of vanadium available for precipitation in ferrite, partly because it is incorporated in the highly-stable Ti-containing inclusions responsible for restricting grain growth, and partly because of the tendency for V(C,N) to deposit in austenite on the pre-existing (Ti,V)N-particles. If accelerated cooling is applied after rolling, it is to be expected that growth of pre-existing (Ti,V)N via epitaxial deposition of V(C,N) will proceed to a lesser extent and, concomitantly, that the relative reduction in ΔR_p for Ti-V-N steels, as compared with Ti-free grades, will be smaller; this is what is found in practice (see previous section).

Very similar observations to the ones discussed above have been made by Houghton et al. (10) on 0,01Ti-0,05Nb steels. Their materials were controlled rolled and it is likely that the compound (Ti,Nb)N-inclusions were formed during the hold period between predeformation and finishing. The demarcation between Ti- and Nb-rich zones in the particles examined by them was also much sharper than has been found for inclusions in the present Ti-V-N steels, which suggests that the interdiffusion of V and Ti in fcc MX-compounds is considerably faster than that of Nb and Ti.

SUMMARY

An investigation pertaining to the grain-coarsening resistance, hot-roll processing and precipitation strengthening of Ti-V-N steels has uncovered the following:

i) In austenite containing Ti-only or Ti with <0,04%V, the dispersion of TiN or (Ti,V)N-particles responsible for restraining grain growth is quite stable at the GCT. Abnormal growth of selected grains can occur even when the vast majority of other grains are pinned by inclusions which are neither ripening nor dissolving.

ii) The addition of vanadium and nitrogen, in excess of the stoichiometric amount (w.r.t.TiN), to a Ti-steel results in only a marginal decrease in grain-coarsening resistance *in the as-continuously-cast condition.*

iii) The GCT of a given Ti-V austenite is a fairly sensitive function of heating rate; the size of the small 'matrix' grains decreases with increasing heating rate with a concomitant loss of grain-coarsening resistance. This observation suggests that the austenite grain size engendered by $\alpha \rightarrow \gamma$ is greater than the particle-limited grain size, i.e.that existing when normal grain growth is arrested.

iv) The GCT of Ti-V austenite which has previously been *hot rolled* is considerably less than that in the as-continuously-cast condition. This is associated with the unfavourable grain-size distribution developed when V(C,N) dissolves at relatively low temperatures; the finer the V(C,N)-dispersion, the more pronounced is the loss in grain-coarsening resistance. Hence, the GCT is augmented if cooling following prior processing is slow or by intercritically annealing the steel in $(\alpha+\gamma)$.

v) For Ti-V austenite, the particles responsible for the restriction of grain growth at high temperatures are $Ti_xV_{1-x}N$ where x increases with the vanadium level in the steel. For a steel with 0,13%V and 0,011%Ti, the present observations also indicate that x increases with decreasing particle size.

vi) The principal benefit accruing from the presence of Ti during hot rolling is the complete elimination of grain growth of austenite, both between rolling passes and during cooling once rolling has been terminated. An important consequence of this is that relatively fine ferrite grain sizes can be achieved in as-hot-rolled Ti-V steels even when the finish-rolling temperature is relatively high (900-1000°C); fine statically-recrystallized grains are preserved down to Ar_3 (recrystallization rolling).

vii) For steels with $\sim$0,01%Ti, the statically recrystallized grain size, for given conditions of strain, temperature and pre-existing grain size, decreases with increasing levels of V and N. Hence, the overall degree of grain refinement engendered by a given rolling scheme is greater for a Ti-steel with say 0,1%V and 0,02%N than one with only 0,04%V and 0,01%N.

viii) The precipitation-strengthening contribution to the as-hot-rolled yield stress derived from V(C,N)-particles formed during or subsequent to the $\gamma\rightarrow\alpha$ transformation, is lower for Ti-V-N steels than for corresponding alloys without titanium; the effect is especially pronounced at low rates of cooling. The vanadium and nitrogen available for precipitation strengthening are diminished both via combination with Ti as stable (Ti,V)N-particles and via continued growth of the latter after the termination of hot rolling, through epitaxial deposition of V(C,N) *in austenite*.

ACKNOWLEDGEMENTS

The investigation reported here was supported by Union Carbide Corporation, Metals Division. It is a pleasure to acknowledge the stimulating cooperation with Michael Korchynsky of that organization. The steels studied were provided by Svenskt Stål AB, Oxelösund and special thanks are due to Åke Josefsson and Tommy Werlefors of Svenskt Stål for helpful guidance and discussion.

REFERENCES

1. Roberts, W., A.Sandberg, T.Siwecki and T.Werlefors, these proceedings.
2. Roberts, W., Swedish Institute for Metals Research Report No. 1333 (1978).
3. Matsuda, S. and N.Okumura, Trans.Iron & Steel Inst.Japan, 18, 198-205 (1978).
4. O'Donnel, D., British Steel Corp. Report GS/PROD/420/2/75C (1975).
5. Horigome, T., S.Kanazawa et al. in "Welding of HSLA (Microalloyed)Structural Steels", Eds. A.B.Rothwell and J.M.Gray, pp. 679-705, ASM, Metals Park, Ohio (1978).
6. George, T.J. and J.J.Irani, J.Australian Inst. Metals, 13, 94-106 (1968).
7. George, T.J. and N.F.Kennon, J.Australian Inst.Metals, 17, 73-80 (1972).
8. Hellman, P. and M.Hillert, Scand.J.Metallurgy, 4, 211-219 (1975).
9. Siwecki, T., A.Sandberg and W.Roberts, to appear in the report series of the Swedish Institute for Metals Research.
10. Houghton, D.C., G.C.Weatherly and J.D.Embury, in "Thermomechanical Processing of Microalloyed Austenite", Eds. A.J.DeArdo, G.A.Ratz and P.J.Wray, pp. 267-292, Met.Soc. A.I.M.E., Warrendale, Pennsylvania (1982).
11. Siwecki, T., A.Sandberg, W.Roberts and R. Lagneborg, as ref.10, pp. 163-194.
12. Gladman, T., D.Dulieu and I.D.McIvor, in "Microalloying 75", Ed.M.Korchynsky, Vol.1, pp. 32-55, Union Carbide Corp., New York (1976).