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The effect of titanium and reheating temperature on the microstructure and strength of plain-carbon, vanadium- and niobium-microalloyed steels

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A series of plain-carbon, vanadium- and niobium-microalloyed steels with or without titanium addition were used to evaluate the effect of a small amount of titanium addition on the properties of steels. Titanium inhibits austenite grain coarsening during reheating and grain refinement was observed when the reheating temperature was below the austenite grain coarsening temperature. The lower the reheating temperature, the less was the observed precipitation strengthening effect of V(C, N). The addition of titanium to microalloyed steels reduces the precipitation strengthening effect of V(C, N) but has no visible effect on that of Nb(C, N). The mechanism of reducing the strengthening effect of V(C, N) is possibly caused by the depletion of available nitrogen content for V(C, N) formation.

1. Introduction

During the past two decades the technology of microalloying and thermomechanical treatment of steels has been extensively developed. This has resulted in significant progress in the production and application of high-strength low-alloy (HSLA) steel. Among the three commonly mentioned microalloying elements such as noibium, vanadium and titanium, the application of titanium has scarcely been reported. This may be due to the fact that titanium is more liable to oxidation [1] so that the recovery of titanium in steelmaking is both low and unstable. Consequently, the variation of product properties is considerable. Recently new steel-making techniques have been available such as vacuum degassing and alloy wire feeding in tun-dish and mould. These new techniques decrease the titanium loss and enable more accurate titanium content control in steel. Furthermore, the beneficial effects of titanium on the steel properties such as reducing the austenite grain size during rolling [2, 3], controlling the shape of sulphide inclusions [4] and suppressing grain coarsening in the heat-affected zone (HAZ) of weldment [5–9] have been reported. These developments have motivated steel makers to add a small amount of titanium (around 0.015%) to steel to improve the properties of steel, especially for weldability enhancement. It is well known that a small amount of titanium added to steel will form very stable TiN particles in steel during cooling from solidification.

These particles can hardly be altered in the subsequently thermomechanical processing [3]. Even in the high-temperature region of the HAZ during welding, the TiN particles are able to restrict the coarsening of austenite grains and refine the transformed microstructure. The tougness of the HAZ can thus be improved.

Although the beneficial effect of titanium on weldability has been widely accepted and applied, its effect on the properties of the base metal is still unclear. For example, it has been found that the addition of titanium to vanadium-bearing steel will decrease the precipitation strengthening effect of V(C, N) [10], but the mechanism and the method of recovering the strength loss are not well known. It is also unclear whether niobium-bearing steel suffers a strength loss in the case of titanium addition.

The purpose of this study is to evaluate the effect of a small amount of titanium addition on the properties of plain-carbon, vanadium- and niobium-bearing steels.

2. Experimental procedure

Twelve experimental steels were prepared form 125 kg vacuum melt heats and cast as ingots 80 mm in thickness and 160 mm in width. The chemical compositions of these steels are listed in Table I. The first six steels in this table were used to evaluate the effects of titanium and reheating temperature on the properties of plain-carbon, vanadium- and niobium-microalloyed steels.

The steels designated as B, V and Nb are plain-carbon, vanadium- and niobium-bearing steels without titanium addition. The compositions of steels T, VT and NbT were similar to those of steels B, V and Nb, respectively, except that the latter contained around 0.014 wt % Ti. The last six steels listed in this table contained a similar amount of vanadium but the titanium and nitrogen contents were varied. These steels were used to study the effects of titanium and

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TABLE I The chemical compositions of experimental steels

Steel	Composition (wt %) C	Si	Mn	P	S	Al	V	Nb	Ti	N (p.p.m.)
B	0.096	0.31	1.35	0.005	0.008	0.020	–	–	–	36
T	0.094	0.31	1.37	0.005	0.007	0.021	–	–	0.014	38
Nb	0.097	0.31	1.38	0.005	0.008	0.020	–	0.032	–	33
NbT	0.098	0.31	1.36	0.005	0.008	0.020	–	0.031	0.012	34
V	0.096	0.32	1.39	0.005	0.008	0.024	0.083	–	–	42
VT	0.096	0.32	1.37	0.005	0.008	0.024	0.083	–	0.014	37
V1	0.096	0.32	1.37	0.007	0.007	0.021	0.087	–	–	81
V2	0.096	0.32	1.35	0.007	0.008	0.021	0.086	–	0.015	72
V3	0.100	0.31	1.33	0.007	0.007	0.022	0.085	–	–	103
V4	0.100	0.31	1.31	0.006	0.007	0.023	0.085	–	0.015	86
V5	0.104	0.28	1.48	0.010	0.007	0.022	0.090	–	–	122
V6	0.104	0.28	1.48	0.010	0.006	0.021	0.090	–	0.009	87

nitrogen contents on the precipitation strengthening of V(C, N). The base composition of all steels was controlled almost to be the same, i.e. 0.1C–0.3Si–1.4Mn (wt %).

Before rolling the steels were heated at a temperature varied from 1050 to 1250° C for 2 h. During rolling the temperature was measured by an optical pyrometer and the finishing rolling temperature was always controlled at around 900° C by changing the interpass waiting time. The rolling reduction per pass was around 20% and the final plate thickness was 12 mm.

For tensile tests the specimens were sectioned in the longitudinal direction of the plate. The tensile specimens were 8 mm in diameter in reduced area and 50 mm in gauge length.

Thin-foil specimens for the observation of precipitates by transmission electron microscopy (TEM) were mechanically ground to about 100 μm and then chemically thinned to about 60 μm. The final thinning was obtained using a twin-jet electropolisher and an alcohol–15% perchloric acid electrolyte. The thin foils were examined in a Jeol CV 2 TEM at 100 kV.

3. Results and discussion

The effect of reheating temperature on the ferrite grain size and strength of plain carbon and titanium steel is shown in Fig. 1. It can be seen that at 1150 and 1250° C the effect of reheating temperature on the ferrite grain size and strength is insignificant, and the difference in grain size and strength of these two steels is negligibly small. However, when the reheating temperature was lowered to 1050° C the ferrite grain sizes of the two steels were significantly diminished. Consequently, both the yield strength and tensile strength of these two steels were correspondingly increased. It was found that the grain refinement and subsequent strengthening of titanium-treated steel were more obvious than those of plain-carbon steel, as indicated by the fact that the strength of titanium steel was higher than that of plain-carbon steel when the reheating temperature was 1050° C.

The reason for grain refinement on lowering the reheating temperature to 1050° C was partially due to the deformation effect. It has been reported that the lower the deformation temperature and the more extensive the rolling process, the finer the recrystallized austenite grains that can be obtained [11, 12]. However, the major effect is believed to originate from the finer initial austenite grain size after reheating at 1050° C.

As shown in Fig. 2, following austenization above 980° C for 2 h, these two steels exhibit three stages of discontinuous grain growth behaviour as previously reported [13]. Below the grain coarsening temperature, which is around 1000° C for plain carbon steel and 1100° C for titanium steel, the austenite grain sizes were uniform and fine and did not grow significantly with temperature until the grain coarsening temperature was reached. In the grain coarsening temperature region some grains began to grow extensively at the expense of the surrounding fine grains. This produced a mixed grain structure. At higher temperatures the grains became uniform again but were very large.

From this result it can be seen that at 1050° C titanium steel was completely within the fine-grain

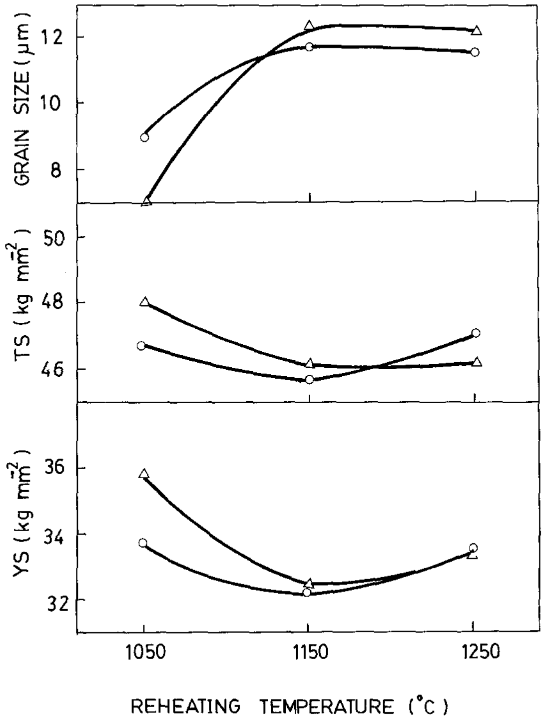

Figure 1 Variation of ferrite grain size and strength with austenization temperature of (○) plain-carbon steel B (Table I) and (△) titanium steel T.

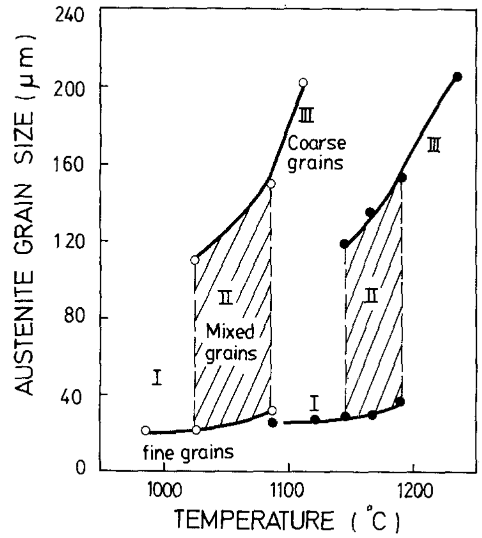

Figure 2 Variation of austenite grain size with austenization temperature of (○) plain-carbon steel B (Table I) and (●) titanium steel T.

region, but the plain-carbon steel was just at the early stage of grain coarsening. At 1150° C the austenite grain size of the plain carbon steel was uniform and large while the titanium steel contained a mixture of fine and coarse grains. Because the finer initial austenite grains can be retained after reheating at 1050° C rather than at 1150 and 1250° C, smaller austenites are probably inherited from rolling and through recrystallization which are then transformed to a finer ferrite structure. A small amount of titanium addition forms TiN particles in steels which prevent austenite grain growth at high temperatures [2, 3]. This results in a higher grain coarsening temperature for the titanium steel as shown in Fig. 2. Apparently, the more uniform and finer austenite structure of the titanium steel compared with that of plain carbon steel at 1050° C makes the former of finer ferrite grain size and higher strength when the reheating temperature is lowered to 1050° C.

The effect of reheating temperature on the ferrite grain size and strength of niobium steel and Nb–Ti steel is shown in Fig. 3. It can be seen that the ferrite grain size of these two steels is finer than that of plain-carbon steel and titanium steel. The grain size is independent of reheating temperature, regardless of titanium being added or not. In the rolling process used in this experiment niobium has a strong effect on refining the ferrite grain size. This effect is apparently more prominent than that of refining the initial austenite structure by titanium addition or decreasing the reheating temperature.

As shown in Fig. 3, although the effect of reheating temperature on the ferrite grain size is negligible, the strength of the two steels was decreased with decreasing reheating temperature. It can also be seen that the effect of titanium addition on the structure and strength of niobium-microalloyed steel was insignificant.

Fig. 4 shows the effect of reheating temperature on the ferrite grain size and strength of vanadium steels and V–Ti steel. It can be seen that both the ferrite grain size and the change of ferrite grain size with reheating temperature were similar to those of plain carbon steel and titanium steel. Apparently, vanadium does not have a grain refinement effect in this experimental rolling process.

It was also found that although the ferrite grain size decreased with decreasing reheating temperature, the strength also showed the same trend. This suggests that the mechanism responsible for a decrease in

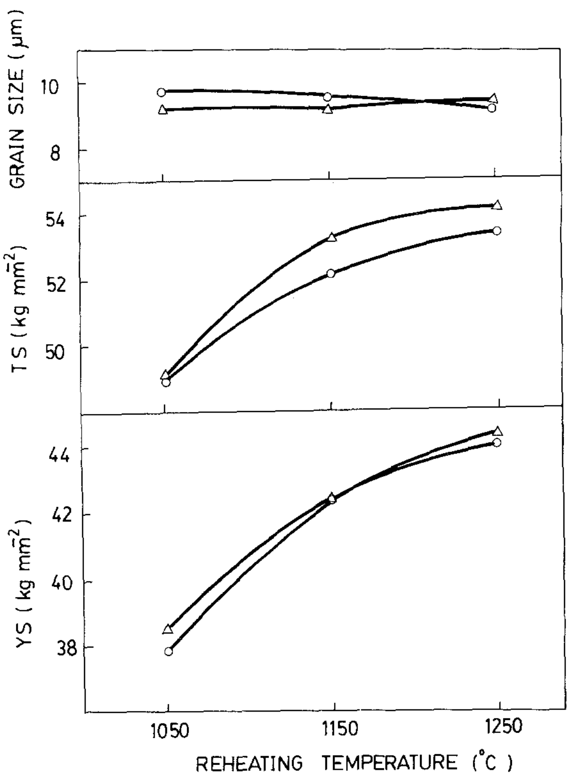

Figure 3 Variation of ferrite grain size and strength with the austenization temperature of (○) niobium steel Nb (Table I) and (△) Nb–Ti steel NbT.

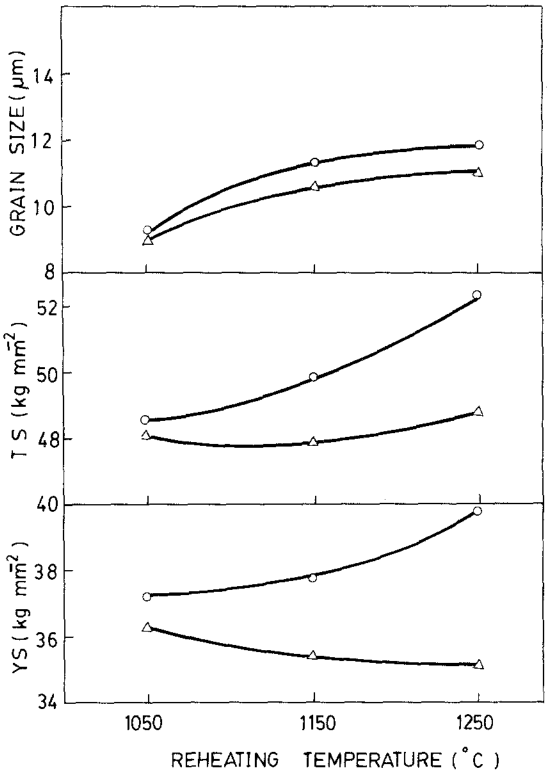

Figure 4 Variation of ferrite grain size and strength with the austenization temperature of vanadium steels without and with titanium addition: (○) steel V (Table I), (△) steel VT.

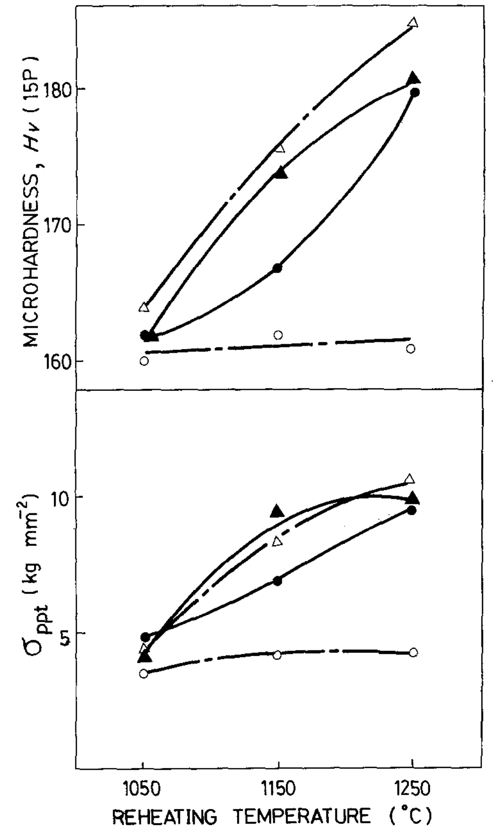

Figure 5 Variation of ferrite matrix hardness and contribution of precipitation strengthening to the yield strength with the austenization temperature of vanadium and niobium steels without and with titanium addition: (●) steel V (Table I), (○) steel VT, (▲) steel Nb, (△) steel NbT.

strength is more important than that for increase in strength by grain refinement as the reheating temperature is lowered. This phenomenon was also observed in the results of niobium steel and Nb–Ti steel as mentioned previously. From Fig. 4 it can also be seen that the addition of a small amount of titanium to vanadium-microalloyed steel decreased the strength significantly. The decrease in strength was more noticeable in the case of reheating at higher temperatures.

From quantitative metallurgy the contributions from different strenghtening mechanisms to the yield strength (YS) can be dissociated according to the following equation [14]:

$$\mathrm{YS} = \sigma_0 + \sigma_{\mathrm{ss}} + K\bar{d}^{-1/2} + \sigma_{\mathrm{ppt}} + \sigma_{\mathrm{d}} \qquad (1)$$

where $\bar{d}$ is the average grain size of ferrite, and K represents the difficulty of transmitting slip across grain boundaries and is around 1.81 kg mm$^{-3/2}$ [15]; σ_0 is the intrinsic strength of the ferrite lattice and is around 6.5 kg mm^{-2} [16], and σ_{ss} is the contribution to strength from solid solution hardening which can be calculated [17] from the equation

$$\sigma_{\mathrm{ss}}\,(\mathrm{kg\,mm^{-2}}) = 3.25\,(\%\,\mathrm{Mn}) + 8.4\,(\%\,\mathrm{Si}) \quad (2)$$

Since the first four terms in Equation 1 are normally known, and the strengthening from dislocation hardening σ_{d} is negligibly small as the finishing rolling temperature is above the Ar_3 transformation temperature, Equation 1 can be used to determine the contribution to strength from precipitation hardening, σ_{ppt}. Fig. 5 shows the calculated σ_{ppt} and the microhardness measured on the ferrite matrix of these steels as a function of reheating temperature. It can be seen that for these steels the contribution of precipitation hardening to yield strength or ferrite matrix strength decreased with decreasing reheating temperature. Since the silicon and manganese contents of these steels are similar, the difference in the hardness of the ferrite matrix can be attributed to the difference in the effect of precipitation strengthening. Based on this analysis it can be realized that the decrease in strength with decreasing reheating temperature for vanadium- and niobium-microalloyed steels with and without titanium addition, as shown in Figs 3 and 4, results from a smaller strengthening effect from precipitation. It is also found that a small amount of titanium addition to the vanadium-microalloyed steel decreased the precipitation hardening effect significantly (Fig. 5). This results in the great strength loss of V–Ti steel as shown in Fig. 4.

The decrease of precipitation strengthening on

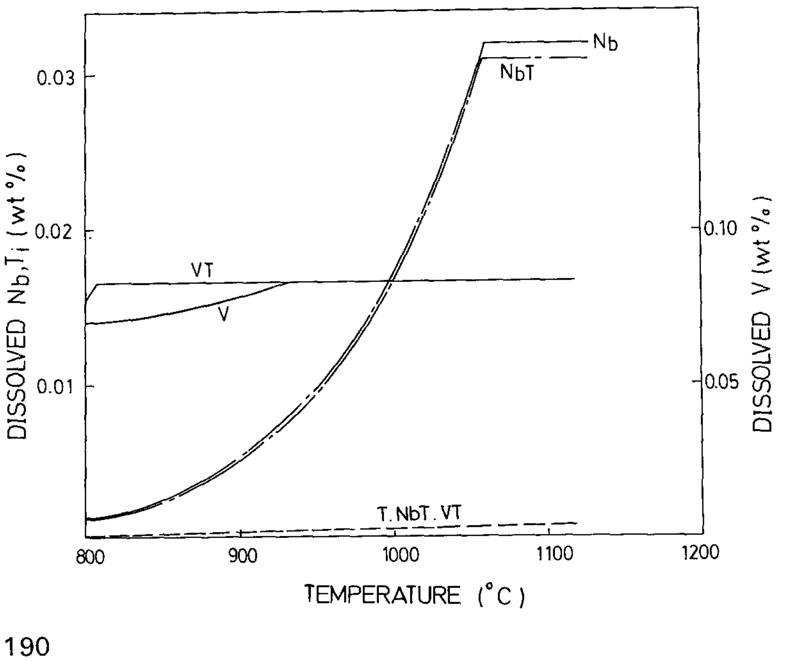

Figure 6 Variation of calculated dissolved alloy contents with the austenization temperature of experimental steels: (——) vanadium, (---) niobium, (– – –) titanium content.

lowering the reheating temperature is considered to have two possible explanations. One arises from the incomplete dissolution of alloying elements as the reheating temperature is decreased [18, 19]. It is well known that the major precipitation hardening effect of microalloying elements comes from their carbide, nitride or carbonitride which form in the ferrite matrix either during transformation on the austenite–ferrite interface or from transformed supersaturated ferrite [20, 21]. For this reason only the alloy content which has dissolved during reheating treatment has the effect of strengthening the ferrite matrix by its precipitates.

According to the solubility product equations [22–24]

$$\begin{aligned} \log([\mathrm{Nb}][\mathrm{C}]) &= -7900/T + 3.42 \\ \log([\mathrm{Nb}][\mathrm{N}]) &= -8500/T + 2.80 \\ \log([\mathrm{Ti}][\mathrm{C}]) &= -7000/T + 2.75 \\ \log([\mathrm{Ti}][\mathrm{N}]) &= -8000/T + 0.32 \\ \log([\mathrm{V}][\mathrm{C}]) &= -9500/T + 6.72 \\ \log([\mathrm{V}][\mathrm{N}]) &= -8300/T + 3.46 \end{aligned} \tag{3}$$

it is possible to calculate the dissolved alloy contents at the reheating temperatures by an established computer program. In V–Ti steel and Nb–Ti steel the free nitrogen and carbon were initially calculated according to the solubility product equations of TiC and TiN, and then the calculated free carbon and nitrogen were used to calculate the dissolved vanadium and niobium according to their compositions and solubility product equations. The calculated results are shown in Fig. 6. It can be deduced that almost all of the titanium added to steels forms very stable TiN which can only slightly be dissolved even at the highest temperature used in this study. In vanadium-microalloyed steels (without or with titanium addition) all of the vanadium in steel should be dissolved even at 950° C. The complete dissolution temperatures of Nb(C, N) or niobium-microalloyed steels without or with titanium addition are around 1060° C, which is close to 1050° C, the lowest reheating temperature used in this study.

From this thermodynamic analysis, the dissolved alloy content and its subsequent precipitation strengthening effect should be independent of reheating temperature except in niobium-microalloyed steels without or with titanium addition at 1050° C. However, in thermokinetics the dissolution of alloy carbides and nitrides is a thermally activated diffusion-controlled process, so that time is needed to dissolve these carbides and nitrides. The higher the reheating temperatures is, the higher both the diffusivity and driving force for dissolution are and the closer to the equilibrium content the actual amount of dissolved alloy can be.

Another possibility of lower precipitation strengthening from a lower reheating temperature is considered to be the discrepancy in the amount of precipitation in the austenite phase. It has been found that the nose of the precipitation–time–temperature (PTT) curve of Nb(C, N) and V(C, N) is around 900° C in the austenite phase [25, 26], and deformation accelerates the precipitation process [27]. The lower the reheating temperature in the range of this study was, the more deformation was obtained in the vicinity or closer to the nose temperature of the PTT curve. This facilitates the precipitation of alloying elements in the austenite phase and depletes the amount of alloy elements in solution. This results in less precipitation strengthening effect as a consequence of a smaller amount of alloy precipitating in the ferrite phase.

The TEM micrographs in Fig. 7 show the V(C, N) particles of vanadium steel reheated at 1050° C (Fig. 7a and b) and 1250° C (Fig. 7c). Fig. 7a shows the undissolved V(C, N). Its size is very large and around 100 nm. This evidence suggests that the V(C, N) particles are not completely dissolved at the reheating temperature. Fig. 7b shows smaller particles around 20 nm in size which are believed to have formed in the austenite phase during rolling. Fig. 7c shows very fine particles around 5 nm in size. These particles are believed to form in the ferrite phase and to make the

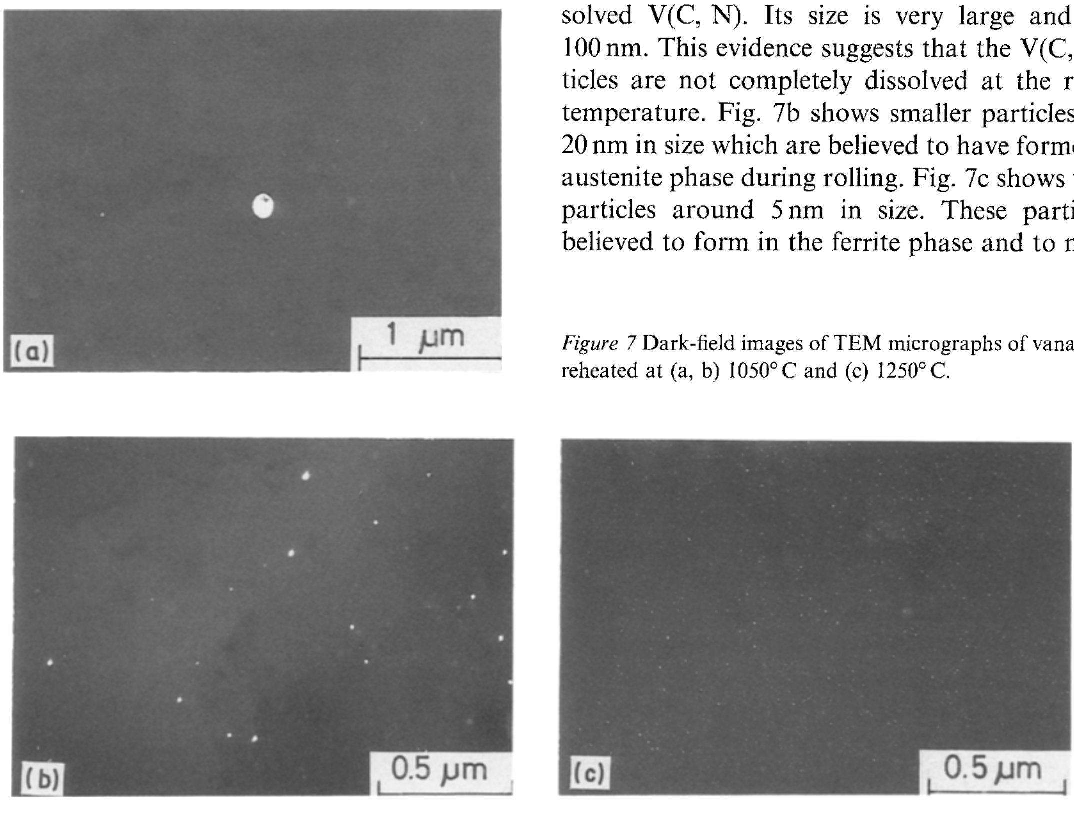

Figure 7 Dark-field images of TEM micrographs of vanadium steel reheated at (a, b) 1050° C and (c) 1250° C.

main contribution to the precipitation strengthening of steels. It was found from the TEM observation that the higher the reheating temperature was, the higher the volume fraction of precipitates formed in the ferrite phase.

The effect of titanium addition in lowering the precipitation strengthening effect of vanadium has been reported by some researchers [10]. Two mechanisms have been proposed to explain this phenomenon. One proposed that V(C, N) and TiN have identical crystal structures (fcc) and very similar lattice parameter, 0.413 to 0.424 nm and 0.424 nm, respectively; it is feasible that the stable TiN particles can function as nucleation centres for V(C, N) precipitation in austenite, and the rate of precipitation of V(C, N) may well be accelerated by the pre-existing TiN particles via direct growth on these particles and skip the nucleation step; consequently, the available vanadium content which can precipitate in the ferrite matrix to product a strengthening effect is eliminated [10]. In consideration of Nb(C, N), it also has the identical crystal structure to that of TiN and a very similar lattice parameter, i.e. 0.444 to 0.447 nm. Consequently the titanium addition to niobium-microalloyed steel should decrease the precipitation strengthening from Nb(C, N) as in the case of V(C, N). However, the experimental results showed the pre-existing TiN did not decrease the precipitation hardening effect of Nb(C, N).

Another proposed explanation of decreasing precipitation strengthening of V(C, N) from titanium addition is that titanium combines with nitrogen to form TiN which depletes the available nitrogen content for VN formation. VN is considered to have a stronger strengthening effect than that of VC [28, 29]. To confirm this explanation, a series of vanadium-microalloyed steels with different contents of titanium and nitrogen were melted, reheated at 1150 and 1250° C, rolled to plate and the tensile properties evaluated. The dissolved nitrogen content at the reheating temperature and the contribution of precipitation to the yield strength were measured and calculated by the method mentioned previously. The results are shown in Fig. 8. It is found that at the same reheating temperature the precipitation strengthening effect of V(C, N) is increased with increasing dissolved nitrogen content at the reheating temperature, and independent of titanium addition. From this result it is proposed that the precipitation strengthening effect of V(C, N) is sensitive to the availability of nitrogen for the formation of V(C, N). The decrease of the precipitation strengthening effect of V(C, N) from titanium addition is attributed to the depletion of nitrogen content in solution by TiN formation, and the diminished strengthening effect is possibly regained by supplementing nitrogen which is consumed by titanium as TiN.

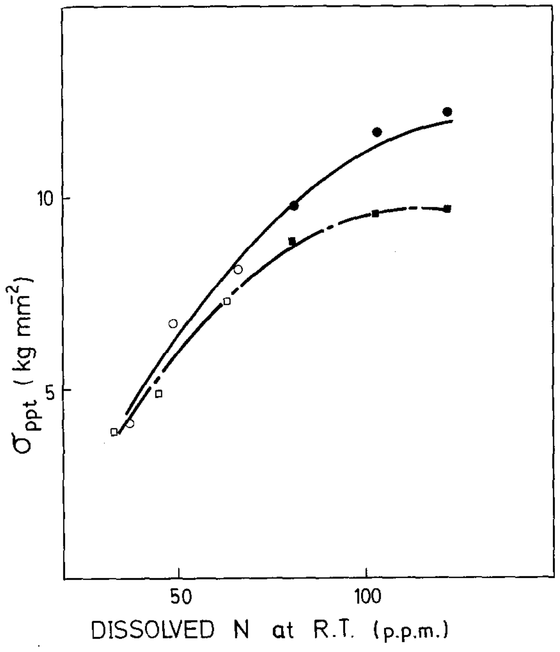

Figure 8 Variation of contribution of precipitation strengthening to the yield strength with the calculated dissolved nitrogen content at reheating temperature (■, □) 1150° C and (●, ○) 1250° C: (●, ■) titanium-free; (○, □) titanium-treated.

4. Summary and conclusions

1. A small amount of titanium addition to steel can inhibit the grain growth of austenite and raise the austenite grain coarsening temperature during reheating. The austenite and the subsequent transformed ferrite grain size can be refined as long as the reheating temperature is not higher than the austenite grain coarsening temperature of the steel. In niobium-microalloyed steels the grain refinement effct is surpassed by niobium itself.

2. The lower the reheating temperature, the less the observed precipitation strengthening effect of V(C, N) and Nb(C, N). Incomplete dissolution of microalloying elements during reheating and a larger amount of strain-induced precipitation in the austenite phase during rolling are possibly attributed to the lower precipitation strengthening effect.

3. The addition of titanium to steels significantly decreases the precipitation strengthening effect of V(C, N), but has no visible effect on that of Nb(C, N). The precipitation strengthening effect of V(C, N) is strongly dependent on the availability of nitrogen content for V(C, N) formation. The decrease of strengthening effect of V(C, N) due to titanium addition is believed to be caused by the depletion of nitrogen in solution for the formation of TiN.

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References

1. A. McLEAN and D. A. R. KAY, in Proceedings of "Microalloying 75", Washington, DC, 1975 (Union Carbide Corporation, New York, 1977) p. 215.
2. L. J. CUDDY and J. C. RALEY, *Met. Trans.* **14A** (1983) 1989.
3. S. MATSUDA and N. OKUMURA, *Tetsu-to-Hogane* **62** (1976) 1209.
4. L. MEYER, F. HEISTERKAMP and W. MUESCHENBORN, in Proceedings of "Microalloying 75", Washington,

DC, 1975 (Union Carbide Corporation, New York, 1977) p. 153.

5. I. WATANABE, M. SUZUKI, K. TSUKADA, Y. YAMAZAKI and T. TOKUNAGA, *NKK Tech. Rep. Overseas* **38** (1983) 33.
6. Y. KUSUHARA, E. KOBAYASHI, F. OHNISHI, I. HIRAI, K. AMANO and R. TARUI, *Kawasaki Steel Tech. Rep.* **13** (1985) 77.
7. H. KAJI, S. TAKASHIMA, T. SHIMOKATA and H. KAMINO, *Kobe Steel Eng. Rep.* **35** (1985) 122.
8. F. TERASAKI, T. HASHIMOTO and Y. KOMIZO, *Sumitomo Metals J.* **37** (1985) 64.
9. Y. OHNO, Y. OKAMURA, K. UCHINO, S. YANO and S. MATSUDA, in Proceedings of Conference on HSLA steels, edited by D. P. Dunne and T. Chandra (AIME, Wollongong, Australia, 1984) p. 129.
10. T. SIWECHI, A. SANDBERG and W. ROBERTS, in Proceedings of Conference on HSLA steels: Technology and Applications, Philadelphia, 1983, edited by M. Korchysky (ASM, Metal Park, Ohio, 1983) p. 619.
11. C. OUCHI and T. OKITA, *Trans. ISIJ* **24** (1984) 726.
12. Y. MATSUMURA and H. YADA, *ibid.* **27** (1987) 492.
13. T. GLADMAN and F. B. PICKERING, *J. Iron Steel Inst.* **204** (1966) 298.
14. A. M. SAGE, D. M. HAYES, C. C. EARLEY and E. A. ALMOND, *Met. Tech.* **3** (1976) 293.
15. W. B. MORRISON, B. MINTZ and R. C. COCHRANE, *Trans. ASM* **59** (1966) 824.
16. B. W. CHRIST and G. V. SMITH, *Acta Metall.* **15** (1967) 809.
17. F. B. PICKERING and T. GLADMAN, Iron and Steel Institute Special Report No. 81 (Iron and Steel Institute, Randon, 1963) p. 10.
18. V. J. POGORZHELSKYJ, Y. J. MATROSOV and A. G. NASIBOV, in Proceedings of "Microalloying 75", Washington, DC, 1975 (Union Carbide Corporation, New York, 1977) p. 100.
19. R. W. K. HONEYCOMBE, *Scand. J. Met.* **8** (1979) 238.
20. P. L. MANGONON and W. E. HEITMANN, in Proceedings of "Microalloying 75", Washington, DC, 1975 (Union Carbide Corporation, New York, 1977) p. 159.
21. I. WEISS and J. J. JONAS, *Met. Trans.* **11A** (1980) 403.
22. K. NARITA, *Trans. ISIJ* **15** (1975) 145.
23. K. J. IRVINE, F. B. PICKERING and T. GLADMAN, *J. Iron Steel Inst.* **205** (1967) 161.
24. S. MATSUDA and N. OKUMURA, *Tetsu-to-Hagane* **62** (1976) 1209.
25. J. J. JONAS and I. WEISS, *Metal Sci.* **13** (1979) 238.
26. M. G. AKBEN, I. WEISS and J. J. JONAS, *Acta Metall.* **29** (1981) 111.
27. I. WEISS and J. J. JONAS, *Met. Trans.* **10A** (1979) 831.
28. T. SIWECKI, A. SANDBERG, W. ROBERTS and R. LANEBORG, in Proceedings of Conference on Thermomechanical Processing of Microalloyed Austenite, Pittsburgh, 1982, edited by A. J. DeArdo, p. 163.
29. N. K. BALLIGER and R. W. K. HONEYCOMBE, *Met. Trans.* **11A** (1980) 421.

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