NIOBIUM IN HIGH STRENGTH STEELS FOR OIL COUNTRY TUBULAR GOODS

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Abstract

This paper reviews the present and potential use of niobium in high strength oil country tubular goods (OCTG). High strength OCTG used in sour and gas well applications are generally microalloyed with niobium to improve both the strength and the resistance to sulphide stress cracking (SSC). One of the benefits of niobium is to produce a finer grained microstructure during austenitizing. Furthermore, niobium plays a more important role in preventing grain growth in the new heat treatment processes, such as accelerated cooling after rolling and induction quenching, which have been investigated for obtaining ultra fine grains. Another important effect of niobium is precipitation hardening due to niobium carbide. Austenitizing niobium-bearing steels at high temperature enhance the finer niobium carbide precipitation during subsequent tempering. The niobium addition, therefore, makes it possible to temper at higher temperatures giving an improvement in SSC resistance.

Introduction

Exploitations of deep oil and gas wells demand high strength oil country tubular goods (OCTG). However, high strength steels used in producing wells containing corrosive hydrogen sulphide have been faced with problems of sulphide stress cracking (SSC). Thus numerous studies have been conducted over recent decades to reduce the SSC susceptibility of high strength OCTG. Desirable microstructures resistant to SSC are generally considered to be quenched and tempered microstructures with fine prior austenite grains and uniformly dispersed carbides particles. For conventional high strength OCTG such as C90 with specified minimum yield strength (SMYS) of 620MPa (90ksi) and C100 with SMYS of 689MPa (100ksi) grades, the beneficial effect of niobium has been to produce a finer grained austenite microstructure by pinning effect due to fine Nb(C,N) carbonitrides (1).

C110 grade with SMYS of 758MPa (110ksi) has been developed in the 1990s (2-11). For such high strength grades, microalloying with niobium is generally required for obtaining an optimum combination of strength and SSC resistance. Furthermore, new heat treatment processes for obtaining ultra fine grains have been investigated, such as accelerated cooling after rolling (9) and induction quenching (10). Niobium is important in refining the microstructure in such new processes. Additionally, it is found that austenitizing niobium-bearing steels at high temperatures is effective in enhancing the subsequent temper softening resistance by secondary precipitation hardening.

This paper classifies the effects of the niobium addition and proposes the best combination of these effects to optimize the strength and the SSC resistance for OCTG.

Niobium Microalloying in Quenching and Tempering Process

The beneficial effect of niobium on the SSC resistance of C90 and C100 grades in quenched and tempered conditions is widely recognized (1). During the 1990s, C110 grade was developed for the demand of higher strength grades (2-11). Table I summarizes the studies concerning high strength OCTG during the last decade. Such high strength grades are generally microalloyed with niobium, producing Nb(C,N) carbonitride particles (6,8). The carbonitrides prevent the grain growth, resulting in the production of a fine grained microstructure during austenitizing. It is the most important attribute of niobium for obtaining the optimum SSC resistance.

The effect of austenitizing conditions and niobium addition on grain size numbers is shown in Figure 1 (3). The niobium bearing steel HMN has a smaller grain size than that as niobium free steels HC, HM and LM, with the same austenitizing conditions. Figure 2 shows the relationship between grain size and SSC resistance evaluated by uniaxial constant load tests (3). The R_s value is defined as the highest survive stress normalized by yield strength. Refinement of the grain size enhances the SSC resistance at the yield strengths higher than 700MPa. There is no significant difference in R_s values between the niobium free steel HM with grain size number of 9.4, and the niobium bearing steel HMN with grain size number of 10.0. This suggests that the benefit of niobium appears mainly through grain refinement.

Table I Microalloying with niobium in high strength OCTG (1-11)

Ref. No.	Grade	Chemical Compositions (mass%)				Heat Treatment	Test methods
		C	Cr	Mo	Nb		
1)	C100	0.29	1	0.5	0.03	QT	Constant load, DCB 3 point bend, SSRT
2)	C110	0.2 ~ 0.3	0 ~ 2	0 ~ 0.5	0.03	QT	DCB, Constant load
3)	C110	0.2 ~ 0.3	0.3 ~ 1	0.1 ~ 0.8	0.03	QT	Constant load
4)	C110	0.22	0.5	0.8	0.03	QT	Constant load, DCB 3 point bend, CT
5)	C110	0.33	1	0.8	0.03	QT	Constant load
6)	C110	0.29	1	0.7	0.03	QT	SSRT
7)	C110	0.3	1	0.8	0.04	QT	Constant load, DCB
8)	C110	0.02 ~ 0.3	1	0.5 ~ 0.7	0.03	QT	DCB
9)	C110	0.26	1	0.5	0.03	Accelerated Cooling+QT	SSRT
10)	C125	0.24	0.6	0.8	?	Induction QT	Constant load, DCB 4 point bend, CT
11)	C110	0.25	1	0.7	0.03	QT	Constant load DCB

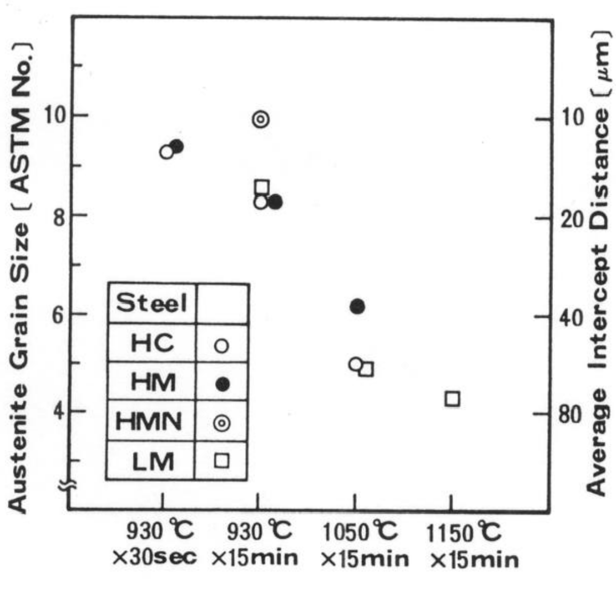

Figure 1: Effect of austenitizing conditions on grain size (3).

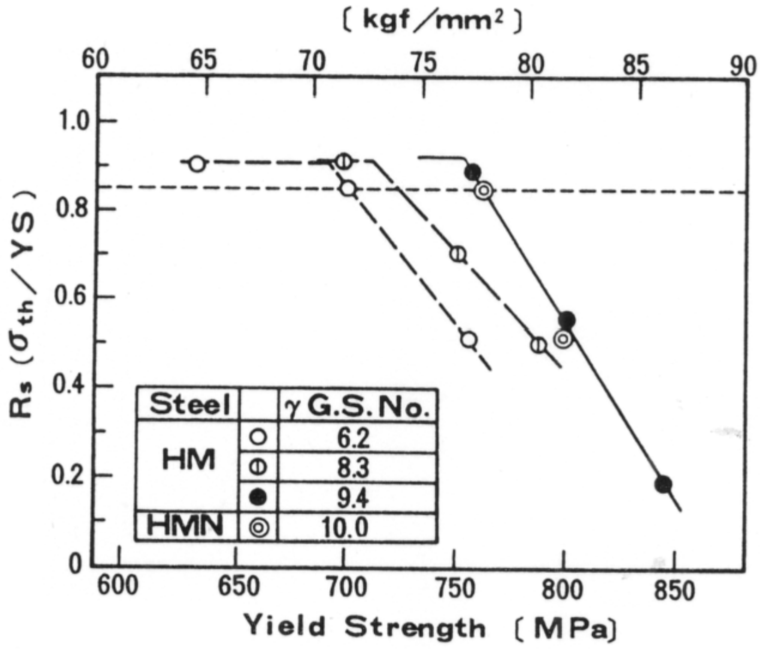

Figure 2: Effect of grain size on SSC resistance (3).

The change in SSC fracture surface depending upon the strength is shown in Figure 3 (3). At yield strengths greater than 750MPa, fracture surfaces exhibit significant intergranular cracking as shown in photograph No.2, No.4, No.5 and No.6. This fractographic investigation reveals that refinement in grain size enhances SSC resistance by reducing SSC susceptibilities at grain boundaries. High SSC susceptibilities at high strengths are attributed to lenticular cementite precipitation at grain boundaries by low temperature tempering (6).

Uniaxial constant load tests according to the National Association of corrosion engineers (NACE) standard TM-0177-A, have probably been most frequently employed for evaluating SSC resistance (2-3). Additionally, it is reported that sulphide fracture toughness K_{ISSC} in double cantilever beam tests (5) and elongation in slow strain rate tensile tests (6) are also improved by grain refinement.

Table II Chemical compositions of steels investigated (mass%) (3)

Steel	C	Mn	Cr	Mo	Nb
HC	0.20	1.46	0.49	-	-
HM	0.19	1.47	0.52	0.20	-
HMN	0.19	1.46	0.52	0.20	0.03
LM	0.20	0.51	0.51	0.20	-

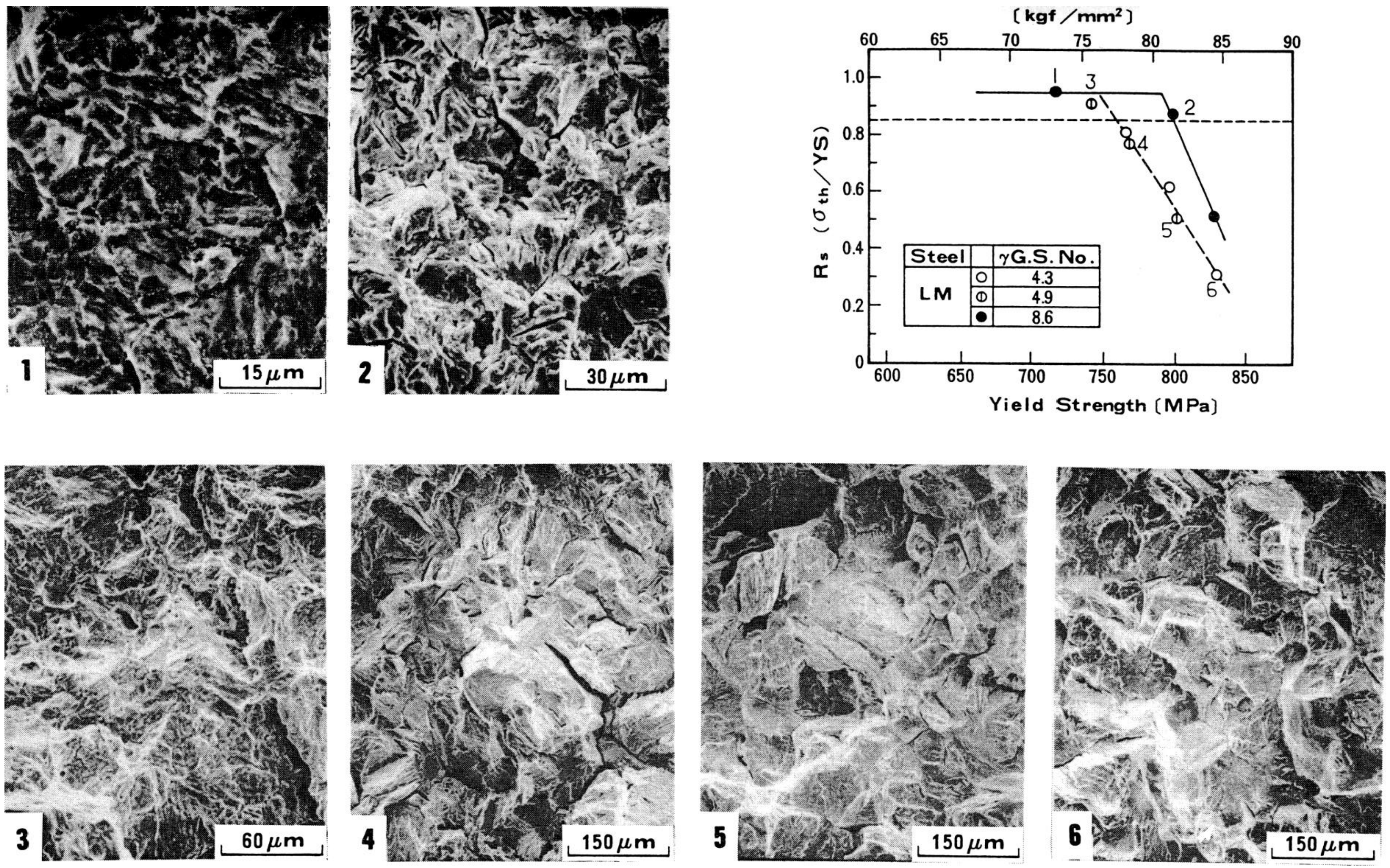

Figure 3: Change in SSC fracture morphology (3).

Ultra Fine Grain by Accelerated Cooling and Induction Heating

New processes for obtaining ultra fine grains have been investigated (9,10). Figure 4 shows the refinement in grain size by accelerated cooling process after hot rolling (9). Steel A free from niobium has been normally quenched and tempered after hot rolling. The steel A has coarse austenite grains. Steel B bearing 0.03% niobium produced through a same process as the steel A, has smaller grains. Steel C with 0.03% of niobium with accelerated-cooling after hot rolling, has the smallest grain size. Figure 5 compares elongations of the three steels in both atmospheric and corrosive environments containing hydrogen sulfide, evaluated by slow strain rate tensile tests. Steel C with ultra fine grain size possesses superior elongation values. This result suggests that ultra fine grains improve the SSC resistance.

Induction heat treatments have also been studied. C125 grade with SMYS of 861MPa (125ksi) produced by an induction quench and tempering process have been investigated (10). The steel with grain size number of 9.4 have been evaluated in sour environments at different hydrogen sulphide partial pressures as shown in Figure 6 (10).

Table III Steels investigated (mass%) (9)

Steel	C	Mn	Cr	Mo	Nb	Cooling after hot rolling
A	0.25	1.16	-	-	-	Normal cooling
B	0.27	0.62	1.01	0.24	0.034	Normal cooling
C	0.26	0.52	0.94	0.47	0.027	Accelerated cooling

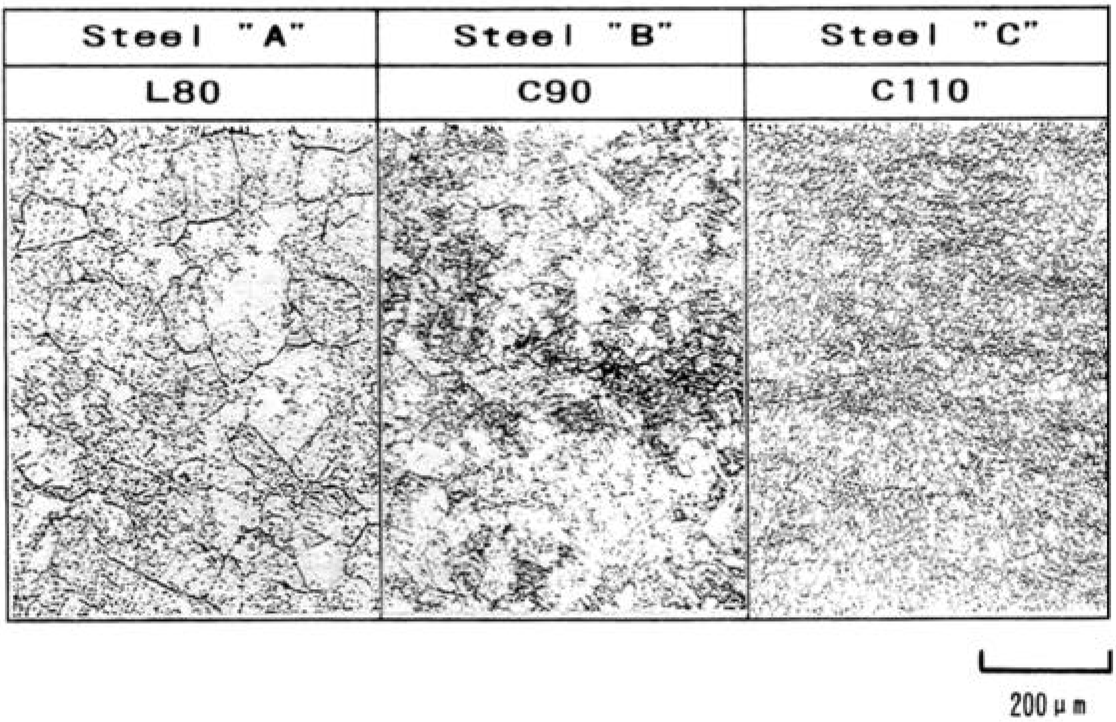

Figure 4: Effect of accelerated cooling on grain size (9).

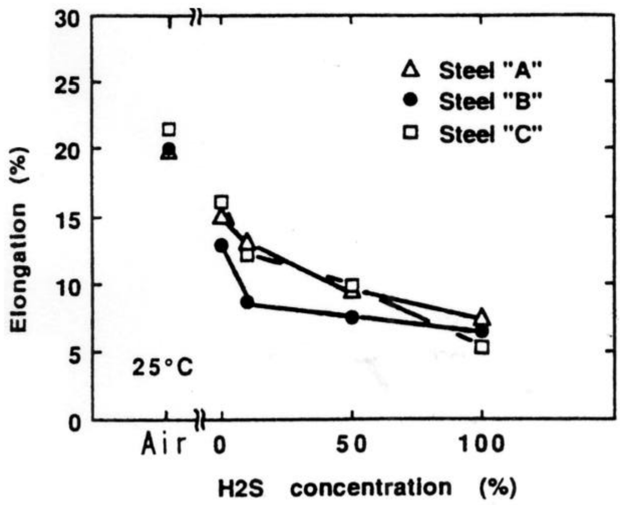

Figure 5: Effect of accelerated cooling on SSC resistance (9).

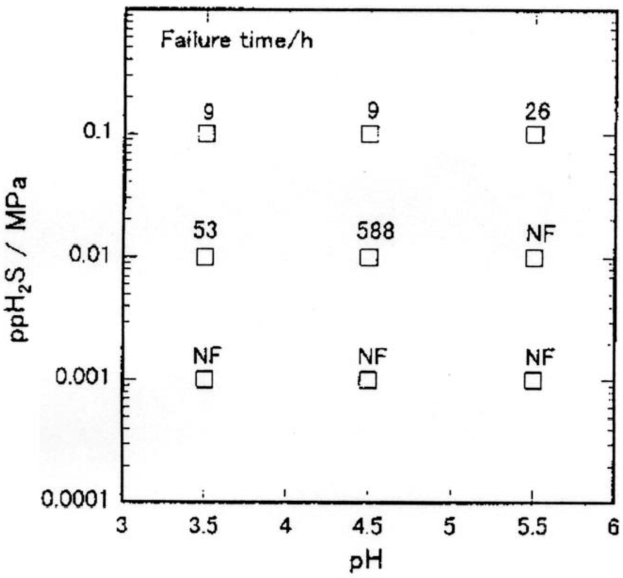

Figure 6: SSC test results for C125 (10).

Niobium Precipitation Hardening by High Temperature Austenitizing

There are few studies concerning secondary hardening behaviour of niobium microalloying in OCTG steels. That is because niobium is insoluble in steels at normal austenitizing temperatures. This paper deals with the secondary precipitation hardening by austenitizing niobium-bearing steels at high temperatures.

Austenitizing at temperatures above 1200°C allows sufficient solution of niobium followed by water quenching. During subsequent tempering, niobium precipitates as very fine niobium carbides. Figure 7 compares temper softening resistance of steels with various amounts of niobium austenitized between 900°C and 1250°C. After austenitizing at 900°C, the increase in niobium shows no beneficial effect on temper softening resistance. Austenitizing at 1200°C enhances the strength of those steels investigated up to 0.1% niobium.

Table IV Chemical compositions of steels investigated (mass%)

Steel	C	Mn	Cr	Mo	Nb
0.03Nb	0.24	0.20	0.49	0.70	0.030
0.07Nb	0.23	0.44	0.50	0.71	0.074
0.1Nb	0.24	0.19	0.50	0.70	0.086
0.15Nb	0.22	0.11	0.50	0.76	0.160

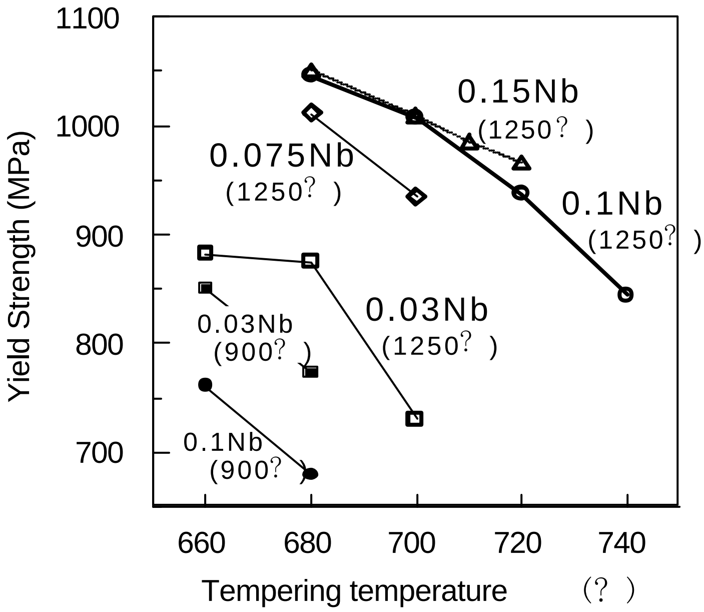

Figure 7: Temper resistance of high niobium steels.After austenitizing at various temperatures.

Figure 8 compares the SSC resistance of the 0.03% niobium steel and the 0.1% niobium steel at similar yield strengths levels. The threshold stress is defined as the highest stress without failure by uniaxial constant load tests. The test environment is the NACE standard aqueous solution of 5% NaCl and 0.5% acetic acid saturated with 0.01MPa of hydrogen sulphide at ambient temperature. The grain size of the two steels are controlled by changing austenitizing temperatures and by rolling after austenitizing, followed by water quenching. A decrease in grain size enhances SSC resistance in the 0.03% steel, showing good agreement with previous works (3). The 0.1% niobium steel has higher threshold values than the 0.03% niobium steel, and keeps the highest values up to a grain size of 150mm.

Figure 9 shows the SSC fracture surfaces of the 0.03% niobium steel and the 0.1% niobium steel with a similar grain size. The 0.03% niobium steel exhibits an intergranular fracture, whilst the 0.1% niobium steel exhibits transgranular fracture.

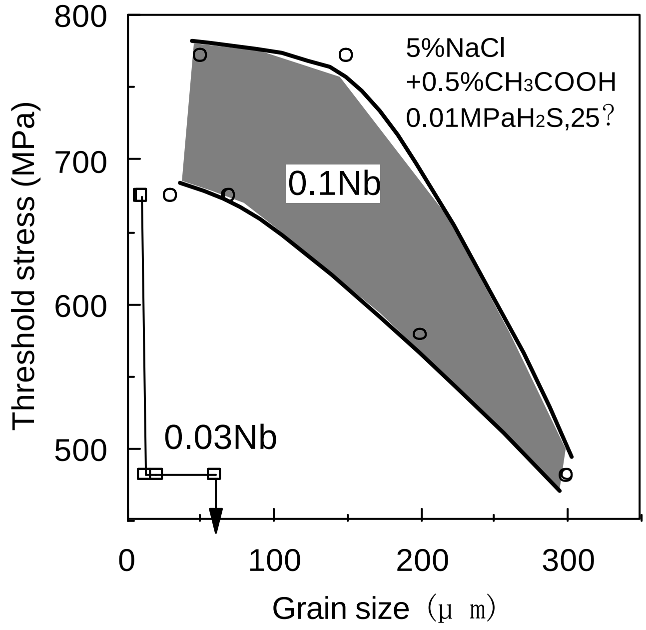

Figure 8: SSC resistance of high niobium steel.

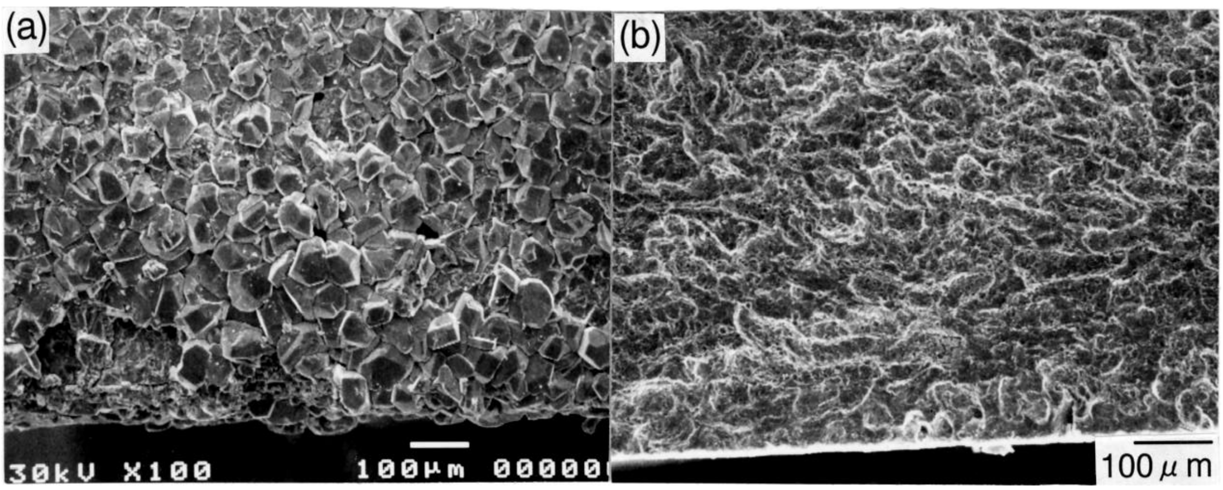

Figure 9: SSC fracture surface (a) 0.03Nb steel (b) 0.1Nb steel.

The beneficial effect of niobium on SSC resistance can be explained by improvement in carbide morphology. Figure 10 shows extraction replica micrographs of the 0.03% niobium steel and of the 0.1% niobium steel. Lenticular cementite precipitates at grain boundaries in the 0.03% niobium steel, which has exhibited intergranular cracking in the SSC tests. Carbides in the 0.1% niobium steel are uniformly dispersed and spheroidized by high temperature tempering, resulting in low SSC susceptibility at grain boundaries. At a higher magnification using thin foils, fine niobium carbides could be observed as shown in Figure 11.

Figure 12 shows hydrogen degassing profiles of the 0.03% niobium steel and of 0.1% niobium steel by a thermal hydrogen analysis after immersion tests in the same solution as the SSC tests. Some studies suggest that fine niobium carbonitrides could be hydrogen trapping sites, resulting in enhancement in SSC resistance (6). However, hydrogen degassing profiles in this study indicate that increasing niobium has no pronounced effect on hydrogen absorption. It would be because the small interface around fine niobium carbides is too small to trap sufficient hydrogen.

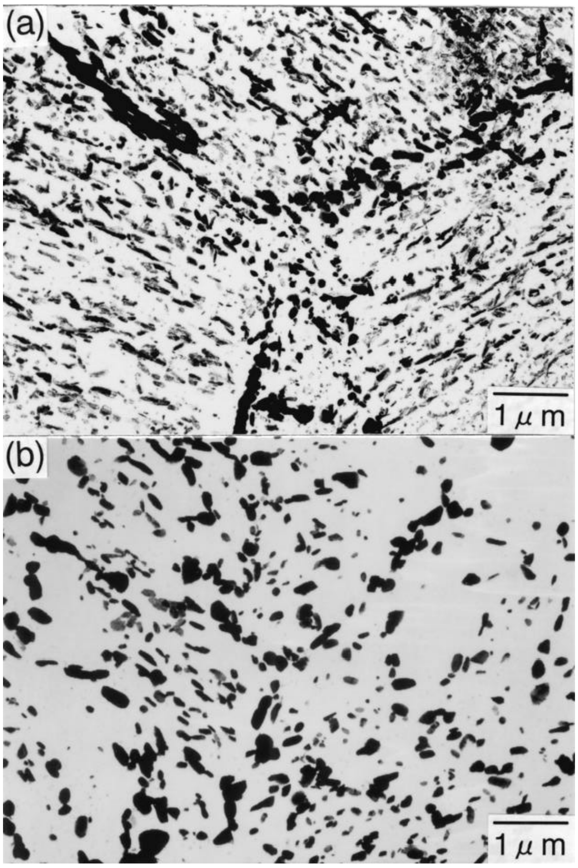

Figure 10: Carbides dispersion (a) 0.03Nb steel (b) 0.1Nb steel.

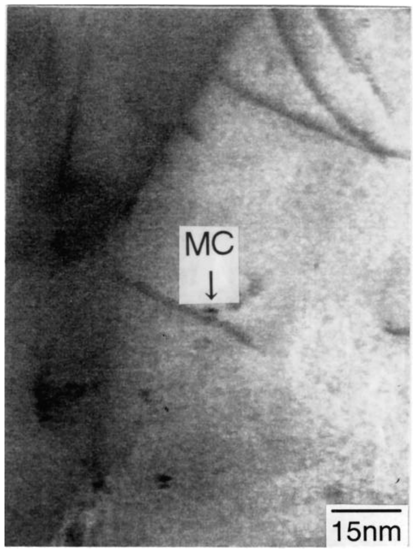

Figure 11: Fine niobium carbides in 0.1Nb steel.

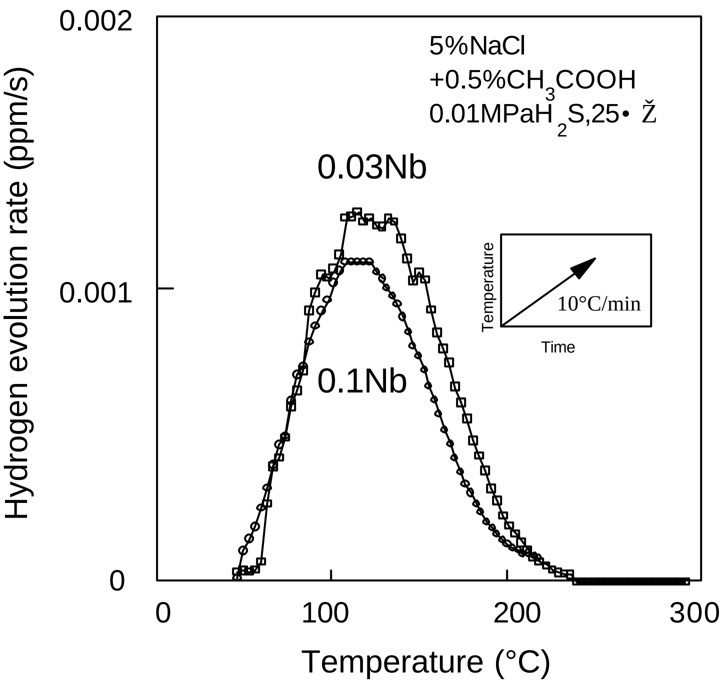

Figure 12: Effect of niobium on hydrogen absorption.

Conclusion

This review deals with the present and potential use of niobium in high strength low alloy oil country tubular goods. In a conventional quench and tempering process, niobium has a beneficial effect on ensuring SSC resistance by microstructural refinement. Ultra fine grain processes such as accelerated cooling after rolling and induction austenitizing, enhanced the effect niobium microalloying. Furthermore, austenitizing at high temperatures could use more of niobium for temper softening resistance. The possibility of the new material design is proposed, which is a high niobium-bearing steel tempered at high temperature.

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