KAWASAKI STEEL TECHNICAL REPORT

No.19 (November 1988)

Steel Pipe

Development of High Strength C110 Grade Steel and 13% Cr Stainless Steel for OCTG in Corrosive Wells

Kunihiro Kobayashi, Kuniaki Motoda, Takao Kurisu, Toshikazu Masuda, Takao Kawade, Hiroshi Oka

Synopsis :

In sour oil wells, where the danger of sulfide stress cracking (SSC) exists, OCTG with YS levels of up to 95 ksi are conventionally used. To meet higher strength requirements, C110 grade OCTG was developed using a high C, low alloy steel, providing an SSC threshold stress above 90% of the specified minimum yield strength. In sweet wells, where severe weight loss corrosion occurs, 13% Cr stainless steel is widely used. A new method for manufacturing 13% Cr tubulars by the Mannesmann rolling process instead of hot extrusion was developed, and tubulars with good dimension accuracy were produced. Corrosion properties and SSC resistance in CO2 and H2S environments were studied in comparison with other steels.

The body can be viewed from the next page.

Development of High Strength C110 Grade Steel and 13% Cr Stainless Steel for OCTG in Corrosive Wells


Kunihiko Kobayashi
Chief of Tubular Products Lab., Heavy Steel Products Research Dept., I & S Research Labs.


Kuniaki Motoda
Staff Manager, R & D Center Kawasaki Steel Techno-research Corp.


Takao Kurisu
Dr. Sci., Chief of Organic Coating & Steel Composite Lab., Coating Research Dept., I & S Research Labs.


Toshikazu Masuda
Staff Deputy Manager, Technical & Quality Control Sec., Technology & Production Control Dept., Chita Works


Takao Kawade
Staff Assistant Manager, Technical & Quality Control Sec., Technology & Production Control Dept., Chita Works


Hiroshi Oka
Staff Assistant Manager, Small Seamless Pipe Sec., Manufacturing Dept., Chita Works

Synopsis:

In sour oil wells, where the danger of sulfide stress cracking (SSC) exists, OCTG with YS levels of up to 95 ksi are conventionally used. To meet higher strength requirements, C110 grade OCTG was developed using a high C, low alloy steel, providing an SSC threshold stress above 90% of the speified minimum yield strength. In sweet wells, where severe weight loss corrosion occurs, 13% Cr stainless steel is widely used. A new method for manufacturing 13% Cr tubulars by the Mannesmann rolling process instead of hot extrusion was developed, and tubulars with good dimensional accuracy were produced. Corrosion properties and SSC resistance in CO_2 and H_2S environments were studied in comparison with other steels.

1 Introduction

The exploitation and production of oil and gas in deeper wells require steel pipe resistant to corrosion and possible failure due to the presence of hostile gases and ions such as H_2S, CO_2, and Cl^-. In sour wells, where H_2S exists, carbon steels suffer sulfide stress cracking (SSC), while in sweet wells, CO_2 causes general corrosion[1]. Oil country tubular goods (OCTG) of special grades are widely used to cope with these corrosive environments. Kawasaki Steel has broad experience in the production and supply of these OCTG, as indicated by **Table 1**. The yield strength of sour service OCTG material has generally been limited to below the 90-95 ksi SMYS (specified minimum yield strength) level, because higher strength drastically reduces SSC resistance.[2] Demand for higher strength in sour service OCTG is rising, however, as wells become deeper. To meet these demands, Kawasaki Steel developed the world's first C110 grade sour service low alloy OCTG (KO-110S).

For sweet service, 13% Cr stainless steel is widely used in OCTG owing to its superior resistance to CO_2 corrosion[1].

In this report, the development of C110 grade OCTG and 13% Cr stainless OCTG is described.

2 Development of C110 Grade Low Alloy Steel OCTG for Sour Service

2.1 Alloy Design

The target of the C110 grade OCTG was set to have an SSC resistance of 0.80 × SMYS as the threshold stress in accordance with NACE TM-01-77, which is also the value specified for API C90 grade OCTG. The yield strength (YS) range was set at 110-125 ksi, with a minimum tensile strength of 125 ksi.

To determine optimum chemical composition, 30-kg laboratory heats of seven steels were melted using a vacuum induction furnace. The ingots were then forged and hot rolled into 15-mm thick plates, which were heat treated. Chemical compositions are shown in **Table 2**. Steels A to D are modified C90 grade steels (0.25%C);

Table 1 Specifications of Kawasaki Steel's special OCTG for sour or sweet services

	Grade	Chemical analysis (wt%)												YS (ksi)	TS (ksi)	HRC	σ_{th} (ksi)
		C	Si	Mn	P	S	Cu	Ni	Cr	Mo	Nb	V	B				
Sour service	KO-80S	0.16-0.35	≦0.35	≦1.35	≦0.030	≦0.015	≦0.30	≦0.10	≦1.60	0.05-1.10	≦0.050	—	≦0.0040	80-95	≧95	≦22	
	90S	0.16-0.35	≦0.35	≦1.35	≦0.030	≦0.015	≦0.30	≦0.10	≦1.60	0.05-1.10	≦0.050	—	≦0.0040	90-105	≧100	≦24	
	95S	0.16-0.35	≦0.35	≦1.35	≦0.030	≦0.015	≦0.30	≦0.10	≦1.60	0.05-1.10	≦0.050	—	≦0.0040	95-110	≧105	≦25	
	KO-85SS	0.16-0.35	≦0.35	≦1.00	≦0.030	≦0.015	≦0.30	≦0.10	0.80-1.60	0.15-1.10	≦0.050	—	≦0.0040	85-100	≧95	≦23	≧70
	90SS	0.16-0.35	≦0.35	≦1.00	≦0.030	≦0.015	≦0.30	≦0.10	0.80-1.60	0.15-1.10	≦0.050	—	≦0.0040	90-105	≧100	≦24	≧80
	KO-110S	0.40-0.50	≦0.35	≦1.00	≦0.030	≦0.007	≦0.30	≦0.10	0.80-1.60	0.15-1.10	≦0.050	≦0.070	—	110-125	≧125	≦31	
Sweet service	KO-13CR-75	0.18-0.22	≦1.00	0.30-0.70	≦0.020	≦0.005	≦0.25	≦0.50	12.0-14.0	—	—	—	—	75-90	≧95	≦22	
	80	0.18-0.22	≦1.00	0.30-0.70	≦0.020	≦0.005	≦0.25	≦0.50	12.0-14.0	—	—	—	—	80-95	≧95	≦23	
	95	0.18-0.22	≦1.00	0.30-0.70	≦0.020	≦0.005	≦0.25	≦0.50	12.0-14.0	—	—	—	—	95-110	≧105	≦26	

Table 2 Chemical compositions of laboratory heats

(wt%)

Steel	C	Si	Mn	P	S	Cr	Mo	Nb	V	Ti	Al
A	0.24	0.25	0.64	0.015	0.004	1.01	0.56	0.031	—	0.009	0.069
B	0.26	0.25	0.52	0.008	0.004	2.03	0.59	0.053	0.077	0.026	0.065
C	0.26	0.26	0.54	0.006	0.005	2.83	0.59	0.052	0.077	0.025	0.076
D	0.26	0.25	0.51	0.009	0.003	1.98	0.99	0.056	0.087	0.021	0.065
E	0.43	0.17	0.62	0.010	0.003	1.00	0.75	0.034	—	—	0.059
F	0.45	0.27	0.62	0.012	0.003	1.04	0.80	0.035	0.052	0.032	0.066
G	0.46	0.26	0.81	0.012	0.003	1.45	1.01	0.062	—	—	0.065

steels E to G are new alloy systems with a higher C content (0.45%).

When these high C steels are quenched and tempered, C110 grade yield strength can be achieved by using higher tempering temperatures than those for medium C (0.25%) steel, as shown in **Fig. 1**. SSC test results for these steel plates (longitudinal direction) are shown in **Fig. 2**. Steel F shows a threshold stress of 0.925 × SMYS, which satisfies the target and is superior to the other experimental steels. The superior SSC resistance of steel F is ascribed to the high quench hardenability and uniform distribution of spheroidized carbides obtained by tempering at high temperature.

The continuous cooling transformation (CCT) diagram of steel F (**Fig. 3**) shows that a martensitic structure can be obtained over a wide range of cooling rates. The comparison of carbide morphologies in steels A and F (**Photo 1**) reveals that the carbides in steel F are more uniform and well spheroidized than those in medium carbon steel A. Based on laboratory scale tests, the 0.45%C-1%Cr-0.8%Mo steel with Nb, V, Ti, and Al was selected for C110 OCTG.

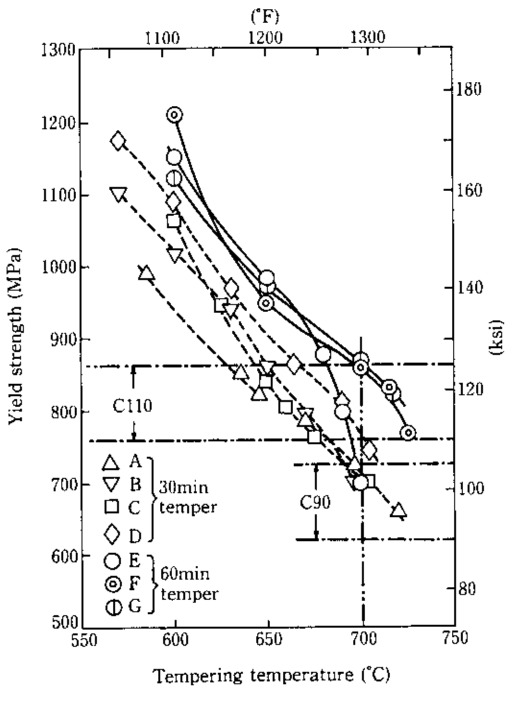


Fig. 1 Relationship between yield strength and tempering temperature of laboratory heats for C110 trials

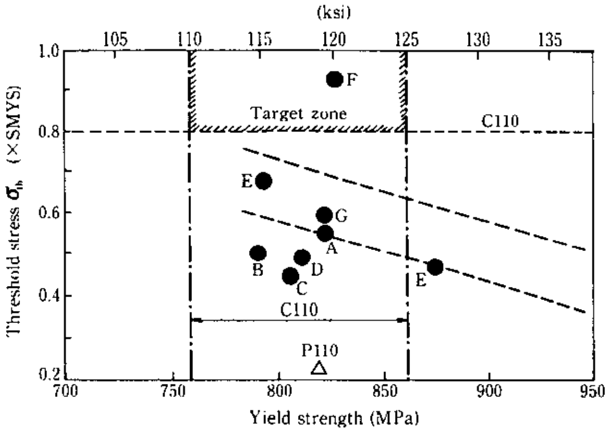


Fig. 2 Results of NACE SSC test in laboratory trials for C110

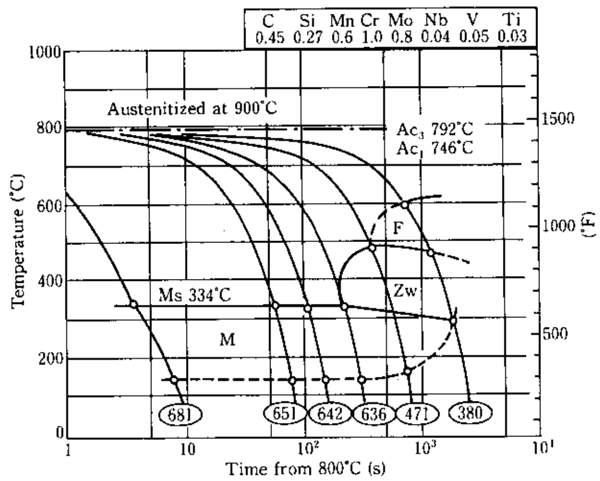
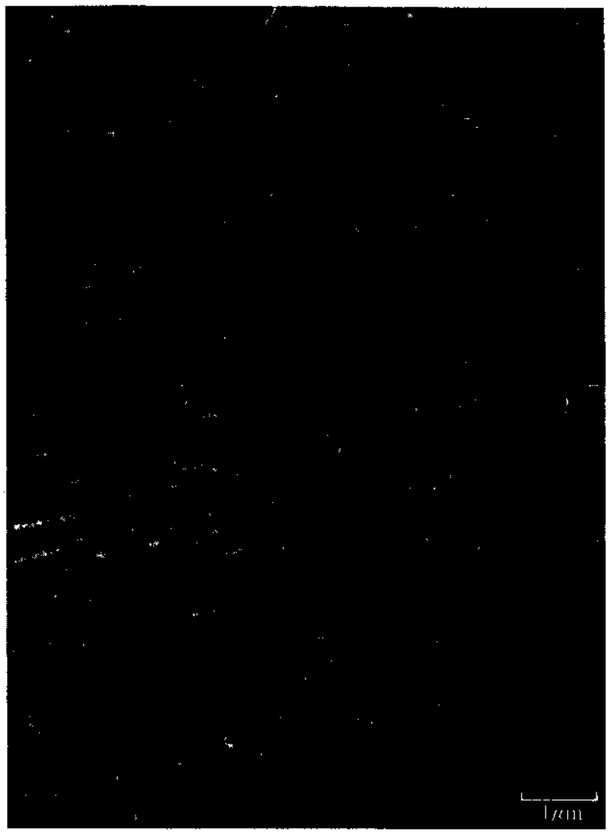


Fig. 3 Continuous cooling transformation diagram for steel F (Encircled figures denote Hardness, HV-10 kg.)

2.2 Production of Pipe

A steel of the same chemical composition (**Table 3**) as steel F was melted in a 5-t vacuum induction furnace and rolled into round billets. Pipes of 7″ × 0.507″ and 7″ × 0.785″ were then fabricated by the plug mill process. These pipes were subjected to external water quenching or immersion oil quenching followed by tempering at various times and temperatures.

Tensile properties of the pipes are shown in **Table 4.**



Upper : Steel A, tempered at 685°C
Lower : Steel F, tempered at 715°C

Photo 1 SEM micrographs showing carbide morphology of steels A and F for C110 trial

The microstructure is tempered martensite, and the austenite grain size is as small as ASTM Grain Size No. 10 (**Photo 2**). Cross-sectional hardness distribution is very uniform, both in the through-wall direction and by quadrants (**Fig. 4** and **Table 5**).

2.3 SSC Resistance of the C110 Pipes

The SSC resistance of these pipes was evaluated by the NACE test (TM-01-77), Shell bent beam test (S_C), and DCB test (K_{ISCC}). The test results are summarized in Table 4. Stress versus time-to-failure plots in the NACE test are shown in **Fig. 5**. The relationship between yield strength and threshold stress is shown in **Fig. 6.** Threshold stresses in the pipes with the specified yield strength are between 0.90 and 1.00 × SMYS. These values are, when compared with the conventional

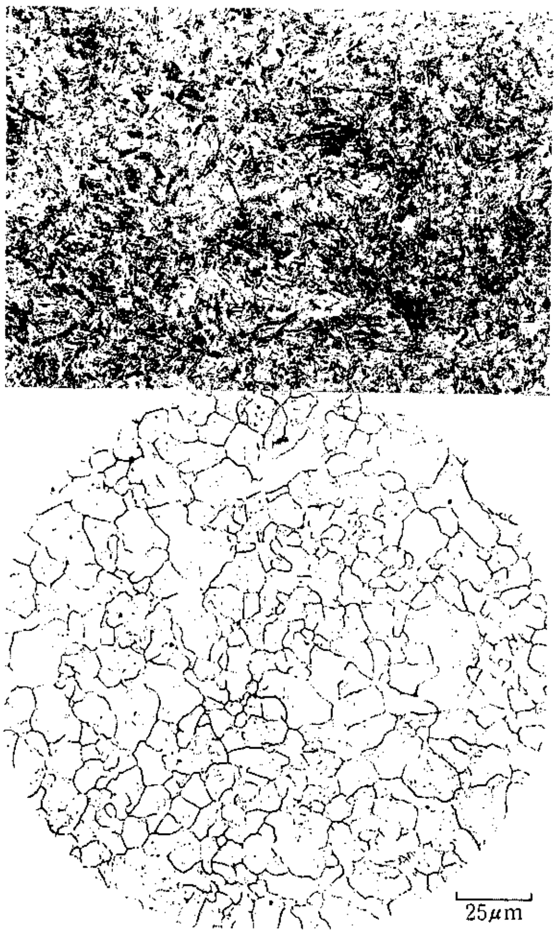
Table 3 Chemical composition of the steel for production trials of C110 pipes (wt%)

C	Si	Mn	P	S	Cu	Ni	Cr	Mo	Ti	V	Nb	Al
0.45	0.25	0.61	0.008	0.004	0.01	0.01	1.03	0.80	0.034	0.052	0.040	0.067

Table 4 Tensile properties and SSC test results of actual pipe production trials

Sample No.	Size (OD×WT)	Quenching method	Tempering condition	YS (ksi)	TS (ksi)	El (%)	σ_{th} *1 (ksi)	S_C *2 (10ksi)	K_{ISCC} *3 (ksi $\sqrt{in}$)
1	7″×0.507″	WQ	710°C×40min	129	140	24.5	88.0 (0.800×SMYS)	7.2	22.4
2	7″×0.507″	WQ	710°C×55min	125	135	24.7	99.0 (0.900×SMYS)	9.9	23.7
3	7″×0.507″	WQ	715°C×45min	120	130	28.2	110.0 (1.000×SMYS)	10.1	32.4
4	7″×0.507″	WQ	715°C×55min	112	121	27.7	104.5 (0.950×SMYS)	12.0	32.3
5	7″×0.788″	WQ	710°C×40min	125	135	28.9	107.3 (0.975×SMYS)	8.4	24.5
6	7″×0.788″	WQ	710°C×55min	120	130	30.3	110.0 (1.000×SMYS)	11.1	25.6
7	7″×0.788″	WQ	715°C×45min	119	128	32.5	110.0 (1.000×SMYS)	11.2	31.2
8	7″×0.788″	WQ	715°C×65min	113	123	32.2	104.5 (0.950×SMYS)	12.4	29.5
9	7″×0.788″	OQ	700°C×40min	115	130	32.3	105.9 (0.963×SMYS)	12.5	26.5

*1 NACE test (TM-01-77) *2 Shell bent beam test *3 DCB test



Upper : Microstructure (Nital)
Lower : Austenite grain size (No.10.2)

Photo 2 Microstructures in a C110 grade pipe of 7″ × 0.788″ (sample No. 6)

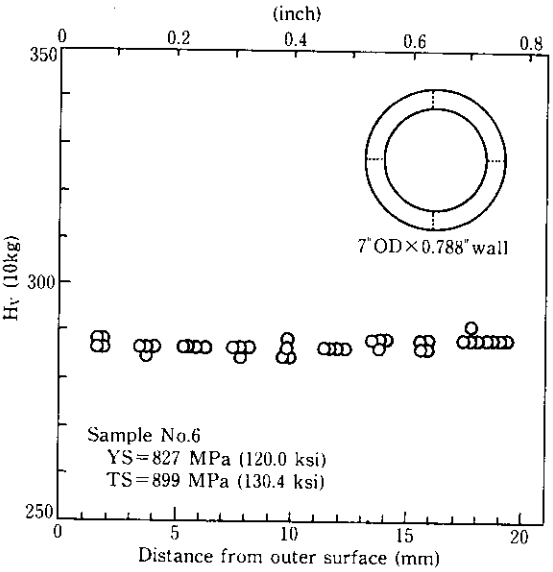


Fig. 4 Through-wall hardness distribution in a 7″ × 0.788″ pipe after tempering

Table 5 Circumferential distribution of hardness of C110 pipe (7″ × 0.788″, sample No. 6)

Quadrant No.	Position average (HRC)			Maximum variation (HRC)
	O.D.	Mid-Wall	I.D.	
1	28.2	28.0	28.2	0.2
2	28.3	28.4	28.5	0.3
3	27.9	27.7	27.9	0.4
4	28.5	28.3	28.4	0.2

Cr-Mo steels shown in Fig. 6, extraordinarily high and meet the C110 requirement by a sufficient margin.

A subsequent production trial using a 30-t heat showed similar results, assuring the reliability of the newly developed low alloy material and C110 grade tubulars.

Results of the S_C and K_{ISCC} tests lay within the upper range of the scatter band of results obtained with con-

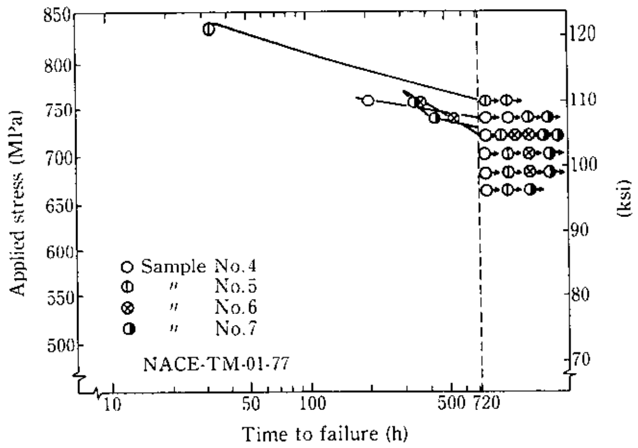


Fig. 5 Applied stress vs time to failure plots for 7″ × 0.788″ C110 grade pipes

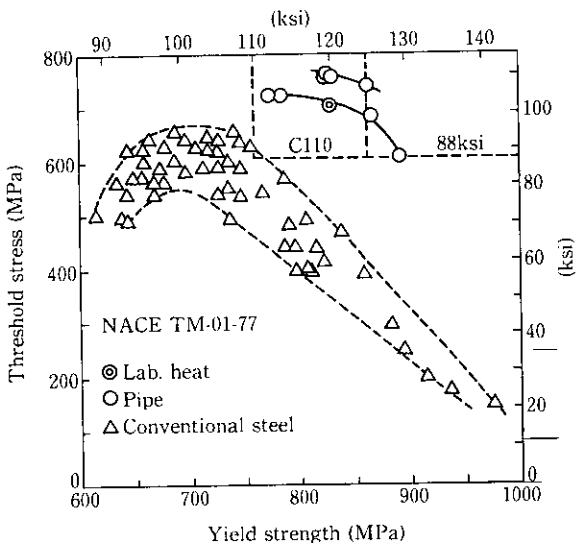


Fig. 6 Comparison of threshold stress of newly developed C110 grade steel with conventional Cr-Mo Steels

ventional steels[3].

3 13% Cr Stainless Steel OCTG for Sweet Service

3.1 Alloy Design

Due to their poor workability at high temperatures, 13% Cr stainless steel tubulars are generally manufactured by the hot extrusion process. The hot workability of 13% Cr steel was found to be improved when impurity elements such as sulfur were reduced.

Figure 7 shows the ductility (reduction of area) of round bar specimens in tensile tests at high temperatures after soaking at 1250°C. As S content is reduced, ductility improves markedly at temperatures around 1100°C, which are the temperatures for piercing and mandrel mill rolling in the conventional Mannesmann

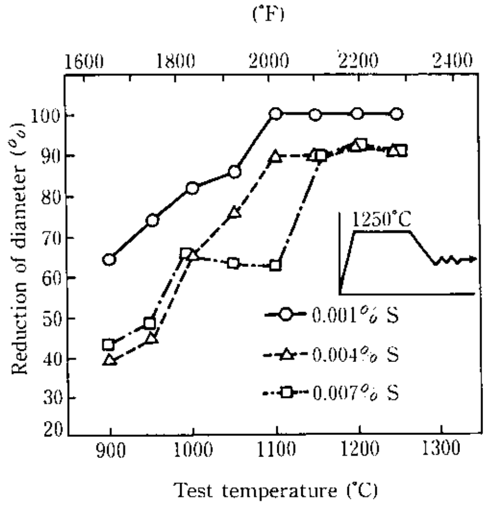


Fig. 7 Effect of S content on hot workability of 13% Cr stainless steels obtained in high temperature tensile test

pipe rolling process.

Based on these findings, a chemical composition with S content held below 0.005%, as shown in Table 1, was specified for the 13% Cr steel, making it possible to manufacture 13% Cr tubulars in the Mannesmann mandrel mill rolling process.

3.2 Production of Pipe

In the manufacture of pipe, the hot metal is first dephosphorized and desulfurized in the torpedo car and K-BOP converter, after which RH-degassing is conducted to reduce impurities and controll chemical composition. Continuously cast slabs of the resulting steel are rolled into round billets as intermediate material for seamless pipe manufacturing.

In pipe manufacturing by Mannesmann process, care must be taken in connection with the following points. (Details are described elsewhere[4]).

(1) Piercing conditions must be optimized to prevent inner surface defects, sticking, and pipe eccentricity.
(2) The shape of roll grooves must be optimal to ensure easy stripping of the mandrel bar.
(3) Temperature must be controlled to prevent defects and ensure the quality.

When adequate care is taken in regard to these technical points, 13% Cr tubulars with good dimensional accuracy can be manufactured on a commercial scale. Examples of the distribution of dimensions in 2 7/8″ × 0.217″ tubing are shown in **Fig. 8**.

The tensile properties of upset tubing are shown in **Table 6**. With proper heat treatment, the strength of the upset portion is little different from that of the pipe body. The microstructure is a typical tempered martensitic structure, as shown in **Photo 3**.

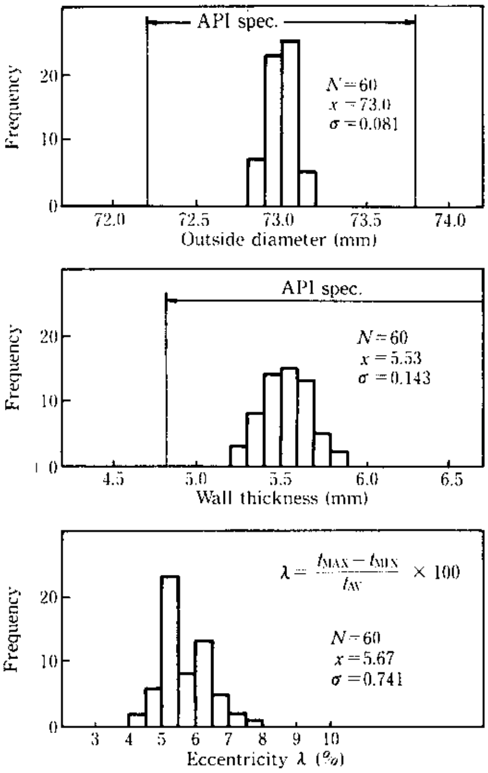


Fig. 8 Accuracy of pipe dimensions of 13% Cr steel tubing of 2 ⅞″ × 0.217″ (73.0 × 5.51 mm)

Table 6 Tensile properties of pipe body and upset portion of KO13CR80 tubing (2 ⅞″ × 0.217″)

	YS (ksi)	TS (ksi)	El (%)	YR (%)
Pipe body	85.6	108.1	42.5	79.2
Upset portion*	86.5	110.1	33.7	78.6

* Subsize specimen

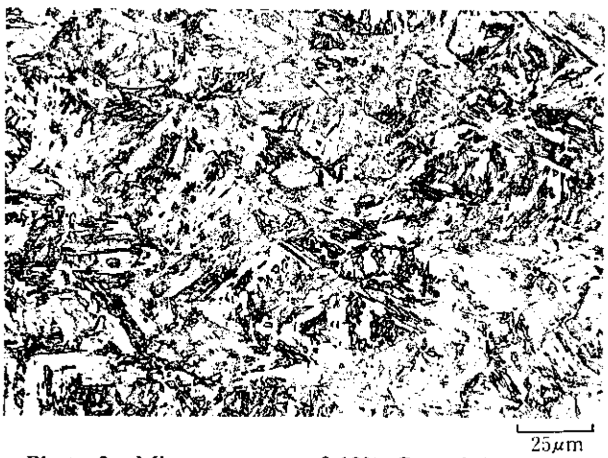


Photo 3 Microstructure of 13% Cr stainless steel

3.3 Corrosion Resistance of 13% Cr Stainless Steel Pipes

Corrosion and SSC resistance were studied in comparison with other typical steels used for OCTG. The chemical compositions of these materials are listed in **Table 7**. Polished coupons were used for corrosion tests in an immersion cell and autoclave with NaCl solutions containing CO_2. Corrosion rates were calculated from the weight losses of the test coupons.

(1) Effect of Temperature

The temperature dependence of the corrosion rate under a condition of 30 atm CO_2 partial pressure is shown in **Fig. 9**. The 13% Cr steel shows a maximum corrosion rate of around 1 mm/year at the tempeature of 150°C. Below this temperature, the rate is much less than that of low alloy steel. Low alloy steels and carbon steels show a corrosion rate

Table 7 Chemical compositions and tensile properties of steels for corrosion tests

Steel	Compositions (wt.%)								YS (ksi)	TS (ksi)
	C	Si	Mn	P	S	Ni	Cr	Mo		
Carbon steel	0.25	0.25	1.40	0.019	0.004	—	—	—	95.3	112
Low alloy steel	0.25	0.26	0.52	0.010	0.004	0.01	1.00	0.04	97.9	112
13%Cr	0.20	0.55	0.60	0.016	0.001	—	13.1	—	86.0	116
22%Cr	0.02	0.51	1.51	0.016	0.001	5.40	22.2	3.10	76.8	103

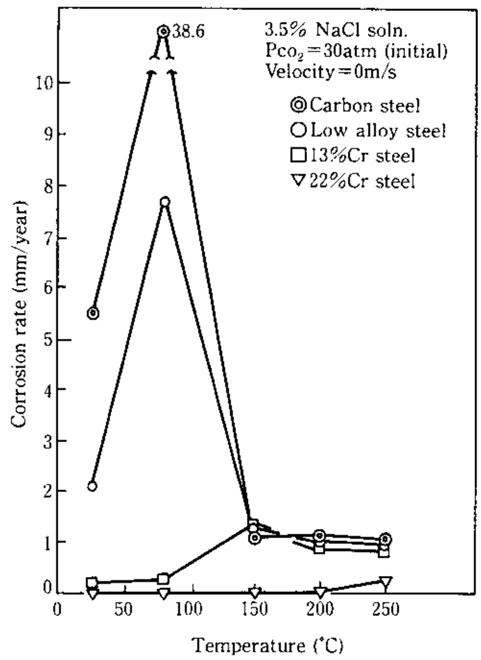


Fig. 9 Effect of temperature on corrosion rate under 30 atm of CO_2

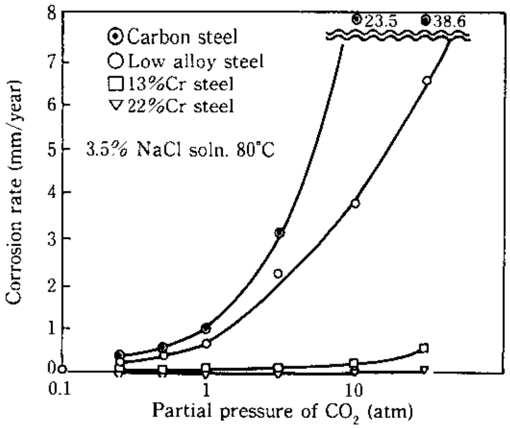


Fig. 10 Effect of CO_2 partial pressure on corrosion rates at 80°C

of 8 to 40 mm/year at around 80°C, more than 10 times greater than that of the 13% Cr steel. The maximum service temperature of the 13% Cr steel is thus limited to 150°C.

(2) Effect of CO_2 Partial Pressure

The partial pressure of CO_2 has a strong effect on corrosion rates in carbon or low alloy steels, as shown in **Fig. 10**. The 13% Cr steel, however, is very resistant to CO_2 corrosion, even at increasing CO_2 partial pressures.

(3) Effect of H_2S Partial Pressure on SSC

The SSC resistance of the 13% Cr steel in NaCl solution containing various amounts of H_2S was studied using 3 point bent beam specimens. At an applied stress of 0.8 × SMYS, cracking was not observed at up to 0.1 atm H_2S, as shown in **Fig. 11**. This critical partial pressure falls to less than 0.1 atm H_2S, however, if the applied stress is raised to 1.0 × SMYS.

4 Conclusions

For sour service OCTG, C110 grade tubulars were developed using 0.45% C low alloy steel. The threshold stresses of the tubulars in the NACE SSC test were above 0.90 × SMYS, with specified yield stresses of between 110 and 125 ksi.

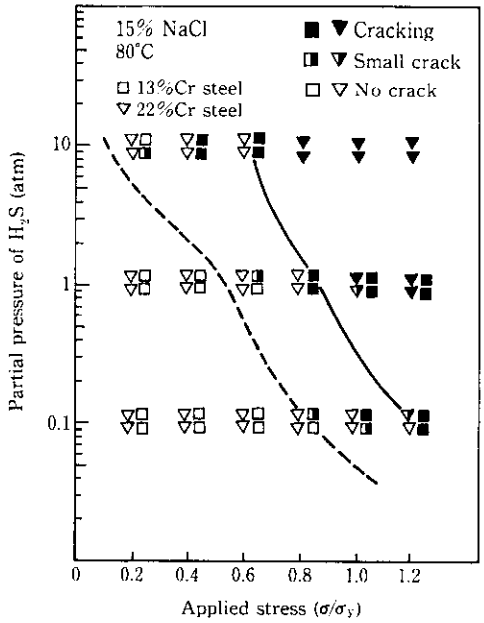


Fig. 11 Effect of applied stress and H_2S partial pressure on the SSC susceptibility of 13% Cr and 22% Cr steels

For sweet service OCTG, a Mannesmann rolling manufacturing process for 13% Cr tubulars was developed. Dimensional accuracy was good and productivity high in actual production. Over 5 000 t of 13% Cr tubulars have been produced by this process and shipped to customers.

References

1) R. D. Kane and W. K. Boyd: "Materials Technology for Oil and Gas Production", Proceedings of Alloys for 80s, Climax Molybdenum Company, Michigan (USA), June (1980)
2) K. Takitani, S. Hasuno, A. Ejima, H. Kawasaki, Y. Kitahaba, and H. Nishi: *Kawasaki Steel Technical Report*, No. 4 (1981), 31-39
3) K. Motoda and T. Masuda: "Development of 110-ksi Grade OCTG with Good Resistance to Sulfide Stress Corrosion Cracking", OTC 5483, Offsore Technology Conference, Houston (USA), April (1987)
4) T. Masuda, T. Terada, T. Kawade, F. Togashi, and T. Kurisu: *Iron Steelmaker*, **12**(1985)4, 33-41