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High Strength $2^1/_4$ and 3% Cr-1% Mo Steels with Excellent Hydrogen Attack Resistance*


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Synopsis:

To develop 300-mm thick alloy-modified $2^1/_4$ Cr-1 Mo steels for pressure vessels to be operated at 900°F and a hydrogen pressure of 3 ksi, laboratory study and factory-scale production trial were carried out. The main results obtained follow:

(1) *The addition of 0.25~0.30% V, 0.015~0.020% Nb and a small amount of B, and the reduction of Si content to less than 0.1% realizes the modified $2^1/_4$ Cr-1 Mo steel. The steel satisfies the target values of strength and toughness as proposed by MPC and API after PWHT whose tempering parameter is 20.6×10^3, and also gives good resistivity to hydrogen attack.*

(2) *The addition of 0.20% V and 0.020% Nb and the reduction of Si to less than 0.1% improve creep rupture strength and resistivity to hydrogen attack of the 3 Cr-1 Mo steels, though both properties are inferior to the modified $2^1/_4$ Cr-1 Mo steel.*

(3) *These modified Cr-Mo steels give low susceptibility to reheat cracking during PWHT and good properties of narrow gapped SAW joints.*

1 Introduction

Heavy oil desulfurization facilities at petroleum refineries are currently operated at about 850°F (454°C) and about 2 ksi (13.7 MPa) in hydrogen pressure. As the materials for pressure vessels, $2^1/_4$ Cr-1 Mo steels with excellent hydrogen attack resistance are used. It is expected, however, that these facilities will be operated at about 900°F (482°C) and about 3 ksi (20.6 MPa) in hydrogen pressure in the future to improve operational efficiency. Conventional $2^1/_4$ Cr-1 Mo steels cannot be used under these severe operating conditions. Consequently $2^1/_4$ and 3 Cr-1 Mo steels with hydrogen attack resistance and creep rupture strength improved by the addition of alloying elements are required. For this reason, MPC (The Materials Properties Council) and API (American Petroleum Institute) in USA have continued activities to standardize alloy-modified $2^1/_4$ Cr-1 Mo steels. It was agreed that the ordinary-temperature tensile strength (TS) be increased to the level of 85 to 110 ksi in ASTM Standards and that an allowable design stress value of 22.2 ksi at 900°F be newly adopted in Sec. VIII, Div. 2 of ASME Boiler and Pressure Vessel Code.[1] In response, Kawasaki Steel conducted systematic research into the improvement of high-temperature strength by the addition of V and Nb, the effect of V addition on hydrogen attack resistance, reduction of the reheat cracking sensitivity of welds in V-bearing steels, etc. Especially in connection with the effect of V addition on the improvement of the hydrogen attack resistance, the authors investigated changes in the morphology, composition and distribution of precipitates attributable to V addition and examined the improvement mechanism by such precipitates.

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Table 1 Chemical compositions of laboratory steels used (mass %)

Steel	C	Si	Mn	P	S	Cr	Mo	V	Nb	Ti	Al	B	REM*
A	0.13	0.05	0.52	0.004	0.001	2.37	1.09	0.25	0.021	—	0.03	—	—
B	0.13	0.06	0.52	0.004	0.001	2.37	1.09	0.31	0.021	—	0.03	—	0.004
C	0.13	0.06	0.53	0.003	0.001	2.43	1.10	0.35	0.021	—	0.03	—	0.006
D	0.13	0.06	0.51	0.003	0.001	2.33	1.07	0.30	0.021	0.010	0.03	0.0019	0.004
E	0.15	0.06	0.50	0.006	0.001	2.21	1.00	—	—	—	0.01	—	—
F	0.14	0.15	0.50	0.007	0.003	3.10	0.97	—	—	—	0.02	—	—

* Rare earth metals

Table 2 Chemical compositions of industrially produced steels (mass %)

	Steel	Steel making	C	Si	Mn	P	S	Cr	Mo	V	Nb	Ti	Al	B	REM	Sn	Sb	As	[S]*1
a	2¼Cr-1Mo-V-Nb-B	EF-LRF 33 t	0.14	0.06	0.54	0.003	0.0008	2.39	1.03	0.25	0.013	—	0.044	0.0010	0.006	0.001	0.0005	0.002	−0.00014
b	2¼Cr-1Mo-V-Nb-Ti-B	VIM 5 t	0.13	0.09	0.51	0.005	0.0010	2.44	1.01	0.29	0.020	0.011	0.023	0.0014	0.005	0.001	0.0005	0.002	−0.00057
c	3Cr-1Mo-V-Nb	EF-LRF 35 t	0.14	0.07	0.53	0.004	0.0010	3.05	1.03	0.21	0.020	—	0.016	—	—	0.001	0.0004	0.002	0.001

*1 $[S]=S-\frac{32}{40}Ca-\frac{32}{140}REM$

This report describes the results of this fundamental research and those of extensive verification tests performed to evaluate strength, toughness, etc. and mock-up tests to evaluate susceptibility to reheat cracking, etc., both conducted on V- and Nb-added 2¼ and 3 Cr-1 Mo steels. The chemical compositions of these steels were designed on the basis of the results of the fundamental research and the materials were produced by way of trial in a commercial plant. Incidentally, a portion of the results of tests conducted by the MPC/API task group on the company's steels was used in the overall evaluation.

2 Experimental Procedures

2.1 Test Materials

2.1.1 Fundamental experiments

Chemical compositions of test steels made by 100-kg vacuum induction melting are given in **Table 1**. Steels A, B and C have the basic compositions of ordinary 2¼ Cr-1 Mo steels and contain 0.25 to 0.35% V and 0.02% Nb. Steel D contains trace amounts of Ti and B in addition to the components of steel B with 0.3% V. Steels E and F, used as comparative materials, are 2¼ Cr-1 Mo steel and a 3 Cr-1 Mo steel, respectively, of ordinary composition. In all these steels, Si content was set at low levels to prevent temper embrittlement and increase creep rupture strength[2]. The P and S contents were also set at low levels to reduce temper embrittlement and the susceptibility of welds to reheat cracking, respectively. The steels were hot rolled to a plate thickness of 30 mm. Quenching treatment was then conducted at a heating temperature of 950°C and at a cooling rate of 0.25°C/s corresponding to that observed in the middle of the thickness of a 300-mm thick plate during water quenching. Subsequently, post-weld heat treatment (PWHT) of a tempering parameter TP = 20.6×10^3 was conducted at 690°C for 24.5 h.

Table 3 PWHT conditions of industrially produced steels

Steel (Thickness)	Tempering	PWHT	TP*
a (300 mm)	650°C, 6 h	690°C, 22.0 h	20.6×10^3
b (300 mm)	650°C, 6 h	690°C, 23.8 h	20.6×10^3
c (350 mm)	650°C, 7 h	690°C, 24.5 h	20.6×10^3

* Tempering parameter $= T(\mathrm{K})[20+\log t(\mathrm{h})]$

2.1.2 Industrial production

Chemical compositions of steels made by way of trial in a commercial plant are given in **Table 2**. Steels a and c are EF-LRF refined steels forged and rolled to plate thicknesses of 300 mm and 350 mm, respectively. Steel b is a VIM (vacuum induction melting) refined steel rolled to a plate thickness of 50 mm. In all these steels, quenching treatment from 950 to 1 050°C was followed by PWHT with a tempering parameter TP = 20.6×10^3, as shown in **Table 3**. The quenching treatment of 50-mm thick plates of steel b was conducted simulating the cooling rate in the middle of the thickness of a 300-mm thick plate during water quenching. Incidentally, steels treated with various TPs were prepared for each steel grade in order to clarify the TP dependence of strength and toughness. Steel a is a 2¼ Cr-1 Mo steel with 0.25% V and 0.013% Nb and B. Steel b has slightly greater V and Nb contents than steel a and contains a trace amount of Ti. Steel c is a 3 Cr-1 Mo steel with 0.21% V and 0.020% Nb. Steels a to c are characterized by very low levels of impurity elements such as P, S, Sn, Sb, and As. Steels a and b contain REMs (rare-earth metals). Incidentally, Steel b was a test material supplied to the MPC/API task group.

2.2 Experimental Methods

2.2.1 Fundamental experiments

Specified test pieces and test conditions were used in the room-temperature tensile test (ASTM A370, E8), high-temperature tensile test (ASTM A370, E21), 2-mm V-notch Charpy impact test (ASTM A370, E23), creep rupture test (JIS Z2272), etc. To evaluate hydrogen attack resistance, Charpy impact test pieces were exposed to a hydrogen atmosphere in an autoclave at 600°C and 49 MPa for various lengths of time. Hydrogen attack resistance was evaluated from changes in absorbed energy at 0°C. Oblique Y-groove restraint cracking test pieces (JIS Z3158) were used in the reheat cracking test of welds. In welding test beads, cold cracking was prevented by preheating to 250°C. PWHT evaluation was then carried out by the usual method in terms of the cracking ratio in five sections. With respect to the examination of microstructures, a 200-kV scanning transmission electron microscope (STEM) was used to observe the morphology of precipitates and an energy dispersive X-ray spectrometer (EDX) was used to analyze their chemical composition.

2.2.2 Industrial production

The same methods as described in 2.2.1 were used in the mechanical testing and hydrogen attack test of the base metal. The room- and high-temperature tensile properties and impact properties of steels a and c were investigated at widely varying PWHT conditions. The G.E. type step cooling method was adopted for accelerated embrittlement in the temper embrittlement test. The cylinder type restraint cracking test method shown in **Fig. 1** was used to investigate the hydrogen attack resistance of the heat-affected zone of welds, and the implant test method shown in **Fig. 2** was employed to investigate the reheat cracking resistance of welds. These two last tests were conducted at Ishikawajima-Harima Heavy Industries Co., Ltd. and AMAX, Inc., respectively, as part of the activities of the MPC/API task group[1]. Welded joints of steels b and c were produced by the narrow-gap two-electrode SAW method in the same manner as welding by a commercial machine (preheating and interpass temperatures, 170 to 200°C; heat input, 3.0 to 3.4 MJ/m), and weld metals were investigated. The joint properties of steel c were also investigated, which was also subjected to the high-temperature fatigue test and fracture toughness test. Incidentally, test pieces with parallel sections (ϕ 10 mm, parallel section length 30 mm) were used in the high-temperature fatigue test, which was conducted under the test conditions of axial strain control, chopping wave, $\dot{\varepsilon} = 1 \times 10^{-3}$/s at 482°C. To investigate fracture toughness, K_{IC} and $K_{IC}(J)$ were measured by CT test. The R curve method for multiple test pieces was used in measuring J_{IC}.

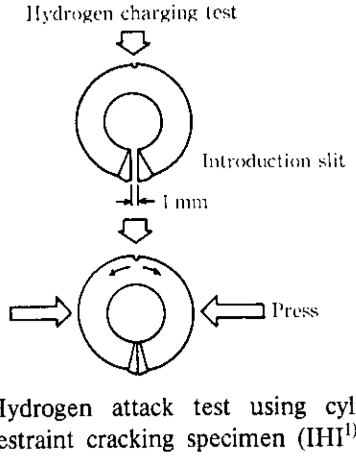


Fig. 1 Hydrogen attack test using cylinder type restraint cracking specimen (IHI[1])

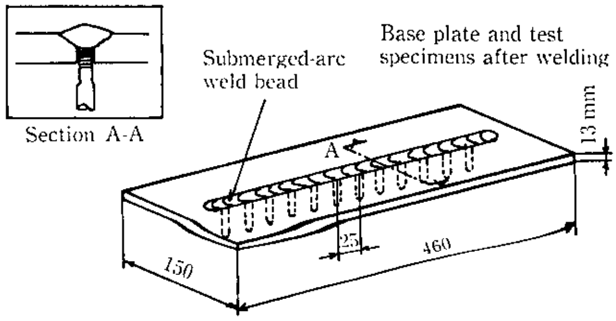


Fig. 2 Welding procedure of reheat cracking test (Implant test, AMAX[1])

3 Results and Discussion

3.1 Composition Design of High-Strength 2 ¼ and 3 Cr-1 Mo Steels

3.1.1 Improvement of high-temperature strength by addition of V and Nb

Tensile stress values of steels A to E at room temperature and 400 to 500°C are shown in **Fig. 3**. Both strength at room temperature and at high temperatures improved with the addition of V and Nb. TS increased with increasing amounts of V added, reaching a maximum at 0.30% V, and tending to decrease at V contents over 0.30%. Steel D, produced by adding Ti and B to a 0.30% V-Nb steel, showed still higher TS.

The creep rupture stresses of steels A to D rearranged by the Larson-Miller parameter are shown in **Fig. 4**. The characteristics of a 2 ¼ Cr-1 Mo steel of ordinary composition are indicated by hatching. All steels A to D had higher creep rupture strength than the steel of ordinary composition, due to the addition of V and Nb. As with TS, steel D, with Ti and B additions, showed the highest creep rupture strength. The creep rupture strength of this steel at 482°C (900°F) in 10^5 h (corresponding to LMP of 18.88×10^3) was high at 235 MPa. The amount of solute Nb increased with increasing heating temperature. Thus Nb contributes

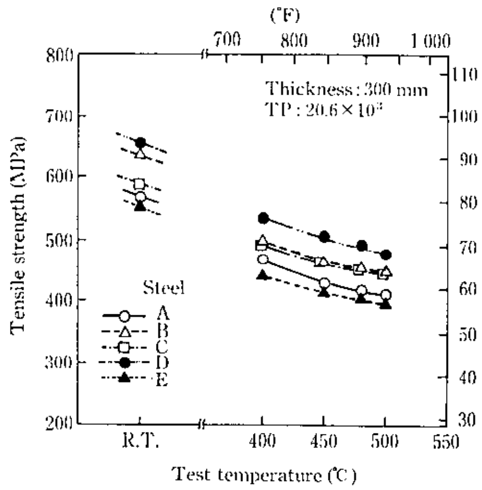


Fig. 3 Tensile strength at elevated temperature of laboratory steel

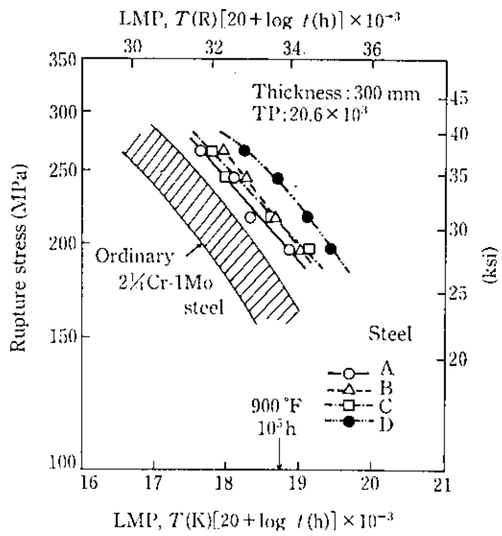


Fig. 4 Relation between creep rupture stress and Larson Miller's parameter in laboratory steel

greatly to the improvement of hardenability[3]. In addition, Nb is a precipitation hardening element, and thus is considered to have improved the strength of these test steels.

3.1.2 Effect of V addition on hydrogen attack resistance

As described earlier, Charpy impact test pieces were subjected to a hydrogen atmosphere at 600°C and 49 MPa. The relationship between the ratio of absorbed energy at 0°C after and before exposure ($_{V}E_0^*/_{V}E_0$) and hydrogen exposure time is shown in **Fig. 5**. Both the 2 ¼ Cr-1 Mo steel (steel E) of ordinary composition and the 3 Cr-1 Mo steel (steel F) of ordinary composition underwent hydrogen attack after short-term hydrogen exposure, and $_{V}E_0^*/_{V}E_0$ decreased greatly. A comparison of these two steels revealed that a decrease in the ratio $_{V}E_0^*/_{V}E_0$ occurred in the 2 ¼ Cr-1 Mo steel in a

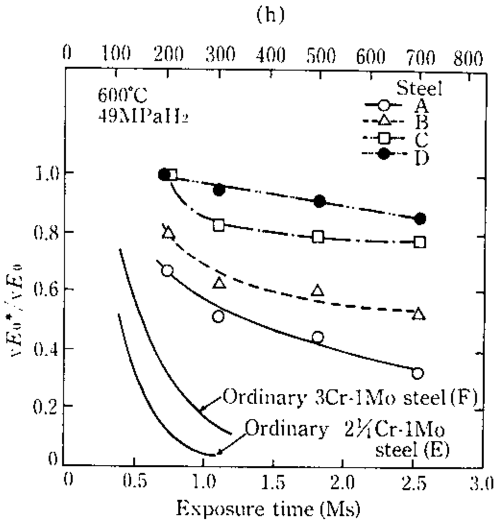


Fig. 5 Effect of exposure time to hydrogen gas atmosphere on absorbed energy at 0°C

shorter exposure time than in the 3 Cr-1 Mo steel. In contrast, all steels A to D with V additions of 0.25 to 0.30% showed smaller changes in $_{V}E_0^*/_{V}E_0$ than steels E and F of ordinary composition; hence, the V-added steels offered excellent hydrogen attack resistance. According to the Nelson diagram, operating conditions of 900°F and a hydrogen pressure of 3 ksi such as those expected in the future are within the safe region of hydrogen attack for the 3 Cr-1 Mo steel. These results suggest that the addition of V will make it possible to use 2 ¼ Cr-1 Mo steels under the future operating conditions. Steels A to D show different susceptibilities to hydrogen attack depending on the amount of V added. In other words, steels A, B, and C (in increasing order of V addition) show a progressively smaller reduction in $_{V}E_0^*/_{V}E_0$ due to hydrogen exposure, and accordingly better resistance to hydrogen attack. In addition, steel D, to which Ti and B were added in addition to 0.30% V, shows a smaller decrease in $_{V}E_0^*/_{V}E_0$ than steel C with 0.35% V. Thus it is apparent that the addition of trace amounts of Ti and B, in addition to V, is also effective in improving hydrogen attack resistance.

3.1.3 Effect of REM addition on reheat cracking resistance of V-bearing steels

The reheat cracking sensitivity of 2 ¼ Cr-1 Mo steels of ordinary composition due to PWHT is generally considered to be lower than that of 1 ¼ Cr-½ Mo steels. However, it was feared that crack sensitivity might increase with the addition of V. In steels of ordinary composition, crack sensitivity is influenced by S content, and when the [S] value given by the following equation is of a negative value, reduced reheat cracking sensitivity is obtained[4].

$$[S] = \left(S - \frac{32}{40} \times Ca - \frac{32}{140} \times REM\right) \times 10^4$$

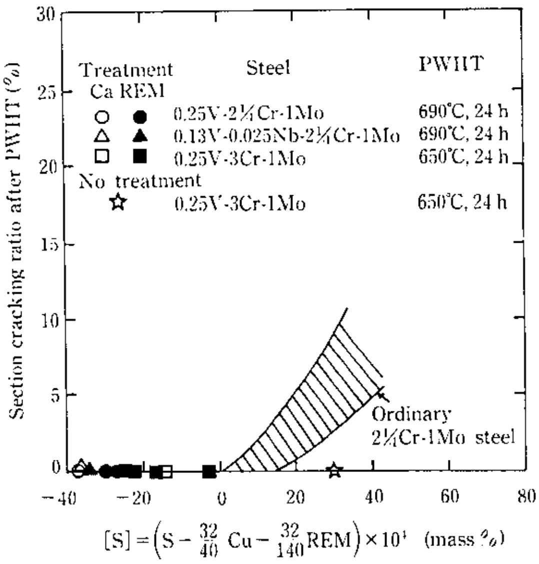


Fig. 6 Results of oblique Y-groove restraint cracking test

Results of the oblique Y-groove restraint cracking test conducted on several kinds of V-bearing and V- and Nb-bearing steels subjected to Ca or REM treatment are shown in **Fig. 6**. Even in V-bearing steels, the section cracking ratio can be reduced to zero if S content is minimized and, additionally, a negative [S]-value is secured by REM or Ca treatment.

3.1.4 Changes in microstructure due to V addition and hydrogen attack resistance

Fracture surfaces of Charpy impact test pieces of hydrogen-exposed steel D with added V, Ti, and B, and steel E of ordinary composition are shown in **Photo 1**. Steel E undergoes intense hydrogen attack and the adjoining methane bubbles at the grain boundaries bond together, showing smooth grain-boundary fracture surfaces. However, steel D shows dimple fracture surfaces and no trace of methane bubbles, indicating that this steel suffered virtually no hydrogen attack. Therefore, the condition of precipitates in these two steels was investigated in order to clarify the mechanism by which the addition of V and other elements brings about improvement in strength and hydrogen attack resistance. STEM images and EDX spectra of precipitates in carbon extraction replicas are shown in **Photo 2**. Steel E (ordinary composition) shows coarse precipitates 0.2 to 0.4 μm in width and 0.3 to 0.8 μm in length that precipitate in the grains and at the grain boundaries and fine needle-like precipitates 0.01 to 0.05 μm in width and 0.2 to 0.5 μm in length that precipitate in the grains only. The former coarse precipitates are carbides with Cr and Fe as their main metallic components, and have crystal structures of M_7C_3 type or $M_{23}C_6$ type. The latter fine precipitates are carbides with Cr and Mo as their main metallic components, have the crystal struc-

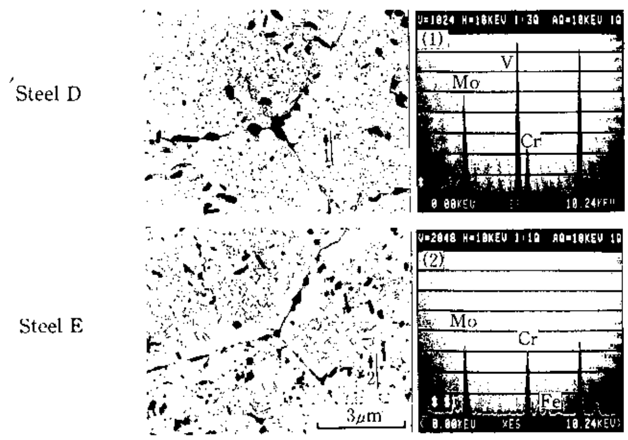
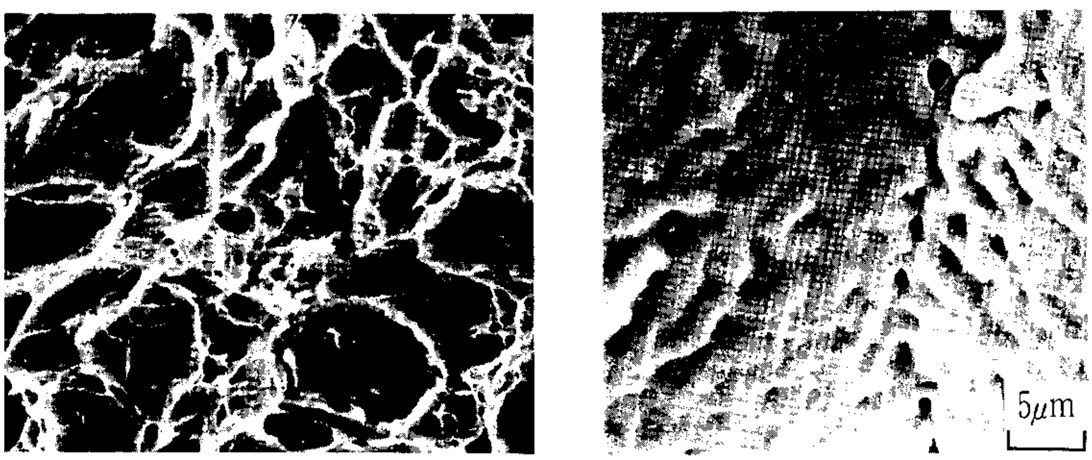


Photo 2 Typical morphologies of precipitates and their compositions



Steel D Steel E

Photo 1 SEM micrographs of fracture surfaces after exposure to hydrogen ture of M_2C type, and form precipitation-free zones (PFZs) at grain boundaries. In steel D, two types of precipitates of different morphology were observed. Coarse carbide precipitates 0.05 to 0.2 μm in width and 0.3 to 0.7 μm in length were observed in the grains and at the grain boundaries. The main metallic components of these precipitates were Cr and Fe, and the V content was 10 at. % or less. These precipitates had almost the same properties as the coarse carbides in steel E of ordinary composition. The other precipitates were fine granular precipitates about 0.05 μm in diameter. These precipitates distribute uniformly not only in the grains but at the grain boundaries, and their main components are V, Mo and Cr. Therefore, the latter precipitates differ greatly in distribution, morphology, and composition from the fine needle-like precipitates with Mo and Cr as their main components which were observed in steel E.

Hydrogen attack is caused by the formation of methane bubbles due to the reaction of grain-boundary carbides with hydrogen. The suppression of the methane formation reaction by the stabilization of carbides and the prevention of the growth of methane bubbles by an increase in the grain-boundary strength are considered effective in preventing hydrogen attack. As mentioned above, there is no great difference in the composition of the coarse grain-boundary carbides of the two steels. Therefore, when this point is taken into consideration, the effect of V addition on hydrogen attack is considered to be closely related to the uniform dispersion of fine precipitates near the grain boundaries when the formation of PFZs is prevented, which in turn results in an increase in grain-boundary strength. The increase in the grain-boundary strength caused by the formation of fine precipitates also contributes greatly to the improvement in the creep rupture strength when V is added.

3.1.5 Composition design

In the composition design of 2¼ Cr-1 Mo steels, the addition of 0.25 to 0.30% V aimed at precipitation hardening, the addition of 0.015 to 0.020% Nb aimed, in combination with high-temperature quenching, at improving hardenability, and the addition of trace amounts of B are effective in increasing the high-temperature strength and creep rupture strength. A reduction in Si content contributes to an increase in the creep rupture strength[2], and accordingly Si content was set at 0.1% or less. The addition of large amounts of V improves resistance to hydrogen attack markedly, and properties much better than those of conventional 3 Cr-1 Mo steels were obtained by adding 0.30% V. Ti and B were also added in trace amounts to improve hydrogen attack resistance. On the other hand, the addition of large amounts of V increases susceptibility to reheat cracking during PWHT. To counteract this, S content was lowered and REMs were added to secure a negative [S]-value. Temper embrittlement was suppressed by a combination of a reduction in impurity elements such as P, Sn, Sb and As, and the lowering of Si content.

Since 3 Cr-1 Mo steels have a ¾% higher Cr content than 2¼ Cr-1 Mo steels, their hardenability is high, making it unnecessary to utilize B for hardening, even at plate thicknesses of 350 mm. With 3 Cr-1 Mo steels, hardening by V, Nb will suffice. Furthermore, susceptibility to reheat cracking is low due to the high Cr content, and reheat cracking is not greatly promoted by V, so REM addition was unnecessary.

On the basis of these considerations, a composition design was made and steels were made by way of trial in a commercial plant.

3.2 Properties of Trial Steels

3.2.1 Room- and high-temperature tensile properties and impact properties vs. PWHT conditions

PWHT conditions are determined by the plate thickness and welding procedure. The relationship between PWHT conditions for a wide range of tempering parameters and strength properties at room temperature and 482°C is shown for steels a and b in **Fig. 7** and steel c in **Fig. 8**. In all the steel grades, the TS properties at room temperature and 482°C met the target values set by MPC under PWHT conditions with a wide range of tempering parameters. Furthermore, ductility, as indicated by elongation (El) and reduction of area (RA) was good under all the conditions.

The relationship between the impact toughness properties of FATT and TT_{54J} and PWHT conditions of

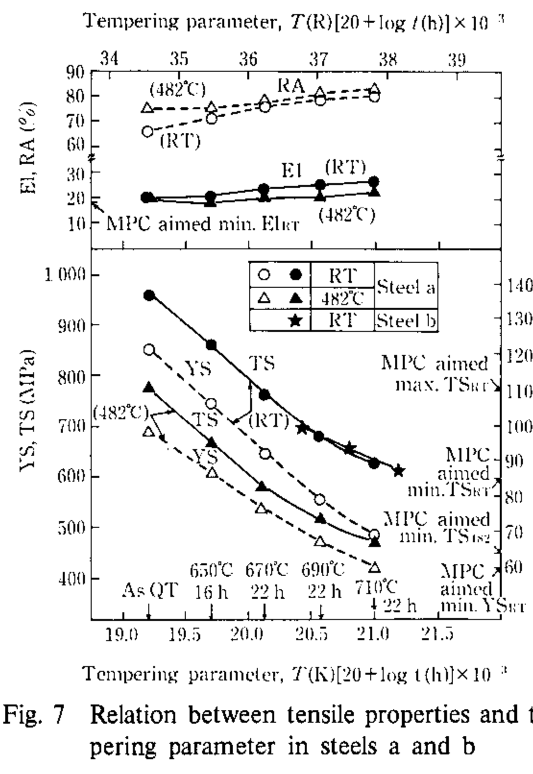


Fig. 7 Relation between tensile properties and tempering parameter in steels a and b

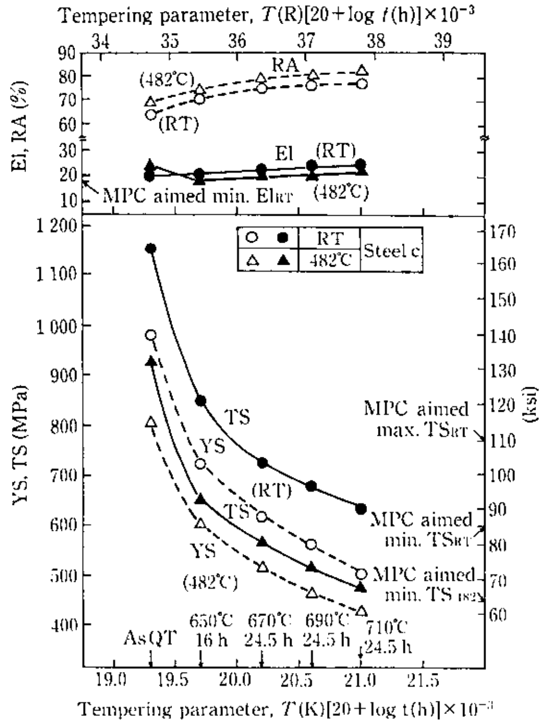


Fig. 8 Relation between tensile properties and tempering parameter in steel c

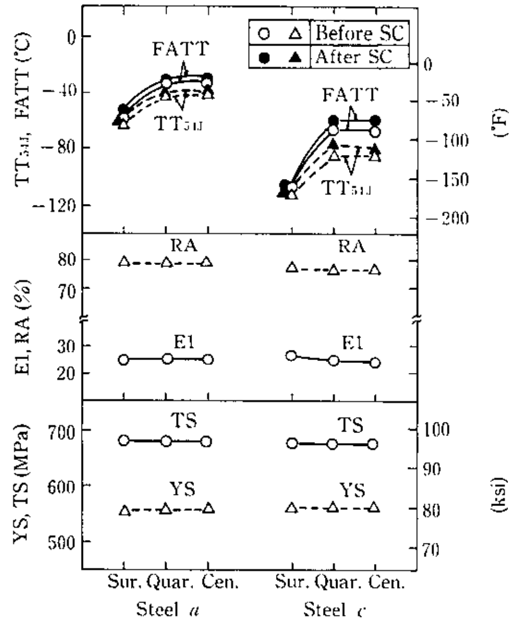


Fig. 10 Variation in mechanical properties with through-thickness location (Steel a, t = 300 mm, 690°C 22 h, TP = 20.6 × 10^3; steel c, t = 350 mm, 690°C, 24.5 h, TP = 20.6 × 10^3)

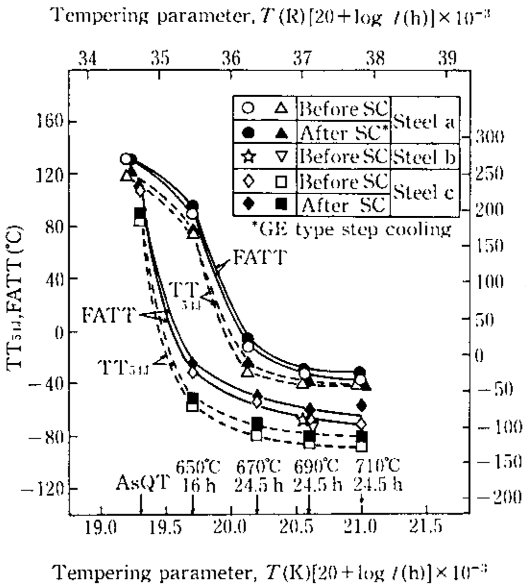


Fig. 9 Relation between toughness and tempering parameter in Steel a-c by 2 mmV notch Charpy impact test (FATT, fracture appearance transition temperature; TT_{54J}, 54J-absorbed energy transition temperature)

steels a to c is shown in **Fig. 9**. Temper embrittlement by step cooling is small in both the 2 ¼ Cr-1 Mo steels and the 3 Cr-1 Mo steels, and toughness is adequate for practical use when the tempering parameter is 20.1 × 10^3 or more for the former and 19.6 × 10^3 or more for the latter.

Results of an investigation into the through-thickness strength and toughness properties of steels a to c are shown in **Fig. 10**. In both steels a and c, the through-thickness strength and ductility change little and are uniform. On the other hand, FATT and TT_{54J} show a remarkable improvement in the surface layer, although they show no difference at ¼ and ½ of the plate thickness in either grade. Steel b was considered to have properties similar to steel a.

3.2.2 High-temperature tensile properties and creep rupture strength

The relationship between the tensile strength and the test temperature of steels a to c is shown in **Fig. 11**. The relationship between the creep rupture properties and the Larson-Miller parameter of the same steels is shown in **Fig. 12**. The conventional design standard values according to ASME Sec. VIII, Div. 2, and the MPC target values for alloy-modified 2 ¼ Cr-1 Mo steel are shown in both figures. In Fig. 12, actual values obtained with a conventional steel are also shown. In steels a to c, MPC target values were achieved for both high-temperature tensile strength and creep rupture strength. The creep rupture strength of steel c was lower than those of steels a and b, due to lower V content. The creep rupture strength of steel c could be expected to increase to the level of steel b if the V content were increased to 0.30%.

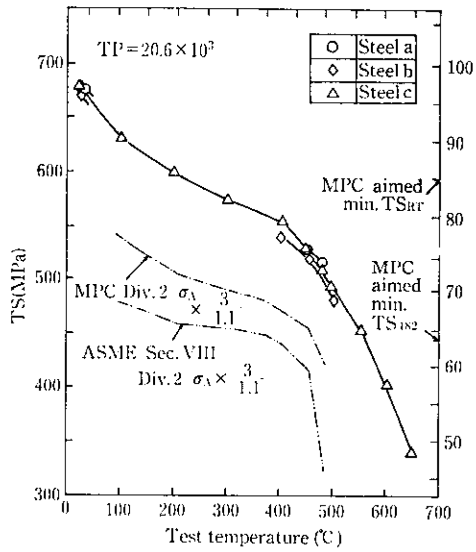


Fig. 11 Tensile strength at elevated temperature in Steel a to c

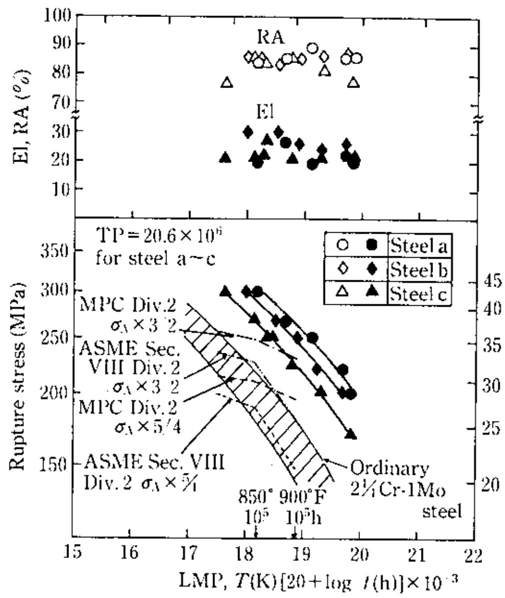


Fig. 12 Relation between creep rupture properties and Larson Miller's parameter in steel a to c

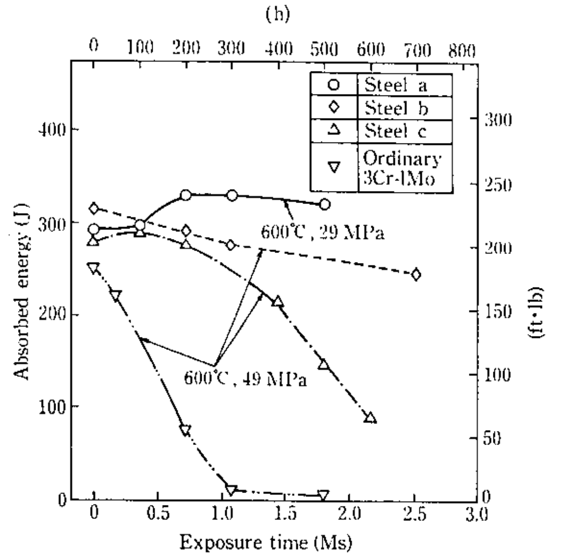


Fig. 13 Effect of exposure time to hydrogen gas atmosphere on absorbed energy at 0°C in 2 mmV-notch Charpy test

Table 4 Results of hydrogen attack tests of synthetic HAZs (IHI[1])

Hydrogen charging / Result / Materials	500°C, (932°F) 20 MPa (2 857 psi)				550°C, (1 022°F) 49 MPa (7 142 psi)	
	400 h		1 300 h		500 h	
	Result	Crack length (mm)	Result	Crack length (mm)	Result	Crack length (mm)
Steel b	N	0	N	0	C	0.5
	N	0	N	0	C	0.6
Ordinary $2^1/_4$Cr-1Mo steel	N	0	N	0	C	1.8
	N	0	N	0	C	2.0

Note 1) N: Not cracked, C: Cracked
2) Heat treatment (1 300°C × 300 s) + (700°C × 15 h)

3.2.3 Hydrogen attack resistance

The relationship between the time of hydrogen exposure and the absorbed energy at 0°C in the Charpy impact test was investigated in steels a to c and the 3 Cr-1 Mo steel of ordinary composition. Results of this investigation are shown in **Fig. 13**. Both steels a and b show good hydrogen attack resistance, and the 2 ¼ Cr-1 Mo steels with added V and Nb have higher resistance to hydrogen attack than steel c, which is a V- and Nb-added 3 Cr-1 Mo steel. The 3 Cr-1 Mo steel also provided substantially improved hydrogen attack resistance in comparison with the 3 Cr-1 Mo steel of ordinary composition due to V-Nb treatment.

A hydrogen attack test using the simulated HAZ specimen shown in Fig. 1 was conducted on steel b and a 2 ¼ Cr-1 Mo steel of ordinary composition. Results of the test are shown in **Table 4**. The hydrogen attack resistance of steel b was improved over that of the steel of ordinary composition. Steels a and c all expected to have similar HAZ properties.

3.2.4 Reheat cracking sensitivity of welds

The reheat cracking sensitivity of welds of steel b during PWHT was investigated by the implant test method shown in Fig. 2. Results of the test are shown in **Fig. 14**. In spite of the addition of 0.29% V, steel b with REM addition and a lowered S content had higher

Table 5 Chemical compositions of weld metals (mass %)

	C	Si	Mn	P	S	Ni	Cr	Mo	V	Nb	Ti
Steel b	0.12	0.17	0.81	0.009	0.004	—	2.53	1.03	0.21	0.020	—
Steel c	0.14	0.21	0.71	0.005	0.003	—	3.14	1.02	0.13	0.008	0.013

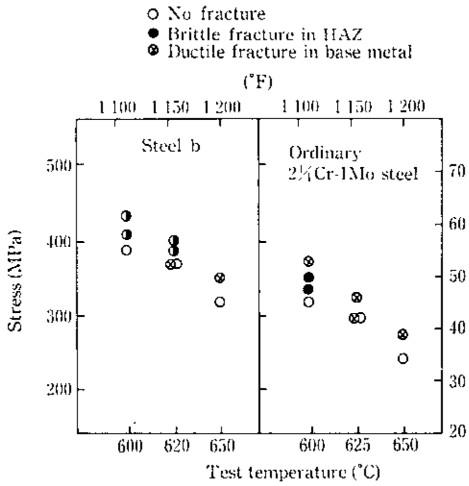


Fig. 14 Results of implant test (AMAX[1])

resistance to cracking at high stresses than the steel of ordinary composition, and hence low susceptibility to reheat cracking. The reheat cracking sensitivity of welds of steels a to c during PWHT was also investigated by the oblique Y-groove restraint cracking test. No cracking was observed in any of the steels. Thus it was ascertained that these steels have low susceptibility to reheat cracking.

3.2.5 Properties of welded joints

Welded joints were prepared using steels b and c. The chemical compositions and mechanical properties of the weld metals of these joints are given in **Tables 5** and **6**, respectively. The strength, ductility and toughness at room temperature of these weld metals are all exceeded the MPC target. Further, MPC's target value for creep rupture strength was achieved in the weld metal of a welded joint prepared using steel b. The tensile strength and toughness of a welded joint (t = 350 mm) prepared using steel c are shown in **Figs. 15** and **16**, repectively. At a tempering parameter of 20.6 x 10^3, tensile strength ranges from 670 to 690 MPa and $TT_{54J} + 3\Delta TT_{54J}$ is −20°C or less, exceeding MPC's target values for both properties.

3.2.6 High-temperature fatigue properties

The fatigue test was conducted at 482°C on steel c treated under two different PWHT conditions (at 650°C for 16 h and at 690°C for 24.5 h). Results of the test are shown in **Fig. 17**. When a comparison was made in terms of the relationship between the whole strain range (ε_{tR}) and the number of cycles to failure (N_f), it

Table 6 Mechanical properties of weld metals

	TP*	YS (MPa)	TS (MPa)	El (%)	Rupture stress 480°C, 10^5h (MPa)	$_vE$ at −18°C (J)	$TT_{54J} + 3\Delta TT_{54J}$ (°C)
Goals of MPC	—	≥413	586 ~758	≥18	≥234	≥54	≤48.9
Steel b	20.6 × 10^3	600	698	19	234	98	−26
Steel c	20.6 × 10^3	546	663	23	—	—	−28

* Tempering parameter = T(K)[20 + log t(h)]

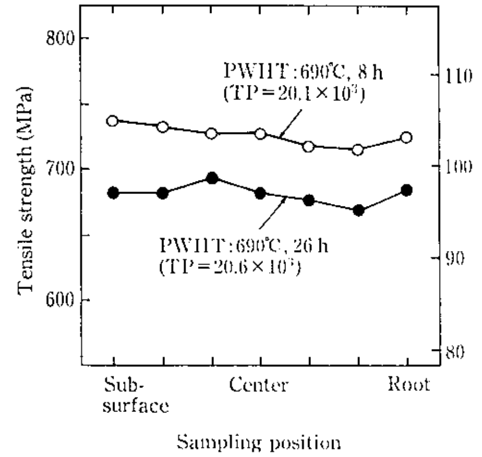


Fig. 15 Tensile strength of 350-mm thick weld joint (steel c)

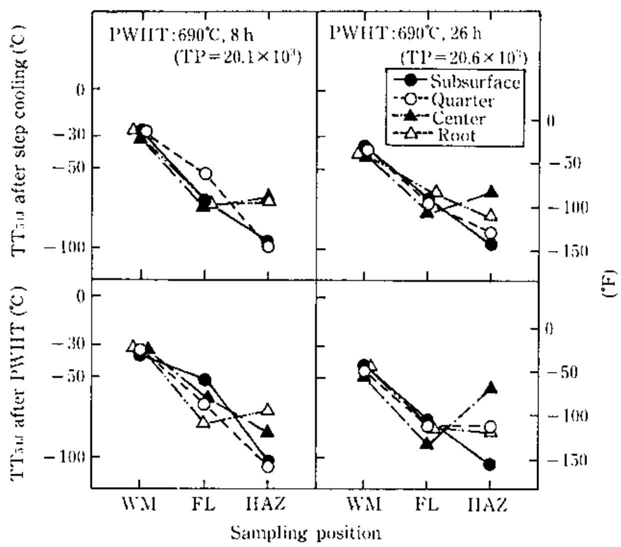


Fig. 16 Toughness after PWHT and stepcooling of 350-mm thick weld joint (steel c)

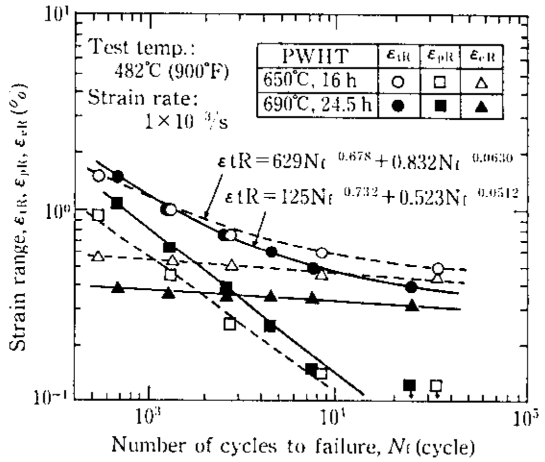


Fig. 17 Relation between strain range and number of cycles to failure (steel c)

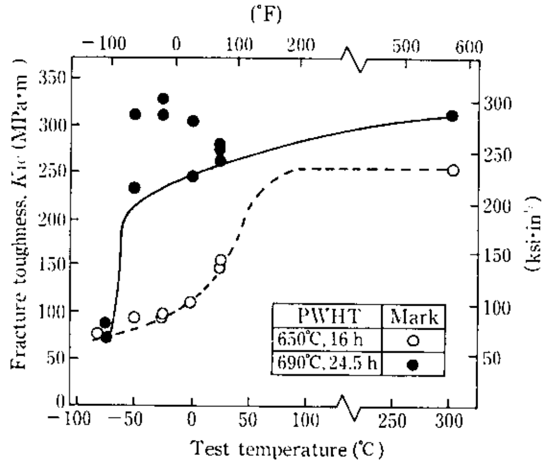


Fig. 18 Relation between fracture toughness (K_{IC}) and temperature (steel c)

was found that the steel treated at 650°C for 16 h, which provides high tensile strength and creep rupture strength, has a longer fatigue life than the steel treated at 690°C for 24.5 h and having low tensile strength and creep rupture strength. This suggests that steels with excellent creep properties have long life in the creep temperature range because the effects of creep damage and atmospheric damage are also important factors in high-temperature fatigue life.

3.2.7 Fracture toughness

The fracture toughness (K_{IC}) test was conducted on steel c treated under two different PWHT conditions (at 650°C for 16 h and at 690°C for 24.5 h). Results of the test are shown in **Fig. 18**. The steel treated at 650°C for 16 h shows K_{IC} of about 90 MPa$\sqrt{m}$ or more at −50 to 300°C, while the steel treated at 690°C for 24.5 h shows K_{IC} of about 230 MPa$\sqrt{m}$ or more at −50 to 300°C. Thus steel c provides sufficient fracture toughness under both of PWHT conditions.

4 Conclusions

Fundamental experiments and trial-manufacture experiments were conducted to develop alloy-modified 2¼ and 3 Cr-1 Mo steels with high creep rupture strength and excellent hydrogen attack resistance for application in 300-mm thick plates for pressure vessels capable of use in a high-temperature, high-pressure hydrogen atmosphere at 900°F (482°C) and at a hydrogen pressure of 3 ksi (20.6 MPa). The following results were obtained:

(1) In 2¼ Cr-1 Mo steels with 0.25–0.30% V, 0.015 to 0.020% Nb, a trace amount of B, and an Si content lowered to 0.1% or less, the target strength values proposed by MPC and API were achieved under PWHT conditions with TP of 20.6×10^3. Good hydrogen attack resistance was also obtained. An increase in susceptibility to reheat cracking during PWHT due to V addition was avoided by lowering S content and adding trace amounts of REMs.

(2) In 3 Cr-1 Mo steels, creep rupture strength and hydrogen attack resistance were greatly improved by adding 0.20% V and 0.020% Nb and lowering the Si content to 0.1% or less. However, 3 Cr-1 Mo steels are inferior to alloy-modified 2¼ Cr-1 Mo steels in these two properties.

(3) Both modified 2¼ Cr-1 Mo steels and modified 3 Cr-1 Mo steels have sufficient toughness for practical use with PWHT of TP of 20.1×10^3 or more and 19.6×10^3 or more, respectively. In both steels, the degree of temper embrittlement by G.E. type step cooling was very small.

(4) Welding materials for narrow-gap SAW suitable for modified 2¼ Cr-1 Mo steels and modified 3 Cr-1 Mo steels were successfully developed, and good weld metal mechanical properties were confirmed. Good welded joint performance can also be expected.

(5) The remarkable improvement in hydrogen attack resistance and creep rupture strength due to the addition of V to 2¼ Cr-1 Mo steels can be explained by an increase in grain-boundary strength due to the formation of densely distributed fine V-Cr-Mo precipitates at the grain boundaries.

References

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