

## **ADVANCED VANADIUM MODIFIED STEELS FOR HIGH PRESSURE HYDROGEN REACTORS**

### **ABSTRACT**

New generation of vanadium modified low-alloy chromium-molybdenum steels for hydrogen reactors has been reviewed. Three steels: 2.25Cr-1Mo-0.25V, 3Cr-1Mo-0.25V-Ti-B, 3Cr-1Mo-0.25V-Nb-Ca standardized according to ASME Boiler and Pressure Vessels Code, Section VIII Division 2 are presented and compared with conventional 2.25Cr-1Mo steel. Metallurgical characteristics, main properties and application limits of the steels has been shown. Microstructure and its effects on in-service degradation phenomena has been indicated.

**Key-words:** *hydrogen reactors, vanadium modified Cr-Mo steels, environmental degradation*

### **INTRODUCTION**

Hydrogen reactors are used for several kinds of processes in refineries and petrochemical plants, such as desulphurisation of hydrocarbons and cracking of heavier hydrocarbon fractions into lighter molecules. These processes are carried out at high temperatures and pressures in the presence of a catalyst.

For more than last 30 years, conventional low-alloy chromium-molybdenum 2.25Cr-1Mo steel has been extensively used for the reactor vessels; to a lesser extent 3Cr-1Mo steel has been also applied. The reactors generally have been operated at temperatures lower than 454°C with hydrogen partial pressure above 10 MPa [1]. Growing demands for higher service temperatures/pressures and increased reactor sizes resulted in larger and heavier reactors with a unit weight up to 1500 metric tons. Many problems with transportation and construction of such reactors were encountered. Moreover, due to the process temperature increase close to the position of 2.25Cr-1Mo curve according to API 941 (Nelson diagram) [2], high temperature hydrogen attack was possible to occur during the reactors' service.

In order to solve these problems, new generation of vanadium modified Cr-Mo steels was developed. The steels are standardized according to ASME Boiler and Pressure Vessels Code, Section VIII Division 2:

- 2.25Cr-1Mo-0.25V steel, approved as Code Case 2098-1 in 1991, allowing several grades with additions of niobium, calcium, titanium and boron,
- 3Cr-1Mo-0.25V-Ti-B, approved as Code Case 1961 in 1992,
- 3Cr-1Mo-0.25V-Nb-Ca, accepted as Code Case 2153 in 1993.

First two reactors made of 3Cr-1Mo-0.25V-Ti-B steel by Japan Steel Work were completed in 1990 [3], and the reactors made of 3Cr-1Mo-0.25V-Nb-Ca were manufactured in 1994 at Kobe Steel, Tagasako Works in Japan [4]. The first 2.25Cr-1Mo-0.25V reactor was fabricated by Nuovo Pignone in Italy in 1995. By the end of 2001 year, 98 vanadium modified vessels had been fabricated all over the world [3].

In this paper metallurgical characteristics, main properties and application limits of vanadium modified reactor steels have been presented. Microstructure and its effects on steel properties have been shown. Improved resistance to in-service degradation phenomena has been indicated.

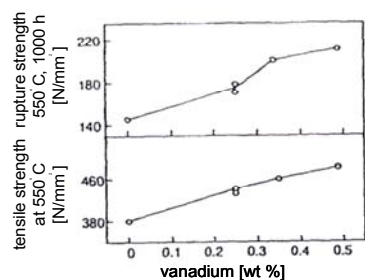
## CHARACTERISTICS OF STEELS AND APPLICATION LIMITS

ASME VIII-2 Code Cases requirements for chemical composition of vanadium modified steels are given in Table 1. Advanced steel making processes, such as a process based on pig iron production in the blast furnace by steel refining in the BOF converter, ladle metallurgy and vacuum treatment are necessary. They provide an extraordinary low content of tramp elements, such as tin, arsenic, antimony and low level of phosphorus, sulphur and oxygen [5].

**Table 1.** Chemical requirements for V modified Cr-Mo steels

Composition, wt. %	2.25Cr-1Mo-0.25V Code Case 2098-1	3Cr-1Mo-0.25V-Ti-B Code Case 1961	3Cr-1Mo-0.25V-Nb-Ca Code Case 2151
C	0.10 – 0.15	0.10 – 0.15	0.10 – 0.15
Mn	0.30 – 0.60	0.30 – 0.60	0.30 – 0.60
P	max. 0.015	max. 0.015	max. 0.015
S	max. 0.010	max. 0.010	max. 0.010
Si	max. 0.1	max. 0.1	max. 0.1
Cr	2.00 – 2.50	2.75 – 3.25	2.75 – 3.25
Mo	0.90 – 1.10	0.90 – 1.10	0.90 – 1.10
Cu	max. 0.25	max. 0.25	max. 0.25
Ni	max. 0.25	max. 0.25	max. 0.25
V	0.25 – 0.35	0.20 – 0.30	0.20 – 0.30
Nb	max. 0.07	-	0.015 – 0.070
Ca	max. 0.015	-	0.0005 – 0.0150
Ti	max. 0.030	0.015 – 0.035	-
B	max. 0.0020	0.001 – 0.003	-

The three modified alloys utilise vanadium addition to enhance tensile strength at elevated temperature and creep rupture strength, and to improve resistance to in-service degradation phenomena, such as temper embrittlement, high temperature hydrogen attack (HTHA) and hydrogen embrittlement [1,3-5]. The effect of vanadium content on the mechanical properties of



**Fig. 1.** Effect of vanadium content on mechanical properties of 3Cr-1Mo steel [3]

3Cr-1Mo steel is shown in Fig. 1. The elevated temperature tensile strength and creep rupture of 3Cr-1Mo-0.25V-Nb-Ca are improved by the addition of niobium [3]. By the addition of calcium into Cr-Mo steels, calcium sulphides form instead of manganese sulphides [3]. In opposite to manganese sulphides, stable calcium sulphides do not dissolve during welding that results in a decreased susceptibility of weldments to stress relief cracking caused by grain boundary segregation of sulphur. The intentional addition of boron in 3Cr-1Mo-0.25V-Ti-B steel increases the hardenability and assures uniform distribution of mechanical properties throughout most heavy cross sections [1]. The addition of titanium helps to maximize the effect of boron.

The modified steels are supplied in quenched and tempered condition. Tempering is carried out at 690-710°C in order to reduce the strength level and to improve impact properties of the quenched steels. The tempering process is performed after the final post weld heat treatment cycle of the reactor. The steels exhibit some decrease in low temperature toughness compared to the conventional steels: 54 J transition temperature (54 J TT) is -29°C and -40°C, respectively [3,4].

Design properties of the conventional Cr-Mo steels and vanadium modified Cr-Mo steels are summarised in Table 2. Higher room temperature strength properties of the modified steels are presented. Increased mechanical properties allow for higher design stresses, leading to a decreased wall thickness and a reduced weight of the reactors.

According to API 941, 0.25 wt.% of vanadium in 2.25Cr-1Mo steel protects the material from HTHA under hydrogen partial pressure  $\leq 13.79$  MPa up to 482°C, compared to 454°C for the conventional 2.25Cr-1Mo alloy. However, despite the vanadium addition, the maximum design temperature permitted by ASME VIII-2 for modified 3Cr-1Mo steels is 454°C at the present time. These steels cannot meet the Division 2 creep rupture requirements at 482°C. It is indicated in Table 2 that application of the modified steels results in lower unit weight of the reactors at a comparable cost.

**Table 2. Comparison of reactor steels: conventional Cr-Mo and V modified Cr-Mo**

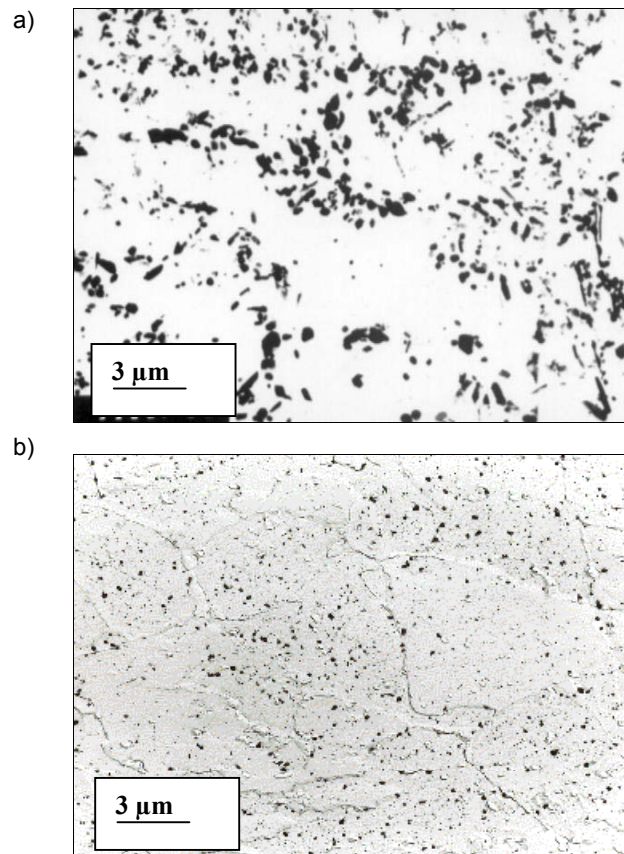
Steel grade	Conventional 2.25Cr-1Mo	2.25Cr-1Mo-0.25V	Conventional 3Cr-1Mo	3Cr-1Mo-0.25V-Ti-B	3Cr-1Mo-0.25V-Nb-Ca
Max. allowed temperature ASME VIII-2	482°C	482°C	454°C	454°C	454°C
Max. allowed temperature API 941	454°C	510°C	510°C	510°C	510°C
Min. Tensile strength	517 MPa	586 MPa	517 MPa	586 MPa	586 MPa
Min. Yield strength	310 MPa	414 MPa	310 MPa	414 MPa	414 MPa
Design stress intensity value, ASME VIII-2	at 454°C 150 MPa	at 454°C 169 MPa	at 454°C 131 MPa	at 454°C 164 MPa	at 454°C 164 MPa
	at 482°C 117 MPa	at 482°C 163 MPa	-	-	-
Wall thickness [1]	at 454°C 338 mm	at 454°C 298 mm	at 454°C 392 mm	at 454°C 307 mm	at 454°C 307 mm
	at 482°C 442 mm	at 482°C 310 mm	-	-	-
454°C design: reactor weight typical cost [1]	1038 metric tons 5.65 £x10 <sup>6</sup>	916 metric tons 5.5 £x10 <sup>6</sup>	1203 metric tons 6.26 £x10 <sup>6</sup>	944 metric tons 5.61 £x10 <sup>6</sup>	944 metric tons 5.61 £x10 <sup>6</sup>
482°C design: reactor weight typical cost [1]	1359 metric tons 7.39 £x10 <sup>6</sup>	953 metric tons 5.72 £x10 <sup>6</sup>	-	-	-

Due to the large wall thickness, the high hardenability and the severe service conditions of the reactors made of vanadium modified Cr-Mo steels, welding needs precaution and careful processing. Welds are always post weld heat treated before service [1,3,5]. Generally, 54 J TT of weld metal and base metal are 20 to 30°C higher than those of the conventional 2.25Cr-1Mo steel, but the transition temperature of heat affected zone is sufficiently low enough compared with those of base metal and weld metal [3].

Delayed hydrogen induced cold cracking is a potential problem of the weldments in the conventional Cr-Mo steels. Low temperature PWHT may be used to prevent the cracking [6]. The tendency towards hydrogen cracking of the vanadium modified steels appears to be similar. As a general precaution, only low weld fluxes and welding conditions that guarantee very low hydrogen input should be used for this kind of steels [5].

### MICROSTRUCTURE AND ITS EFFECT ON IN-SERVICE PROPERTIES

In-service behaviour of the reactor Cr-Mo steels strongly depends on the type and morphology of carbide phase. Vanadium modification provides fine, vanadium-rich carbides, evenly distributed in the metal matrix. Fine carbide particles in quenched and tempered 2.25Cr-1Mo-0.25V steel are compared with coarse carbides in 2.25Cr-1Mo steel in Fig. 2. Four types of carbides were identified in the modified steel:  $M_7C_3$ ,  $M_{23}C_6$ ,  $M_6C$  and  $M_2C$ . All the types of the carbides contained vanadium, as well differentiated amounts of chromium, iron and molybdenum [8]. The thermodynamic stability of carbides in the modified steels is much greater than vanadium-free precipitates [7].



**Fig. 2.** Carbides in conventional 2.25Cr-1Mo steel (a) and modified 2.25Cr-1Mo-0.25V steel (b), carbon extraction replicas, scanning electron microscope

### Temper embrittlement

A good near room temperature toughness of steel is one of important factors for safe operation hydrogen reactors during shutdowns and startups. Low alloy Cr-Mo steels are known to be prone to temper embrittlement caused by long tempering and/or elevated service in a temperature range of about 370-560°C [1,9,10]. The grain boundary segregation of impurities and tramp elements was shown to be the main factor influencing this phenomenon.

It is a current industry practice to limit impurity/tramp elements content in reactor steels according to a relationship called a Watanable number or J factor [11]:

$$J \text{ factor} = 10^4 (P + Sn) (Mn + Si)$$

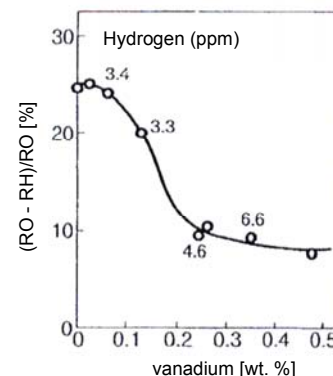
In the above equation the elements are expressed in ppm. It is considered that the resistance of steels to temper embrittlement will be sufficient when J factor is limited to a value of less than 100.

Carbide transformations accompanied by microstructural and microchemical changes cooperate in the embrittling process [12]. A delay in carbide transformation, precipitation or thickening usually leads to a delay in the embrittlement [7]. From this point of view, the presence of stable V-rich carbides is of great importance. Generally, the temper embrittlement susceptibility of vanadium modified Cr-Mo steels is lower compared to the conventional Cr-Mo steels [1,4].

### Hydrogen embrittlement

Hydrogen embrittlement is a cause of concern for high-strength reactor steels during shutdown conditions. At typical hydroprocessing temperatures and hydrogen partial pressures, hydrogen diffuses easily throughout the reactor wall, and hydrogen concentration level reaches about 6-7 ppm maximum. When the reactor is cooled down to rapidly to permit the diluted hydrogen to diffuse out of the steel, delayed hydrogen cracking may occur. Embrittlement usually takes place below 150°C [1].

Fine, evenly distributed vanadium-rich carbides trap the diffusible hydrogen in the steel. As a result, vanadium modified Cr-Mo steels have lower hydrogen diffusion coefficient than the conventional alloys. Lower hydrogen diffusivity improves the resistance to hydrogen embrittlement because hydrogen concentration at the tip of cracks is reduced. In Fig. 3 the effect of vanadium addition in 2.25Cr-1Mo steel on reduction of area of tensile specimen without and with hydrogen charging is shown [13]. It may be seen that ductility loss decreases with an increased vanadium content and the steels containing more than about 0.2 wt.% of vanadium have high resistance to hydrogen embrittlement.



**Fig. 3.** Effect of vanadium addition on ductility loss connected with hydrogen embrittlement. RO - reduction of area of hydrogen-free specimen, RH - reduction of area of hydrogen-charged specimen [13]

### High temperature hydrogen attack

Cr-Mo steels may fail by high temperature hydrogen attack during the reactor service. The hydrogen that diffuses throughout the steel wall reacts with carbon in carbides to form methane.

Depending on service conditions, the reaction takes place at the steel surface or inside the steel that results in surface decarburisation of the material or internal decarburisation connected with formation of cavities/fissure/cracks filled with methane and decrease in mechanical properties [2,14,15].

HTHA limits the maximum operating conditions of hydroprocessing reactors. The guidelines for the maximum recommended temperatures at corresponding hydrogen partial pressures for the modified and the conventional Cr-Mo steels, designated by API 941 are shown in Table 2.

The susceptibility to HTHA is determined by the microstructure of the steel, especially by its alloy carbides  $M_xC_y$ . Higher thermodynamic stability of the carbides results in reduced methane pressure, which gives a driving force for cavities growth, and suppressed hydrogen influence [16]. Precipitation of vanadium-rich carbides in the modified steels enhances the resistance to hydrogen attack. Adding 0.25 wt.% of vanadium to 2.25Cr-1Mo steel, improved resistance to HTHA is achieved, the same as the resistance of 3Cr-1Mo steel with higher chromium content [2].

### **Hydrogen induced overlay disbonding**

All hydrogen reactors must be protected from high temperature sulphide corrosion caused by hydrogen sulphide present in the process stream. The protection is usually provided by austenitic stainless steel weld overlay over the base steel. However, the reactors may often develop disbonding cracks during shutdowns due to hydrogen concentration at the interface of both the steels. The tendency for disbonding appears to increase with increased hydrogen partial pressure, increased operating temperature and faster cooling rates from the operating temperature [1].

The modern vanadium modified Cr-Mo steels do not exhibit as great a susceptibility to disbonding as the conventional steels do. This has been attributed to the lower diffusivity of hydrogen in the vanadium steels caused by hydrogen trapping by fine vanadium-containing carbides [3]. Another explanation deals with formation of low carbon martensite on the weld metal side of the interface instead of high carbon martensite which increases susceptibility to disbonding [17]. This is due to the fact that vanadium carbide precipitations reduce carbon diffusion from the base metal to the weld metal.

## **SUMMARY**

Advanced vanadium modified Cr-Mo steels with additions of niobium, calcium, titanium and boron offer improved performance for hydrogen reactors in the refinery industry and the petrochemical industry compared to conventional Cr-Mo steels. The new steels provide important advantages:

1. Excellent properties against hydrogen degradation, such as
  - hydrogen embrittlement,
  - high temperature hydrogen attack,
  - hydrogen induced overlay disbonding,
2. Good toughness at low temperatures and improved resistance to temper embrittlement,
3. Lower unit weight of the reactors at a comparable cost by increase of steel strength.

## REFERENCES

1. Antalfy L.P., Chaku P.N.: US perspective of modern hydroprocessing reactor metallurgy. *Hydrocarbon Technology Int.* HTI Quaterly, Spring 1996, pp. 39-48.
2. Steels for hydrogen service at elevated temperatures and pressures in petroleum refineries and petrochemical plants. API 941. Fifth edition. American Petroleum Institute, Washington D.C., 1997.
3. Yamada M., Sakai T., Nose S.: Development of Cr-Mo-V-Cb-Ca steel for high pressure and high temperature hydrogenation reactors, in *Application of 2.25Cr-1Mo-V modified steel to hydroprocessing pressure vessels*. Kobe Steel, Ltd., Tagasago, Japan, 1996.
4. Antalfy L.P., West G.T.: The new generation of vanadium modified reactor steels. EFC WP15 Meeting, TotalFinaElf, Paris, France, 2002.
5. Detemple I., Hanus F., Luxenburger G.: Advanced steels for hydrogen reactors. *Hydrocarbon Engineering* 4 (1999), pp. 1-8.
6. Takahashi E., Iwai K.: Omission of intermediate post weld heat treatment (PWHT) by utilising low temperature PWHT for welds in pressure vessels. *Special Technical Publication ASTM STP 755*, ASTM, Philadelphia PA, 1982.
7. Vyrostkova A., Kroupa A., Janovec J., Svoboda M.: Carbide reactions and phase equilibria in low alloy Cr-Mo-V steels tempered at 773-993 K. Part I: experimental measurements. *Acta mater.* 40 (1997), pp. 31-38.
8. Hucińska J., Haras J.: Opracowanie szczegółowego programu i procedur badań nieniszczących reaktorów 0150-R1 i 0150-R2 w Rafinerii Gdańskiej SA pod kątem dopuszczenia ich do eksploatacji na czas dłuższy niż 100 000 godzin oraz badania stanu zerowego reaktorów. Report no. 013448. Gdańsk University of Technology, Mechanical Engineering Faculty, Gdańsk, 1999.
9. Barbacki A.: O przyczynach kruchości niskostopowych stali pracujących w podwyższonych temperaturach. *Hutnik* 45 (1991), pp. 306-310.
10. Tadao Iwadate: Life prediction methodology of high temperature/pressure reactors made of Cr-Mo steels. *First Int. Conf. on Microstructures and Mechanical Properties of Aging Materials*, Chicago, Illinois 1992. Minerals, Metals & Materials Society, Warrendale, Pennsylvania, 1992, pp. 19-26.
11. Watanabe J., Murakami Y.: In: *API Publication 28*. American Petroleum Institute, Washington D.C., 1981.
12. Hudson J.A., Druce S.G., Gage G., Wall M.: Thermal aging effects in structural steels. *Theoret. and Appl. Fracture Mechanics* 10 (1988), pp.123-133.
13. Sakai T., Takagi I., Asami K.: Effect of carbides and inclusions on internal hydrogen embrittlement of Cr-Mo pressure vessels steels. *J. of the Iron and Steel Inst. of Japan.* 72 (1986) pp. 1375-1382.
14. *Corrosion in the Petrochemical Industry*. L. Garverick [ed]. ASM International, Materials Park OH, 1995.
15. Timmins P.F.: *Solutions to Hydrogen Attack in Steels*. ASM International, Materials Park OH, 1997.
16. Shih H. M., Johnson H. H.: A model calculation of the Nelson curves for hydrogen attack. *Acta Metall.* 30 (1982), pp. 537-545.
17. Shinya T., Tomita Y.: Effect of vanadium addition on disbonding of 2.25Cr-1Mo steel weld overlay welded with austenitic steel. *Z. Metallkd.* 88 (1997) pp. 587-589.