Solubility Product of VN in Austenite of High Cr Heat Resistant Steel

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Dissolved V in austenite of 7%Cr–0.4%V–0.09%N steel (hereinafter, % means mass%) was measured and the solubility product of VN was determined as follows:

$$\log([\%V][\%N]) = 4.38 - \frac{8436}{T}$$

where T is the absolute temperature in K. The solubility product obtained is 3 to 5 times larger than those in the literature and about one order larger than that for iron. The decrease in the activity coefficient of nitrogen due to the presence of Cr and V in the experimental steel is responsible for the increase in the solubility product of VN.

KEY WORDS: precipitation; MX; thermodynamics; activity coefficient.

1. Introduction

Micro-alloying technique based on the precipitation of carbo-nitride (hereinafter MX) is very important for developing advanced alloys.¹⁾ A lot of work has been done on high strength steel sheet,²⁾ high toughness steel plate,³⁾ high strength heat resistant steel.⁴⁾ Therefore, the solubility products of MX in carbon steel have been systematically studied and the results have been summarized elsewhere.⁵⁾ However, the experimental data on alloy steel have been limited. Therefore, the solubility products for carbon steel or the calculated data by the thermodynamic data calculation system⁶⁾ have been used for alloy steels instead. However, it is reported that some alloying elements, such as Cr, increase largely the solubility products of MX.⁷⁾ Therefore, the systematical experimental data on alloy steel should be needed.

The authors have reported the solubility products of NbC^{8,9)} and TaC^{10,11)} in austenite of the high chromium heat resistant steel. Among several kinds of MX-type precipitates VN has been also judged to be important for the purpose of maintaining high temperature strength for a long time.¹²⁾ In this study the solubility product of VN in austenite of high chromium alloy steel has been studied experimentally. In determining the solubility product of NbC, we have proposed a new analyzing method that the Nb content in the filtered solution is directly measured by using an inductively coupled plasma atomic emission (ICP). The results obtained are compared with the results of the conventional method and enough reliability of the new method has been established for NbC.⁸⁾ However, this method is not general, so that the reliability of the new method has been examined for VN.

2. Experimental Procedure

2.1. Experimental Steel

A 50 kg ingot was made in a vacuum induction furnace. The ingot was heated at 1250°C and then hot-rolled to a 12 mm plate in a final thickness. The experimental steel is designed on the base of ASTM A213 T91 along a concept that any compound other than VN, such as delta-ferrite, carbide and nitride, does not precipitate in austenite. The chemical composition of the experimental steel is 0.0032%C–0.15%Si–0.51%Mn–7.2%Cr–0.3%Mo–0.41%V–0.091%N and the balance is Fe. The Nb content is less than 0.0005%. Small coupons of 20×20 mm were cut from the plate normalized at 1250°C and then the coupons were normalized at 980–1200°C in air for 1 h. A thin sheet of about 1 g is sliced from the heat-treated specimen, surface layers of which were cut off about 2 mm in order to eliminate the surface damages. The time dependence of the precipitation of VN is also examined up to 100 h at 1100°C and, in this experiment, the coupon was heated in an SiO₂ capsule in order to prevent oxidation and nitridation.

2.2. Analyzing Method

The thin sheet was completely dissolved in 6N-HCl of 50 ml at 70°C and the residue was isolated using nucle-pore filter with 2 μm diameter. V concentration of the filtered solution was determined directly using ICP by means of a calibration method. The reference solutions containing 1, 10, and 20 ppm V were prepared by distilling a standard vanadium reagent using 6N-HCl. The test solution contains constituent elements of the matrix, *i.e.* Fe, Cr, Mo, Mn and Si and, therefore, a wave length of 311.07 nm was selected in order to prevent the interferences from the matrix con-

stituent elements. The detectable limit for V in this study is about 0.42 ppm for the experimental steel.

The solubility product of VN is calculated using the following equation assuming that chemical composition of VN is stoichiometric.

$$[\%V][\%N] = [\%V][\%N_0] \dots\dots\dots(1)$$

where

$$[\%N_0] = \%N_t - \frac{14}{51}(\%V_t - [\%V]) \dots\dots\dots(2)$$

Symbols, $[\%V]$ and $[\%N]$, denote the dissolved V and N in austenite, and V_t , N_t denote the total V and N, respectively. Symbol, $[\%N_0]$, denotes the dissolved N in Fe-V-N alloy which is calculated from the observed values of the dissolved V. The amount of the dissolved vanadium in the matrix, $[\%V]$, is assumed to be equal to the amount of the dissolved vanadium observed.

3. Experimental Results and Discussion

3.1. Thermal Equilibrium

Characteristic features of the present analyzing method are that the duration of heat treatment is relatively short, and that the V content of a filtered solution is directly measured. Therefore, firstly, whether the equilibrium in the precipitation of VN is satisfactorily guaranteed by 1 h heating or not becomes a problem. Therefore, the effects of heating rate and heating duration should be discussed. **Figure 1** shows the Arrhenius plot of the dissolved V. Open marks correspond to rapid heating where a small coupon was put into a pre-heated furnace and temperature of the coupon was reached to an aiming temperature within 5 min at least. Closed marks correspond to slow heating where a coupon was set in a cold furnace and gradually heated up to an aiming temperature taking 3 h. All coupons were held for 1 h at a temperature in both cases. The figure shows that a linear relationship is found in a wide range of temperature by the rapid heating and the regression line may probably correspond to the equilibrium solubility limit of V in austenite. On the other hand, the amount of the precipitates by the slow heating is insufficient at low temperatures as compared with those of the rapid heating. **Figure 2** shows the time dependence of the dissolved V of the rapidly heated specimens at 1100°C. This figure shows that the enough precipitation has been roughly accomplished by the 1 h rapid heating. Therefore, from Figs. 1 and 2 it is found that the equilibrium of the precipitation of VN in austenite is practically realized by a technique of the rapid heating of a small coupon followed by the short time holding at a temperature. The authors have studied the precipitation behavior of TaC and NbC and concluded that the precipitation of MX in austenite is accomplished within a very short time when martensitic steel is heated rapidly beyond the A_{C1} transformation point.⁸⁻¹¹⁾ This phenomenon is caused by the rapid nucleation and subsequent growth of MX on a lot of retained dislocations which are succeeded from martensitic structure. The phenomenon showed in Figs. 1 and 2 can be explained by the same mechanism. Figure 1 shows that the amount of precipitated VN particles in the slowly heated specimens is less than those of the rapidly heated

Fig. 1. The Arrhenius plot of the dissolved V for the different heating patterns.

Fig. 2. The time dependence of the dissolved V of the rapidly heated specimens at 1100°C.

ones. When the specimens are heated slowly, dislocations quenched in martensite are annihilated during heating and, thus, nucleation sites in austenite decrease. Beside this reason, since the 1 h heating time is not enough for the equilibrium, the amount of the precipitates is less at low temperatures as shown in Fig. 1.

3.2. Optical Microscopy and Precipitates

Figure 3 shows optical microstructures of the experimental steel normalized at 1050 and 1200°C for 1 h. Coarse austenitic grains and no delta ferrite were confirmed when normalizing temperature was 1200°C, though the grain size of 1050°C was fine. This figure suggests that MX may be fully dissolved at 1200°C.

Table 1 shows chemical compositions of the extracted residue in the specimens normalized at 1150 and 970°C for 30 min. The residue was electrolytically extracted using the non-aqueous solution (10 mol% acetyl acetone-1 mol% tetramethyl ammonium chloride-methanol). The metallic elements listed in the table were analyzed using ICP. As shown

Fig. 3. Optical microstructures of the experimental steel normalized at (a) 1050°C and (b) 1200°C for 1 h.

Table 1. Chemical compositions of the extracted residue. The specimen was normalized at a temperature listed for 30 min. Content of each element is converted to the relative composition in the residue. (mass%)

	Normalizing temperature (°C)	V	Cr	Fe	Si
Content in specimen	1150	0.038	0.006	0.002	<0.001
	970	0.194	0.028	0.002	<0.001
Content in residue	1150	80.8	12.8	4.2	<2.1
	970	86.2	12.4	0.9	<0.4

Fig. 4. (a) Transmission electron microstructure of the extracted residue of the specimen normalized at 1050°C for 1 h and (b) the diffraction pattern from the same area as (a).

in the table the major metallic element in the residues is V and the residue contains chromium of about 13%. A small amount of Fe or Si is also detected, but the extracted values for Fe or Si in the specimens are roughly constant, respectively, independent of normalizing temperature. Therefore, nonmetallic inclusions excluding VN may be responsible for the detection of these elements.

Figure 4(a) shows a transmission electron micrograph of the extracted carbon replica of the specimen normalized at 1050°C for 1 h. Fine spherical or cuboidal precipitates were observed. A diffraction pattern (Fig. 4(b)) from the same area as Fig. 4(a) shows that the most of the precipitates are judged to be the precipitates of an NaCl type. Figure 5 shows the chemical compositions of the individual particle extracted from the same specimen as Fig. 4, which were determined by energy dispersive spectra (EDS). This figure shows that the major metallic element of the precipitates is vanadium and the precipitates contain about 20% of Cr and 3% of Si. These results lightly differ from the results of ICP listed in Table 1.

The intrinsic non-metallic inclusions may be extracted on the replicas. These unexpected compounds may affect EDS. Even though these unexpected compounds did not irradiat-

Fig. 5. Results of EDS analyses of each MX particle as shown in Fig. 4(a).

ed directly by an electron beam, if those are around an MX particle irradiated, the characteristic X-ray emitted from V atoms in the MX particle irradiates indirectly the unexpect-

ed compounds, and, consequently, the information of the unexpected compounds might be overlapped over the information of EDS from the MX particle. Therefore, Si detected by EDS may be caused by the nonmetallic inclusions extracted, though the reason that the Cr content by TEM-EDS is larger than those of ICP shown in Table 1 should be discussed.

It is reported that V(CN) particles on the extracted replicas from high Cr heat resistant steels of the normalized and tempered state contain about 15% of Cr according to the TEM-EDS analysis.^{13,14)} Other researchers reported the TEM-EDS with an noticeable peak of Cr^{15,16)} and without any peak of Cr.^{12,17)} The above reports are on the normalized and tempered specimens, so that Cr carbides should be around the V(CN) particles of interest. On the other hand, the TEM-EDS information of VN in high Cr steel in the normalized state has not yet been available.

According to the calculation of the thermodynamics calculation system,⁶⁾ the equilibrium composition at 1050°C of MX in the experimental alloy is 78.2% of V, 20.2% of N, 1.5% Fe, and 0.4% Cr (97.6% of V, 1.9% of Fe and 0.5% of Cr for metallic elements). The calculation shows that Cr is little contained in VN. However, the calculation system does not indicate the database for what compositional range of alloy the coefficients in the calculation are reasoned inductively and to what alloy the calculation is applicable. Therefore, it is not so surprising that the results of the calculation do not coincide with the experimental results as shown in Table 1 and Fig. 5.

Certainly, it is not easy to determine precisely the Cr content in the MX particles in the experimental steel. However, it can be concluded that the VN particles in the experimental steel should include a certain amount of Cr.

3.3. Reliability of Present Analyzing Method

At around 1960 the solubility product of MX in steel was determined as follows: After V-containing alloys are equilibrated in an N₂-containing gas flow, N-content of the specimens is determined chemically and then the solubility limits of V and N are determined from changes of the slope in a total V or gas pressure vs. total N content diagram for every temperature and an alloy with a given V-content.^{18,19)} However, this method is not always convenient, because (i) it takes many hours to reach at a state of equilibrium and (ii) many test runs should be needed.

In the late of 1960's the precise chemical analysis of N, C, and Nb in the isolated residue from the solution dissolved by 6 N-HCl had been made. As a result, the crystallographic structure and the solubility products of NbC and NbN in austenite of iron were determined.^{20,21)} This technique reduced the number of test runs.

In the early 1970's, systematic study on the isolation and determination of carbides in steel had been made, and, besides the acid methods, the potentiostatic electrolysis method using the non-aqueous solution had been also recommended for the isolation of MX.²²⁻²⁴⁾ Many kinds of precipitates can be isolated within relatively a short time and, therefore, this method has become the major extraction method for steel and the extracted residue has been analyzed directly.²⁵⁾ In the early 1980's the ICP method has been induced and the accuracy and detectable limit of

Fig. 6. Comparison of the dissolved V measured by the present study (solution method) with the electrolytically extracted residue-ICP method.

analysis have been improved greatly.²⁶⁾ According to both the electrolysis method and ICP method the amount of the metallic element in the residue and, thus, the amount of soluble element in the matrix are determined precisely and speedy. Therefore, the solubility product can be determined easily with the assumption of the stoichiometric form of MX.^{10,11,27)}

However, this method, the combination of the electrolytically extracted residue and ICP, is still inconvenient, because there arises some errors when the amount of the metallic element is comparable with that of the residue. In this case directly analyzing the filtered solution should be necessary. However, ICP is not suitable for analyzing the organic solution.²⁸⁾ Moreover, this method includes several sequential processes, which may arise some errors.

Therefore, Ikeda *et al.*⁸⁾ have developed a simple method where a heat resistant steel of 9%Cr–1%Mo–0.2%V–0.1%Nb is dissolved in 6 N-HCl and the filtered solution is analyzed by ICP directly, and thus, the solubility product of NbC in austenite can be determined. The results are comparable with those of the popular electrolytically extracted residue-ICP method.

Considering the above circumstances in this study the filtered solution after dissolving by 6 N-HCl is directly analyzed by ICP. **Figure 6** shows the correlation between the dissolved V obtained by the present analyzing method and the popular electrolytically extracted residue-ICP method. After normalized at 950°C half of the total V was precipitated as VN and after normalized at 1200°C followed by tempered at 500°C for 2 h the most of V still stayed in the matrix. In both cases we can find a very good coincidence between two methods. Therefore, the present analyzing method is judged to be sufficiently reliable.

3.4. Solubility Product of VN

The dissolved V shown by open circles in Fig. 1 is converted according to Eqs. (1) and (2) into the solubility product of VN in austenite of the experimental steel and the re-

Fig. 7. Solubility product of VN in austenite of the experimental steel and Fe-V-N alloy.

sults are shown in Fig. 7. In the figure the solubility product at 1100°C which was obtained by a specimen heated for 100 h is also shown by a symbol of a star. There is not any significant difference between the solubility product by the 100 h heating and the regression line for specimens heated for 1 h. Therefore, the regression line for 1 h is considered as a solubility product of VN in the equilibrated austenite of the experimental steel and is given by Eq. (3)

$$\log([\%V][\%N]) = 4.38 - \frac{8436}{T} \quad \text{.....(3)}$$

In the figure the calculated data by Thermo-Calc⁶⁾ for both the experimental steel and iron, and the calculated data using the regression equation deduced by Narita *et al.*⁷⁾ are shown. Firstly, it is found that the solubility product of VN in austenite of high Cr steel is much larger than that for iron. It is also found that the solubility product of VN for the experimental steel is much larger as compared with both the data calculated by Thermo Calc⁶⁾ for the composition of the experimental steel and the data calculated using the Narita's regression equation⁷⁾ for 7%Cr-0.4%V-0.09%N steel.

Many researchers have studied the solubility products of VN in austenite for iron^{5,7,18,29-30)} and the results are summarized also in Fig. 7. Turkdogan³¹⁾ also proposed the solubility product of VN for iron, but his equation does not based on the original data and, thus, his data are omitted in Fig. 7. Some scatterings depending on the researchers are recognized, but the maximum difference among the solubility product of iron is within the factor of 3. On the other hand, the solubility product of VN obtained in this study is about 5 times larger than that of Narita *et al.*⁷⁾

In the following sections the reasons for the differences in the solubility product between the present data and the literature data will be discussed.

3.5. Off-Stoichiometric Composition of VN

Equation (1) is induced on the assumption that the composition of VN is stoichiometric. However, a V-N binary phase diagram³²⁾ shows that the minimum composition of

N in MX is roughly given by VN_{0.7}. Therefore, the solubility product for VN_{0.7} was re-calculated and the results were plotted by open triangles in Fig. 8. The solubility product of VN_{0.7} is 1.0 to 1.7 times still larger than those for VN, which depends on normalizing temperature. Therefore, the off-stoichiometric composition of VN cannot explain the difference in the solubility product of VN between the present data and the literature data.

3.6. Effect of Cr on the Solubility Product

(1) Dissolution of Cr into MX

If a compound of MX is formed by the next reaction in steel

a thermodynamic equilibrium constant, K , is given by Eq. (5).

$$K = \frac{a_V^{1-n} \cdot a_{Cr}^n \cdot a_N}{a_{MX}} \approx [\%V]^{1-n} [\%Cr]^n [f_N \cdot \%N] \quad \text{.....(5)}$$

where, [%V], [%Cr], and [%N] are dissolved V, Cr, and N in austenite, and a_V 's, f_N are activities according to the Henry's law and the activity coefficient of N, respectively. In Eq. (5) we assumed that $a_{MX}=1$, $f_Z=1$, and $f_V=1$. Eq. (5) can be rewritten as

$$\log K = \log\{[\%V][f_N \%N]\} + n \log \frac{[\%Cr]}{[\%V]} \quad \text{.....(6)}$$

In Eq. (6) [%N] denotes dissolved N in Fe-Cr-V-N alloy and is given by

$$[\%N] = \%N_t - \frac{14}{51} (\%V_t - [\%V]) \cdot \frac{1}{1-n} \quad \text{.....(7)}$$

Using Eqs. (2) and (7), Eq.(6) can be rewritten as

$$\begin{aligned} \log K = & \log\{[\%V][f_N \%N_0]\} \\ & + \log \left\{ 1 + \frac{\%N_t - [\%N_0]}{[\%N_0]} \cdot \frac{1}{1-n} \right\} + n \log \frac{[\%Cr]}{[\%V]} \end{aligned} \quad \text{.....(8)}$$

Fig. 8. The effects of off-stoichiometric VN and the dissolution of Cr in VN on the solubility product of VN in austenite of the experimental steel.

The 1st term of the right hand side of Eq. (8) is the apparent solubility products for the imaginary VN, in which all of Cr in $V_{0.85}Cr_{0.15}N$ are replaced by V, and it can be confirmed that the 2nd and 3rd terms are both positive for the observed values of [%V], using Eq. (2), and the relations, $n \approx 0.15$ and [%Cr] ≈ 7.2 . Therefore, the 1st term of Eq. (8) is apparently smaller than the observed values of Eq. (3) by the values of the sum of 2nd and 3rd terms of Eq. (8), if K can be assumed constant. It is found assuming $f_N = 1$ that the values of the apparent solubility products for $V_{0.85}Cr_{0.15}N$ are 35–60% smaller than those for (Fig. 8). However, as seen in the figure, the difference between the observed values and the literature data cannot be explained satisfactorily by the dissolution of Cr into MX.

(2) Activity Coefficient

Usually the activity coefficient, f_N , is smaller than unity and the solubility product, [%V][%N], is larger than K by a factor of $1/f_N$. Thermodynamic data for the calculation of the activity coefficient of N in austenite of high Cr steel are limited, however the interaction parameters of the major element of the experimental steel for the activity coefficient of N in liquid iron are available.³³⁾ The interaction parameter of V for in austenite of Fe–V–N alloy is negative and increases with increase in temperature¹⁸⁾ and the extrapolated value for liquid iron (1 650°C) is nearly equal to the experimental value in liquid iron.³³⁾ That is, the correlation between in the liquid state and in the solid state is confirmed in Fe–V–N alloy.

Therefore, the effect of soluble elements on the activity coefficient can be discussed in the liquid state instead of the solid state. Mn, Cr, Mo, and V show the negative effect on f_N and Si, and C increase f_N . According to the database in the liquid state³³⁾ f_N 's of Fe–V–N alloy and the experimental steel in the liquid state are roughly estimated as 0.9 and 0.42, respectively. The interaction parameter of V for f_N is negative and the absolute value is larger than that of Cr, however the contribution of Cr to the activity coefficient is much larger than that of V due to the larger amount of Cr. Therefore, the decrease in f_N , i.e. the increase in the solubil-

ity product of VN, is mainly caused by the increase in Cr content. In the liquid state, f_N of the experimental steel is roughly half of that for Fe–V–N alloy, which may lead that the solubility product of VN in the experimental steel is twice larger than that for the Fe–V–N alloy. On the other hand, according to Thermo Calc⁶⁾ the solubility product of VN in austenite of the experimental steel is 5 times larger than that of Fe–V–N alloy (Fig. 7). Therefore, though there may be some problems in discussing the absolute values of the solubility product, qualitatively we can explain the effect of alloying element on the solubility product of VN in austenite in terms of the activity coefficient in the liquid state. Therefore, it is concluded that the observed increase in the solubility product of VN as compared with that of iron is mainly caused by the decrease in the activity coefficient of N due to the large amount of the dissolved Cr.

3.7. Difference in the Solubility Product between Present Work and the Literature Data

It is shown in Fig. 7 that the solubility product of VN in austenite of high Cr heat resistant steel is larger than that of Narita's data or Thermo Calc. The difference in the Cr content in the MX particles is one of the reasons for the above discrepancy. However, Fig. 8 shows that though the dissolved Cr in VN in the experimental steel certainly decreases the difference between the observed values and the literature, the essential difference is still exist between these data. Since the solubility product due to Narita's data and Thermo-Calc are introduced by extrapolation or regression analysis, it is reasonable to conclude that their data-bases do not include the experimental steel.

The above discussion does not explain satisfactorily the difference between the solubility product of Eq. (2) and that of Thermo Calc or Narita's data. However, Fig. 8 shows that at 1200°C the value of the solubility product is nearly equal to the product of %V_t and %N_t, which suggests that the VN particles should be dissolved completely and grain growth may occur. Certainly, Fig. 3 shows that at 1200°C the grain growth is confirmed. If the solubility product in the literature were true in this steel, fine grains would be

observed. Therefore, Eq. (3) is suitable for the solubility product of VN in the austenite of the high Cr ferritic steel.

4. Conclusions

A heat resistant steel of 7%Cr–0.3%Mo–0.4%V–0.09%N–Fe was normalized for a relatively short time. The specimen was dissolved in 6 N-HCl solution and the filtered solution was analyzed by ICP and the dissolved V in austenite was measured. Assuming stoichiometric composition of VN, the solubility product of VN in austenite is calculated and the following conclusions have been obtained.

(1) The values of the dissolved V measured by the present work are equivalent to those by the conventional combined electrolytically extracted residue-ICP method.

(2) The solubility product of VN in austenite is given by

$$\log([\%V][\%N]) = 4.38 - \frac{8436}{T}$$

where T is the absolute temperature and % denotes mass%.

(3) The solubility product according to the above equation is about one order larger than those of iron and 3 to 5 times larger than those of the literature, which are calculated for the experimental steel.

(4) The observation of the microstructure supports the above equation rather than those of the literature.

(5) The decrease in the activity coefficient of N due to the presence of Cr and V in the matrix rather than the dissolution of Cr into MX is responsible for the increase in the solubility product of VN in this alloy as compared with iron.

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