Phase Equilibria in FeS–XS and MnS–XS (X=Ti, Nb and V) Systems

Hajime MITSUI,¹⁾ Tomoyuki SASAKI,²⁾ Katsunari OIKAWA³⁾ and Kiyohito ISHIDA³⁾

1) Formerly Department of Materials Science, Graduate School of Engineering, Tohoku University. Now at Fukushima Technology Centre, Machiike-dai 1-12, Koriyama 963-0215 Japan. 2) Formerly Department of Materials Science, Graduate School of Engineering, Tohoku University. Now at Nippon Steel Corporation, Muroran Works, Nakamachi 12, Muroran 050-8500 Japan. 3) Department of Materials Science, Graduate School of Engineering, Tohoku University, Aoba-yama 02, Aoba-ku, Sendai 980-8579 Japan.

(Received on January 8, 2009; accepted March 31, 2009)

The phase equilibria in the FeS–XS and MnS–XS (X: Ti, Nb and V) pseudo-binary systems were investigated by using an X-ray diffraction and electron probe micro analyzer. In the FeS–TiS and FeS–VS systems, a mono-sulfide with the NiAs structure form a complete solid solution, while two-phase separation of the mono-sulfide with the NiAs structure is observed in the FeS–NbS system. In all MnS–XS systems, two-phase region of a Mn-rich mono-sulfide and X-rich mono-sulfide exists widely. Solubility of each elements in the Mn-rich mono-sulfide and X-rich mono-sulfide is small, except that of Mn in Nb-rich mono-sulfide.

KEY WORDS: iron sulfide; manganese sulfide; titanium sulfide; niobium sulfide; vanadium sulfide; phase equilibria.

1. Introduction

Since morphology, distribution and composition of non-metallic inclusions in steels have significant effects on their material properties, the control of them is an important subject of investigations in the area of steel making process.¹⁾ In the case of sulfide inclusions, the MnS and FeS are the most popular inclusions and a lot of studies focusing on the relation between solidification condition and the morphology of them have been conducted.^{2–5)} Because phase diagrams are an important tool for understanding the formation mechanism of the MnS and FeS, phase diagram relations on FeS and MnS in steels have also been conducted.^{6–8)} In our previous papers, the systematic studies of the effect of alloying elements on the morphology of MnS^{9–11)} and the calculation of phase diagram based on the CALPHAD approach¹²⁾ have been conducted. The occurrence of the morphology change of MnS in steels was shown to relate with the metastable monotectic reaction and stable eutectic reaction forming the liquid and solid sulfides, respectively. Similar results were also obtained in other alloys such as Fe–Cr alloys^{13,14)} and Cu alloys.¹⁵⁾

Ti, Nb and V are commonly used as alloying elements in steels to improve the material properties. These elements have also strong chemical affinity for sulfur in steels. It has been reported that degree of effective sulfide formation by solute elements in steel decreases in the order of $Zr > Ti > Mn > Nb > V > Cr > Al > Mo > W > Fe$.¹⁶⁾ Thus, a complex precipitation behavior of these sulfides is expected in the commercial steels. In fact, a control of the precipitation of MnS, TiS and Ti₂CS in interstitial-free steels is an

important factor to improve the material properties.¹⁷⁾ The phase diagrams including sulfide phases is one of the most important information to understand these precipitation mechanism and stability of the sulfide phases. The CALPHAD approach is very useful for calculation of phase diagrams in the multi-component and multi-phase system and allows to predict the precipitation mechanism, but the computable sulfide phases in steels are few due to the lack of thermodynamic data of sulfides.

The goal of our research is the development of the thermodynamic database to calculate the phase diagram and phase stability of steels including various kinds of sulfide. We have already developed the thermodynamic database for Fe–Ti–C–Cr–S–Mn–Ni system.^{18,19)} In this study, we focused on the phase equilibria FeS–XS and MnS–XS (XS: TiS, NbS and VS) systems, because Ti, V and Nb are very strong affinity for sulfur in steels. Only a few works about phase stability and phase equilibria of sulfide mixtures in these system have been reported,^{20,21)} although these are essential information to determine the function of the thermodynamic database. For example, Vogel *et al.*²⁰⁾ and Kaneko *et al.*²¹⁾ reported only partial phase equilibria of FeS–TiS system. But their conclusions are conflict. In addition, any information on the phase equilibria of the MnS–XS systems could not be found. Herein, we report the crystal structure and phase equilibria of FeS–XS and MnS–XS mixture sulfide prepared by a powder-synthesizing method.

2. Experimental Procedure

Specimens weighing about 2 g each were prepared by a

powder-synthesizing method using high purity iron, manganese, titanium, niobium, vanadium and sulfur powder. The mixed powders were uniaxially pressed at 250 MPa to form a green compacts with a cylinder shape in a diameter of 15 mm. The green compacts were sealed in evacuated quartz capsules and heat treated at 673 K for 72 h, and then elevated to 1 173 K and kept for 24 h to promote a chemical reaction of each powder. The prepared specimens were cut into four pieces and sealed again in evacuated quartz capsules. The small pieces in the quartz capsule were equilibrated at 1 173–1 573 K, and then the quartz capsule was dropped into ice water.

Microstructure observation and composition analysis of the mirror-polished sections of the specimens were carried out by using an electron probe micro analyzer (EPMA). X-ray diffraction (XRD) was used for the analysis of crystal structure of the equilibrated specimens ground to powder of the FeS–XS systems.

3. Experimental Results

3.1. FeS–XS Systems

Typical backscattering electron images (BEI) of $(\text{Fe}_{0.2}\text{Ti}_{0.8})\text{S}$ mixture annealed at 1 273 K for 10 h is shown in Fig. 1. Black and white color regions are void and metallic phases, respectively and the matrix in gray color is the sulfide phase. According to the EPMA analysis of sulfide phase at several points, the chemical composition of sulfide was almost the same value at every analyzed point. This result suggests that the sulfide phase in Fig. 1(a) is a homogeneous phase. Every samples of the FeS–TiS system showed the similar microstructure.

Figures 2(a) and 2(b) show the typical XRD patterns obtained from $(\text{Fe}_{0.6}\text{Ti}_{0.4})\text{S}$ and $(\text{Fe}_{0.2}\text{Ti}_{0.8})\text{S}$, respectively. The spectrum peaks of Figs. 2(a) and 2(b) can be identified as the NiAs and Ti_8S_9 structure by Joint Committee on Powder Diffraction Standards of International Center for Diffraction Data (JCPDS-ICDD cards), respectively.²²⁾ The NiAs structure is observed a composition region from pure FeS to $(\text{Fe}_{0.4}\text{Ti}_{0.6})\text{S}$ and pure TiS, while several samples with high Ti content show the Ti_8S_9 structure which is called NiAs-type superstructure.²³⁾ This Ti_8S_9 structure phase might be transformed from the NiAs structure phase during the cooling, because the phase transformation from the NiAs to the Ti_8S_9 is very sensitive to the cooling rate.²⁴⁾ The lattice parameters of the NiAs structure were evaluated from the

XRD patterns using the software PowderCell²⁵⁾ and the results are summarized in Table 1 and are plotted in Fig. 2(c) as a function of TiS content. The lattice constant of pure FeS and TiS accords with previous data.²⁶⁾ The *a*- and *c*-axis of the NiAs structure monotonously increases and decreases with increasing TiS content, respectively. These results suggest that the mono-sulfide with the NiAs structure in FeS–TiS binary system forms complete solid solution in the temperature range 1 173 to 1 473 K. According to the

Fig. 2. XRD patterns obtained from (a) $(\text{Fe}_{0.6}\text{Ti}_{0.4})\text{S}$ and (b) $(\text{Fe}_{0.2}\text{Ti}_{0.8})\text{S}$ annealed at 1 473 K for 24 h and (c) composition dependence of *a*- and *c*-axis of (Fe–Ti)S with the NiAs structure.

Fig. 1. Backscattering electron images of $(\text{Fe}_{0.2}\text{Ti}_{0.8})\text{S}$ annealed at 1 273 K.

Table 1. Lattice constant of FeS–XS (X: Ti, V, Nb) systems.

Specimen [mol%]	Temp. /K	<i>a</i> -axis/nm	<i>c</i> -axis/nm	<i>c/a</i> ratio
FeS–TiS				
0.00	1273	0.3473	0.5786	1.666
20.00	1273	0.3454	0.5818	1.684
40.50	1273	0.3428	0.5919	1.727
60.76	1273	0.3404	0.6003	1.764
100.00	1273	0.3297	0.6412	1.945
FeS–VS				
13.81	1473	0.3444	0.5745	1.668
36.44	1473	0.3429	0.5754	1.678
57.63	1473	0.3390	0.5774	1.703
80.91	1473	0.3371	0.5793	1.720
100.00	1473	0.3340	0.5845	1.750
FeS–NbS				
76.20	1273	0.3430	0.5987	1.745
80.60	1273	0.3.61	0.6166	1.835
91.40	1273	0.3326	0.6299	1.894
94.80	1273	0.3315	0.6350	1.916
100.00	1273	0.3310	0.6537	1.975

previous works of FeS–TiS system by Vogel *et al.*²⁰⁾ and Kaneko *et al.*²¹⁾ the miscibility gap between FeS and TiS were drawn in the phase diagram as shown in Fig. 3, although the location of the miscibility gap of them were inconsistent with each other. Vogel *et al.*²⁰⁾ estimated the miscibility gap by a microstructure examination of as-cast alloys and thermal analysis. On the other hand, Kaneko *et al.* evaluated the miscibility gap by the chemical composition analysis of the Fe–Ti–S ternary alloys annealed at 1 223 K for 20 h. Present experimental data is also marked in Fig. 3. The homogeneous solid solution of the NiAs structure is obtained in composition regions where Vogel *et al.*²⁰⁾ and Kaneko *et al.*²¹⁾ reported the miscibility gaps. One of the reasons of these discrepancies among experimental data is considered to be microsegregation formed during a solidification of samples, because samples of both Vogel *et al.*²⁰⁾ and Kaneko *et al.*²¹⁾ were prepared by a melting and solidification, while the samples in the present study were prepared by powder-synthesizing method.

Figure 4 shows the BEI of the $(\text{Fe}_{0.4}\text{V}_{0.6})\text{S}$ mixture annealed at 1 473 K for 24 h. Black color regions are void and crack, and the matrix in gray color is mono-sulfide phase. According to the EPMA analysis of sulfide phase at several

points, the chemical composition of the sulfide was almost the same value at every analyzed point. This result suggests that the sulfide phase in Fig. 4 is a homogeneous phase and every samples of the FeS–VS system showed the similar microstructure. Typical XRD pattern obtained from FeS–VS mixture is shown Fig. 5(a), whose spectrum peaks can be identified as the NiAs structure. The lattice parameters of the NiAs structure evaluated from the XRD patterns are summarized in Table 1 and are plotted in Fig. 5(b) as a function of VS content. The *a*-axis shows a minimum around 10 mol% VS, while *c*-axis monotonously increases and decreases with increasing VS content. These results suggest that the mono-sulfide with the NiAs structure in the FeS–VS binary system forms complete solid solution. This conclusion is consistent with the previous data reported by Kaneko *et al.*²¹⁾ The phase diagram of the FeS–VS system

Fig. 3. Phase diagram of the FeS–TiS pseudo-binary system. x_{Fe} and x_{Ti} are the mole fraction in sulfide.

Fig. 4. Backscattering electron images of $(\text{Fe}_{0.4}\text{V}_{0.6})\text{S}$ annealed at 1 473 K for 24 h.

Fig. 5. (a) XRD pattern obtained from $(\text{Fe}_{0.6}\text{V}_{0.4})\text{S}$ annealed at 1 473 K for 24 h and (b) composition dependence of *a*- and *c*-axis of the $(\text{Fe}, \text{V})\text{S}$ of the NiAs structure.

Fig. 6. Schematic phase diagram of the FeS–VS pseudo-binary system. Phase boundaries between solid and liquid are schematically illustrated. x_{Fe} and x_{V} are the mole fraction in sulfide.

might be the completely soluble type as schematically drawn in Fig. 6.

The micrograph of $(\text{Fe}_{0.7}\text{Nb}_{0.3})\text{S}$ mixture annealed at 1273 K for 3 h is shown in Fig. 7. Black color regions are voids, and the two kinds of sulfides can be observed. The EPMA analysis of these two sulfides reveals that white and gray color regions are niobium-rich and iron-rich monosulfides, respectively. The similar two-phase microstructure was observed in the $(\text{Fe}_{0.5}\text{Nb}_{0.5})\text{S}$ mixture annealed at the temperature range from 1073 to 1273 K, while the single-phase structure is observed in the samples with high Nb content. The local chemical compositions in two-phase samples determined by the EPMA are summarized in Table 2. It is to note that the composition of sulfur deviate from the stoichiometric composition, especially in the Nb-rich sulfide. The solubility of Nb in the Fe-rich sulfide is very

Fig. 7. Backscattering electron images of $(\text{Fe}_{0.7}\text{Nb}_{0.3})\text{S}$ annealed at 1473 K for 3 h.

Table 2. Composition of two-phase structure in the FeS–NbS and MnS–XS pseudo-binary systems.

Specimen [mol %]	Temp./ K	Time/ h	(Fe,Nb)S		(Nb,Fe)S	
			Fe / at. %	Nb / at. %	Fe / at. %	Nb / at. %
FeS-50%NbS	1073	576	48.8	0.67	14.5	28.1
	1173	288	48.5	1.01	15.2	27.5
	1273	120	47.5	1.23	14.0	27.5
MnS-50%TiS	Temp. (K)	Time (h)	(Ti,Mn)S		(Mn,Ti)S	
			Mn / at. %	Ti / at. %	Mn / at. %	Ti / at. %
	1173	24	1.05	45.3	48.7	1.23
	1273	24	1.26	45.2	47.9	1.75
	1473	12	2.34	43.5	47.0	2.59
	1573	5	2.91	43.8	45.5	3.44
MnS-50%NbS	Temp. (K)	Time (h)	(Nb,Mn)S		(Mn,Nb)S	
			Mn / at. %	Nb / at. %	Mn / at. %	Nb / at. %
	1073	576	13.7	30.0	49.5	0.06
	1173	288	13.4	29.9	49.4	0.08
	1273	120	12.8	30.4	49.1	0.09
	1373	60	11.6	31.6	49.0	0.19
	1473	25	11.4	31.6	48.7	0.11
	1573	18	12.6	29.9	48.9	0.14
MnS-50%VS	Temp. (K)	Time (h)	(V,Mn)S		(Mn,V)S	
			Mn / at. %	V / at. %	Mn / at. %	V / at. %
	1173	288	1.53	40.3	47.6	1.92
	1273	120	1.93	39.9	47.1	2.35
	1373	60	2.27	39.5	46.2	3.32
	1473	25	3.03	39.0	44.2	4.84
	1573	18	3.60	38.8	42.1	6.81

small, although the solubility of Fe in Nb-rich sulfide is relatively large. These results accord with the previous experimental data by Kaneko *et al.*²⁰⁾ Typical XRD pattern obtained from two-phase sulfide mixture is shown Fig. 8(a). Both sulfide phases can be identified as the NiAs structure with different lattice constant. The lattice parameters of the NiAs structure of this system evaluated from the XRD patterns are summarized in Table 1 and are plotted in Fig. 8(b) as a function of NbS content. The *a*- and *c*-axis of the NiAs structure increases and decreases with increasing NbS content, although a gap exists in the Fe-rich region. The phase diagram of the FeS–NbS system is drawn in Fig. 9 based on the present results. Since the tie-lines of the miscibility gap do not exist on this plane, the composition of the miscibility gap is expressed by the atomic ratio of metals, $x_{\text{Nb}}/(x_{\text{Nb}}+x_{\text{Fe}})$. The two-phase separation region of the NiAs

Fig. 8. (a) XRD pattern obtained from $(\text{Fe}_{0.8}\text{Nb}_{0.2})\text{S}$ annealed at 1173 K for 3 h and (b) composition dependence of the *a*- and *c*-axis of $(\text{Fe},\text{Nb})\text{S}$ with the NiAs structure.

Fig. 9. Phase diagrams of the FeS–NbS pseudo-binary system. Phase boundaries between liquid and solid phases are schematically illustrated. x_{Fe} and x_{Nb} are the mole fraction in sulfide.

Table 3. Comparison of lattice constant and volume mismatch of sulfides with NiAs structure.

Sulfide	Pearson's handbook		Present work		Molar volume/cm ³	Volume mismatch, ΔV %	c/a
	a -axis/nm	c -axis/nm	a -axis/nm	c -axis/nm			
FeS	0.3456	0.5779	0.3473	0.5786	18.19	-	1.665
TiS	0.3296	0.6398	0.3297	0.6412	18.17	0.128	1.944
VS	0.3340	0.5830	0.3340	0.5845	17.00	6.569	1.750
NbS	0.3320	0.6460	0.3310	0.6537	18.67	2.623	1.975

phase is located in the FeS-rich side. Main factors that affects the range of solubility of two-phase separation in isostructural sulfide system are the volume mismatch and the difference of bonding character such as covalency and ionicity.²⁷⁾ In the case of the oxide, sulfide and halide with the NaCl structure, the solubility of the two-phase separation could be explained by a volume mismatch of the two end-members.²⁷⁾ Lattice constant and volume mismatch of sulfides with the NiAs structure are summarized in **Table 3**. The volume mismatch, ΔV between FeS and XS (X: Ti, V and Nb) is defined by $\Delta V = |V_{XS} - V_{FeS}| / V_{FeS} \times 100$, with V_{XS} the molar volume of the XS, V_{FeS} the molar volume of FeS. The lattice constants of the present results accords with previous data quoted in Pearson's handbook.²⁶⁾ ΔV is less than 10% as listed in Table 3, which values would be small to cause a miscibility gap at high temperature according to the results of the oxide, sulfide and halide with the NaCl structure.²⁷⁾ Namely, the volume mismatch is not main factor for the two-phase separation of the NiAs structure in the FeS–NbS system. The axial ratio is also listed in Table 3. The c/a ratio of FeS is 1.665, which value is near to the ideal ratio $c/a = 1.633$ of the hexagonal closed-packed structure. The c/a ratio of NbS is the largest in the present study as shown in Table 3, namely the difference of the bond characteristic between FeS and NbS is one of the reasons of the two-phase separation of the FeS–NbS system.

3.2. MnS–XS Systems

Sulfide mixture of $(\text{Mn}_{0.5}\text{X}_{0.5})\text{S}$ (X: Ti, V, and Nb) were prepared and annealed at the temperature range from 1 173 to 1 573 K. Typical BEIs of the sulfide mixtures annealed at 1 473 K are shown in **Fig. 10**. Black color region in every image are void. The EPMA analyses reveal that regions referred to as *P* and *Q* are the X-rich mono-sulfide and the Mn-rich mono-sulfide in every systems, respectively. Since the crystal structure of pure XS and pure MnS is the NiAs and NaCl structure, respectively, the crystal structure of the *P* and *Q* phases might be the NiAs and NaCl structures, respectively. The chemical compositions of *P* and *Q* phases at various temperature determined by the EPMA are summarized in Table 2 and are plotted in the phase diagrams as shown in **Fig. 11**. It is to note that the composition of sulfur deviate from the stoichiometric composition, especially in the *P* phase. Since the tie-lines of the phase boundaries do not exist on this plane, the chemical composition of the phase boundaries is expressed by the atomic ratio of metals, $x_X/(x_X + x_{\text{Mn}})$. In the MnS–TiS and MnS–VS systems, each solubility of Mn in the *P* phase and Ti and V in the *Q* phase is less than 0.2 mol. While, in the MnS–NbS system, the solubility of Mn in the *P* phase is about 0.12 mol and that of Nb in the *Q* phase is less than 0.01 mol, thus the two-

Fig. 10. Backscattering electron images of (a) $(\text{Mn}_{0.5}\text{Ti}_{0.5})\text{S}$, (b) $(\text{Mn}_{0.5}\text{Nb}_{0.5})\text{S}$ and (c) $(\text{Mn}_{0.5}\text{V}_{0.5})\text{S}$ annealed at 1 473 K.

phase region lie to the Mn-rich side. Since all of specimens of the MnS–XS systems are in two-phase structure even at 1 573 K, which is the maximum temperature of this study, an invariant reaction point of the MnS–(TiS, NbS, VS) systems might be higher than 1 573 K.

4. Conclusions

The phase stability and phase equilibria of the FeS–XS and MnS–XS (X: Ti, V and Nb) were investigated.

(1) The complete solid solutions of the NiAs phase are formed in the FeS–TiS and FeS–VS systems, while the NiAs phase in the FeS–NbS system separate in the two-phase. The two-phase region of the NiAs phase in the FeS–NbS system lies to the FeS side.

(2) In the MnS–XS (X: Ti, V and Nb) systems, the two-phase region of a Mn-rich mono-sulfide and a X-rich mono-sulfide exists widely. Solubility of each elements in the Mn-rich mono-sulfide and the X-rich mono-sulfide is small, except that of Mn in the Nb-rich mono-sulfide.

Fig. 11. Phase diagrams of (a) MnS-TiS, (b) MnS-VS and (c) MnS-NbS pseudo-binary systems. Phase boundaries between solid and liquid are schematically illustrated. x_X (X: Mn, Ti, Nb and V) is the mole fraction in sulfide.

Acknowledgement

This study was supported by ISIJ Research Promotion Grant and JFE 21st Century Foundation. Support from CREST, Japan Science and Technology Agency and from the Global COE Project is also acknowledged.

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