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Thermodynamic Analysis for Sensitization of Stainless Steel Welding Zone in Nuclear Power Plant Piping System

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1. Introduction

Material degradation in austenitic stainless steel of nuclear power plant piping system in holding great influence on its component integrity. In particular, the intergranular corrosion resistance in welding zone would be decreased by the sensitization, which occurred in welding HAZ(Heat Affected Zone) inevitably. The sensitization on surface of austenitic stainless steel was generated from chrome carbide formation in grain boundary. Corrosion and pitting do happen actively in the Cr-depleted zone so that it has a close relation with the LOCA in the case of primary system. In order for the stainless steel to increase the intergranular corrosion resistance, the carbon content in stainless steel must be decreased or the solution treatment of Cr-carbide could be carried out. The thermodynamic calculation is needed for the resistance improvement with alloying element or the optimum temperature of solution treatment.

2. Methods and Results

2.1. Carbide formation in Fe-C/Cr-C system

Cr-carbide formation is very stable so that it could be compared with Fe-carbide in aspect to carbide stability by carbon activity in phase diagram analysis. Fe-carbide, cementite, is metastable relative to pure iron and graphite since the standard Gibbs free energy for the formation of Fe-carbide is greater than zero over the entire temperature range. It means that the carbon activity should be greater than one for Fe-carbide formation at all temperature.

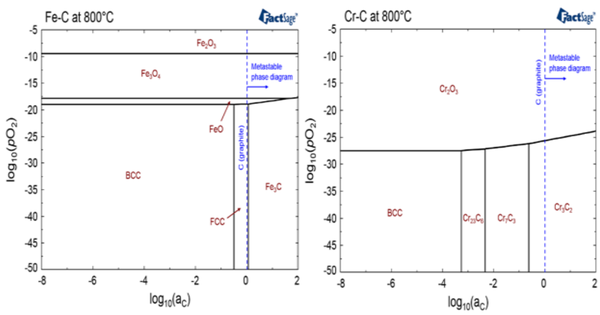

Fig. 1. Phase diagram in Fe-C and Cr-C system.

On other hands, Cr- carbide exists as stable compound thermodynamically once it was formed by carburization differing from metastable Fe-carbide. It was explained by required carbon activity for Cr-carbide formation, which need not to be more than unity over temperature as shown in **Fig. 1**. Therefore, $Cr_{23}C_6$ formed in sensitization during welding process is so stable that Cr-depleted zone can contribute to weld decay.

2.2. Relationship with equilibrium phase fraction and sensitization in SUS304/SUS316

Carbide as $Mn_{23}C_6$ has been formed from 1000°C in SUS304, which could be stable at the temperature under 1000°C in **Fig. 2**. Even if the solid solution carried out for corrosion resistance and strength at high temperature, $M_{23}C_6$ could be formed at 500~800°C. That's why the sensitization can occur properly at this temperature range. Most of the metallic element existed in $M_{23}C_6$ is Cr, which solubility is about 80wt% at sensitization temperature range. Compared with Cr content, 18wt%, Cr solubility in $M_{23}C_6$ can induce Cr-depletion fully in grain boundary at welding zone.

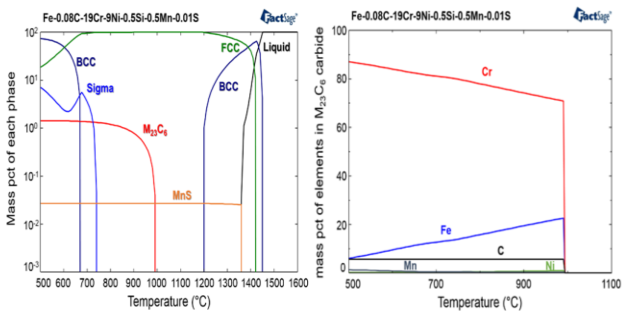

Fig. 2. Equilibrium phase diagram and metallic element solubility of $M_{23}C_6$ in SUS304.

SUS316 was formed with 2~3wt% Mo from SUS304 for pitting corrosion resistance. According to Mo addition, stability region of $M_{23}C_6$ is expanded until 1070°C and phase fraction is also increased in comparison with the case of SUS304. However, Cr solubility was decreased to approximately 60wt% in $M_{23}C_6$, which means 20wt% of Mo was substituted for Cr as shown in **Fig. 3**. Therefore, Mo addition could help to resist the sensitization with regard to lowered Cr loss content. Effect of Mo can contribute to not only pitting corrosion resistance but also suppress Cr-carbide formation even though the small amount of Mo added.

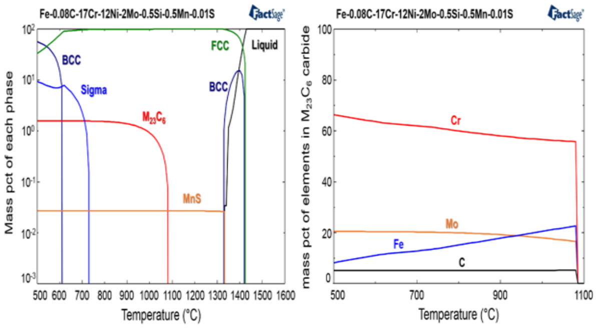

Fig. 3. Equilibrium phase diagram and metallic element solubility of $M_{23}C_6$ in SUS316.

2.3. Prevention on sensitization in Ti-stabilized STS/Nb-stabilized STS.

AISI321 as representative Ti-stabilized stainless steel has a little of Ti content for effect on Cr-carbide stability change as shown in **Table 1**.

Table 1. AISI321 composition (Ti-stabilized alloy)

Comp.	Fe	C	Cr	Ni	Si	Mn	Ti	N	P	S
Conc. (wt%)	Bal.	0.08	17~19	9~12	0~1	0~2	0~0.7	0~0.1	0~0.04	0~0.03

The most significant change of equilibrium phase diagram in AISI is Ti(C,N) formation instead of $Cr_{23}C_6$ as shown in **Fig. 4**. Carbon activity was decreased by reduced carbon content depending on Ti addition. It can make the environment difficult for Cr-rich carbide formation due to lower carbon activity.

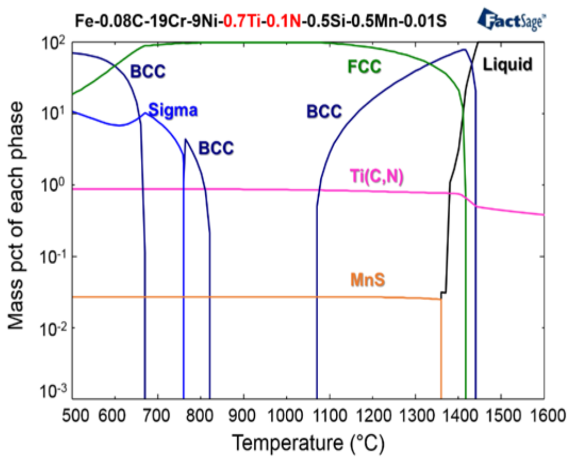

Fig. 4. Equilibrium phase diagram in AISI321.

Nb-stabilized stainless such as AISI347 was developed with Nb addition, which was comprised in about 1wt% as shown in **Table 2**. As carbide former, Nb, can form NbC or NbC_2 with carbon easily in Nb-C phase diagram. In particular, the melting point of NbC is 3500°C so that it could be very stable thermodynamically. Similarly, it seemed that NbC formation affected to suppress the sensitization like as Ti(C,N).

Table 2. AISI347 composition (Nb-stabilized alloy)

Comp.	Fe	C	Cr	Ni	Si	Mn	Nb	P	S
Conc. (wt%)	Bal.	0.08	17~19	9~13	0~1	0~2	0~1.0	0~0.04	0~0.03

As NbC had been precipitated at the temperature where solidification almost finished, its effect might be low a little bit on grain refinement of FCC. However, since Cr-carbide was not shown in phase stability diagram as shown in **Fig. 5**, Nb must be element to prevent on sensitization of austenitic stainless steel.

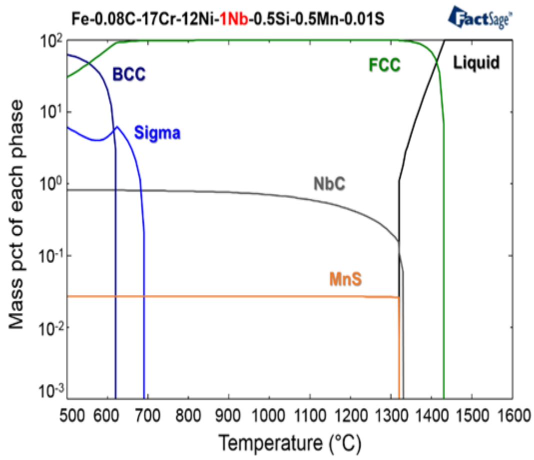

Fig. 5. Equilibrium phase diagram in AISI347.

3. Conclusions

Sensitization analysis through the equilibrium phase diagram and phase fraction calculation with applying FactSage. Based in thermodynamic analysis with FactSage, carbide formation mechanism related to sensitization could be investigated for the purpose of intergranular corrosion resistance in stainless steel. In addition, a new type of austenitic stainless steel development will be attributed to this report results.

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