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First-principles investigation on the composition of Ni-Si precipitates formed in irradiated stainless steels

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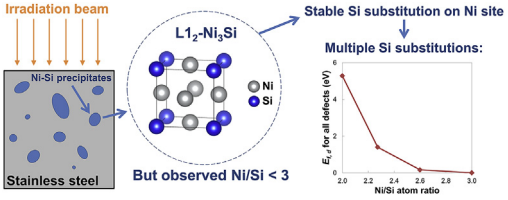
HIGHLIGHTS

- Observed Ni-Si precipitate composition is discussed by modeling.
- Si substitution on Ni sites is the most stable type of single defects in γ′ phase.
- High density of Si substitutions can exist by keeping large enough distances.
- Lattice defects are one key contributor to the small Ni/Si ratio of precipitates.

GRAPHICAL ABSTRACT



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ABSTRACT

Recent atom probe tomography (APT) study has revealed the complicated nature of Ni-Si precipitates in irradiated stainless steels. Although Ni_3Si γ′ phase has been confirmed under transmission electron microscopy (TEM), the Ni/Si ratio of the precipitates detected by APT is smaller than its theoretical value 3. An interpretation of the APT results is provided in this work by considering the lattice defects in the Ni_3Si γ′ phase. Using first principles calculations, Si substitutions on Ni sites were found to be the most thermodynamically stable among all the single defects considered here. Although two such substitutional defects are repulsive to each other, the repulsion decreases quickly as their separation distance grows. By keeping a large enough distance between each other, multiple Si substitutions can appear at high densities in the γ′ phase, which can be one important contributor to the small Ni/Si atom ratio in Ni-Si precipitates observed by APT.

1. Introduction

Austenite stainless steel is used as structural material in light water reactors. During its service time, dislocations and secondary phases will appear in the material as a result of high temperature and high dose irradiation [1,2]. Even in high purity stainless steels such as 304L or 316L, in which carbide formation is suppressed, high densities of Ni-Si precipitates could form. These Ni-Si precipitates were considered to be the γ′ phase (Ni_3Si) by transmission electron microscopy (TEM) study [3,4], and their formation should be closely related to radiation-induced segregation [5]. The

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formation of dense precipitates would lead to the irradiation embrittlement and the irradiation accelerated stress corrosion crack (IASCC) of stainless steel components, and therefore would threaten the structural integrity of light water reactors.

The recent atom probe tomography (APT) research showed that the nature of the Ni-Si precipitates in irradiated stainless steels is more complicated than our previous understanding. Firstly, the precipitate number density observed in APT is one or two orders higher than that previously observed in TEM. The precipitate density was found to be roughly on the order of $10^{21}m^{-3}$ by TEM when the stainless steel is irradiated at light water reactor temperature (~300 °C) [6,7] or at higher temperatures (425–500 °C) [4,8]. In APT, the precipitate density is $(4.2 \pm 2.1) \times 10^{23}m^{-3}$ when irradiated in a pressurized water reactor [9], and is on the order of 10^{22} ~ $10^{23}m^{-3}$ in ion irradiation at 350–360 °C, depending on the dose (0.5–10 dpa) [10–14]. Secondly, by APT observation, it has been found that the precipitate composition does not follow the standard stoichiometry of the γ′ phase (Ni_3Si). The values of the Ni/Si atom ratio of the observed Ni-Si precipitates in APT, which should theoretically be 3 for the γ′ phase, have a large scatter [15]. Even when the Ni/Si atom ratio is averaged among the observed precipitates, the average value is not always close to 3. Table 1 summarizes the Ni-Si precipitate composition tested by APT in 304/316 stainless steels irradiated at 300–400 °C. Although the detailed cluster definitions could be different in these APT data analysis, most of the resultant Ni/Si ratios are smaller than 3. The exception is the value 3.6 reported by Chen et al. However, they also pointed out that their results should have overestimated Ni/Si ratios, because Ni was selected as the only element to identify Ni-Si precipitates in their work [16].

As we know, TEM is focusing on the crystallographic structure of the precipitates while APT is focusing on the microchemistry. It indicates that a large fraction of the Ni-Si precipitates observed by APT does not strictly follow the standard γ′ phase structure. To be more detailed, two possible explanations have been mentioned in previous literature. The first explanation is that the Ni-Si precipitates found in APT may contain other phases with lower Ni/Si ratio. $Ni_{31}Si_{12}$, Ni_2Si, Ni_3Si_2 and NiSi do not have a cubic structure and were not observed in previous TEM observations. G phase ($M_6Ni_{16}Si_7$) can be a reasonable explanation with Ni/Si ratio of 2.3 [17,18]. However, literature data shows that G phase forms in a narrow temperature regime centered around 500 °C, while γ′ phase forms at a much wider temperature range extending to ~300 °C [19–21]. Similarly, some research works listed in Table 1 had used both TEM and APT for precipitate analysis, and γ′ phase was the only Ni-Si phase detected by TEM ([10,17,9,22]). G phase had been found in several cases by Tan et al. [23] and Isobe et al. [24], showing that G phase could form in the temperature regime of 300–400 °C under certain conditions. In the case of Porollo et al. [25], the addition of Ti element should have enhanced G phase formation [19]. As a conclusion, although the possible existence of G phase or the precursors of G phase should not be neglected, most of the TEM data currently available indicates that γ′ phase is the dominant phase for Ni-Si precipitates formed between 300 and 400 °C.

The second possible explanation focuses on the detailed evolution process of the γ′ phase precipitates. There are debate that the precursors of the γ′ phase might have caused the small Ni/Si ratio [10], but no direct proof had been found. While the existence of precursors might be a contributor to the phenomenon, the possible contribution of formed γ′ phase precipitates should also be investigated. In fact, due to the high concentration of alloying elements in stainless steels and the high density of point defects in irradiation conditions, it is highly possible that the formed γ′ phase could deviate from its standard structure by accumulating lattice defects. This possibility was overlooked in previous literature, but is essential to the comprehensive understanding on the precipitate composition observed by APT. Thus, the objective of this work is to investigate the possible contribution of lattice defects in the γ′ phase to the precipitate composition. This possibility is examined by evaluating the relative stability of different defects in the γ′ phase through first principles calculations. The modeling results are compared with experiments in literature to provide an interpretation for the APT observation results. This work would help to better clarify the nature and the evolution process of the Ni-Si precipitates formed in irradiated stainless steels.

Table 1
Literature APT data of Ni-Si precipitate composition in 304/316 stainless steel irradiated at 300–400 °C. Ti or Nb is not alloyed in the stainless steel samples. Errors are given by the standard deviation.

Particle	Alloy composition (wt.%)			T (°C)	Dose (dpa)	Ni-Si ppt[a] composition (at.%)				Ref.
		Ni	Si			Ni	Si	Ni/Si	Composition definition	
Proton	HP304 + Si	12.4	1.05	360	5	34.32 ± 1.83	15.69 ± 1.34	2.18	MSM[b] by Ni + Si. (>100 ppts analyzed)	[10]
	CP304	8.5	0.65			21.69 ± 1.58	7.10 ± 0.97	3.05		
PWR neutron	CW316	12.61	0.62	323	3	19.4	10.8	1.8 (d < 5 nm)	MSM[b] by Si atom.	[17,44]
				323	3	29.4	14.1	2.1 (d > 5 nm)		
				323	11	21.7	11.5	1.9 (d < 5 nm)		
				323	11	31.0	16.0	1.9 (d > 5 nm)		
				305	74	21.6	10.7	2.0 (d < 5 nm)		
				305	74	28.5	14.4	2.0 (d > 5 nm)		
Proton	CP304	8.6	0.67	360	10	–	–	3.6 ± 1.4	MSM[b] by Ni atom.	[16]
Fe^{5+}	CW316	10.60	0.68	350	10	28.2 ± 0.4	12.3 ± 0.3	2.3 (rounded)	Average of ppt core	[12,13]
						25.6 ± 0.4	7.6 ± 0.3	3.4 (torus)		
PWR neutron	CW316	12.10	0.64	360	12	53.9 ± 1.5	38.1 ± 1.4	1.4	Average of ppt core	[14,41]
PWR neutron	304	9.3	0.78	300	24	–	–	<3 (all ppt)	Average of ppt core, defined by half maximum of Ni + Si	[9]
						40–50	15–20	~2.6 (d > 10 nm)	value in concentration profile.(130 ppts analyzed)	
Fe^{2+}	SA304L	10.80	0.56	380	46	20–30	10–20	~1.7	Average of ppt core, by concentration profile.	[18]
	SA304L	10.80	0.56		260	~60	~30	~2	(several well-developed ppts)	
	CW316	10.54	0.73		46	~50	~25	~2		
Fe^{4+}	SA316	11.1	0.59	400	4	25.2	28.2	0.9 (rounded)	Maximum value in concentration profile	[39]
						25.6	25.3	1.0 (torus)		

[a] ppt: precipitate.
[b] MSM: maximum separation method.