Precipitation sequence in Niobium-alloyed ferritic stainless steel [1]

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[1] Fujita, Nobuhiro, H. K. D. H. Bhadeshia, and Masao Kikuchi. "Precipitation sequence in niobium-alloyed ferritic stainless steel." Modelling and Simulation in Materials Science and Engineering 12.2 (2004): 273.

Niobium in ferritic stainless steels

- Automobile industry becoming energy-efficient $\rightarrow$ increase in temperature of exhaust gas
- Material in exhaust:
  - Better high temperature strength
  - Resistance to thermal fatigue
- Solution: Nb based ferritic stainless steel
- Disadvantages: Precipitates at high temperatures and long time scales $\rightarrow$ Decrease in performance.

Experiments

- Nominal composition: 19Cr-0.8Nb wt.%
- Procedure followed:
  - Vacuum melting $\rightarrow$ heating at 1250°C for 30 minutes in an Ar atmosphere$\rightarrow$ hot-rolled and normalized to 900°C$\rightarrow$ Annealing at 1000°C for 10 minutes$\rightarrow$ water quenched$\rightarrow$ Machining$\rightarrow$ isothermal heat treatments at 950°C and 1000°C for 500 hours.
- Characterization done:
  - XRD$\rightarrow$precipitates formed were noted.
  - TEM and EDS with carbon extraction replicas$\rightarrow$ microstructures and particle sizes.

Experimental results

Phase transformation

$$\alpha \rightarrow \alpha + \text{Nb(C,N)} + \text{Fe}_2\text{Nb} + \text{Fe}_3\text{Nb}_3\text{C} \rightarrow \alpha + \text{NbN} + \text{Fe}_3\text{Nb}_3\text{C}.$$

- Equilibrium has $\text{Fe}_3\text{Nb}_3\text{C}$
- NbC and Laves phase dissolves.
- Precipitates $\rightarrow$ more spherical than needle-like.

Table : Presence of precipitates in samples at different experimental conditions: VW, W,S,VS stand for very weak, weak, strong and very strong X-ray intensities

Aging conditions		Precipitates detected		
Temperature (°C)	Time (h)	Nb(C,N)	Fe_3Nb_3C	Fe_2Nb
As annealed at 1000°C		S	VS	W
	1	VS	VS	VS
	8	S	VS	W
950	20	S	VS	W
	50	S	VS	VW
	100	VW	VS	-
1000	20	W	VS	-

Models used: Nucleation

Classical nucleation theory

$$I = \left(1 - \frac{V^{\beta}}{V^{\alpha\beta}}\right) N_0 \frac{kT}{h} exp\left(-\frac{G^* + Q^*}{RT}\right)$$

$$G^* = \frac{16\pi\sigma^3}{3\Delta G_V^2}$$

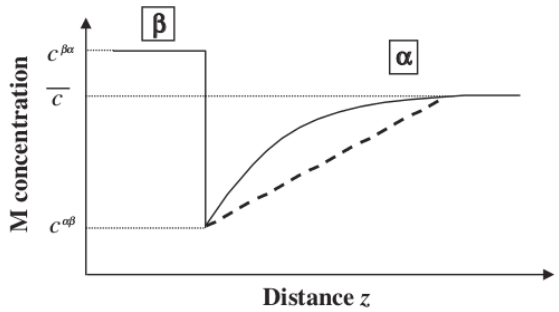
- V^{β} and $V^{\alpha\beta}$ are instantaneous and equilibrium volume fractions of the precipitate.
- N_0 and Q^* are the number density of nucleating sites and activation energy respectively.
- σ and ΔG_V are interfacial energy and volume Gibbs energy change.

Growth: Binary

Growth: governing equation

$$v(c^{\beta\alpha} - c^{\alpha\beta}) = -D\frac{\partial c}{\partial z}$$

- D: diffusion coefficient
- v: growth velocity
- $c^{\beta\alpha}$, $c^{\alpha\beta}$: concentrations at equilibrium
- $\frac{\partial c}{\partial z}$: concentration gradient.

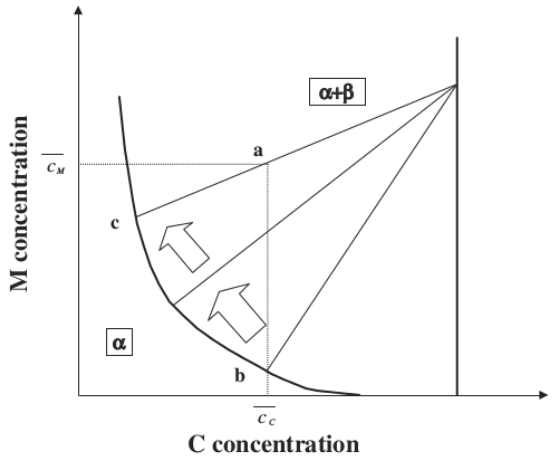


Growth: MC precipitate

Growth: MC governing equation

$$v(c_X^{\beta\alpha} - c_X^{\alpha\beta}) = -D_X \nabla c_X$$

- C: interstitial atom $\rightarrow D_C >> D_{\mathrm{Nb}}$.
- Flux of C and Nb should almost match.
- Movement from b to c and a to c
  - b $\rightarrow$ initial C composition such that C gradient minimized and M gradient maximised.
  - As solute from matrix depleted, the average composition moves from a to c.
  - c $\rightarrow$ Equilibrium



Capillarity

Capillarity equation

$$c_{r,\mathrm{M}}^{\alpha\beta} = \left(1 + \frac{\sigma}{kT}\frac{v^{\beta}}{r}\frac{1-c_{\mathrm{M}}^{\alpha\beta}}{c_{\mathrm{M}}^{\beta\alpha}-c_{\mathrm{M}}^{\alpha\beta}}\right) c_{\mathrm{M}}^{\alpha\beta}$$

- Phase boundaries $\rightarrow$ modified
- Reduces amount of small sized precipitates
- Larger the precipitate, lower is the solute content at its interface $\rightarrow$ drives coarsening

Calculations and results

- CALPHAD description and solubility products$\rightarrow$ Volume Gibbs energy
- Fe-Nb-C system considered
- Parameters varied: N_0 and σ.
- Close agreement with experimental data.
- Interfacial energy 15 times stronger impact than number of nucleation sites.

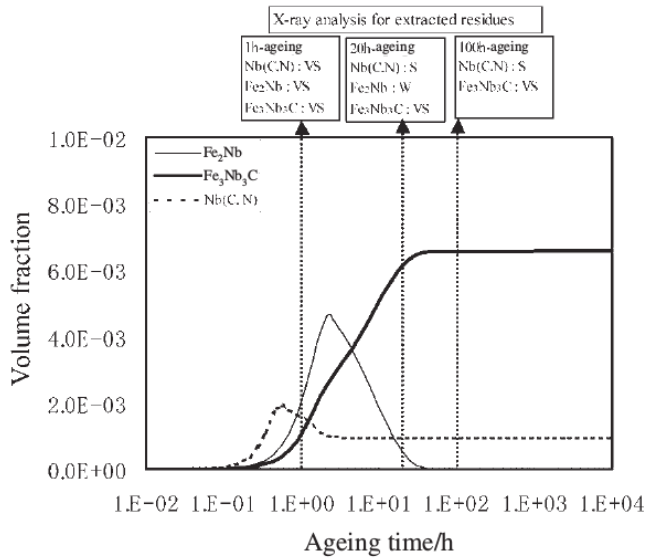
Parameters obtained

Table : Results from modeling

Number density of sites: N_0 (m^{-3})	
NbN	2×10^{12}
Fe_2Nb	3×10^{11}
Fe_3Nb_3C	3×10^{12}
Interfacial energy: σ(J m^{-2})	
NbN	0.230
Fe_2Nb	0.280
Fe_3Nb_3C	0.330

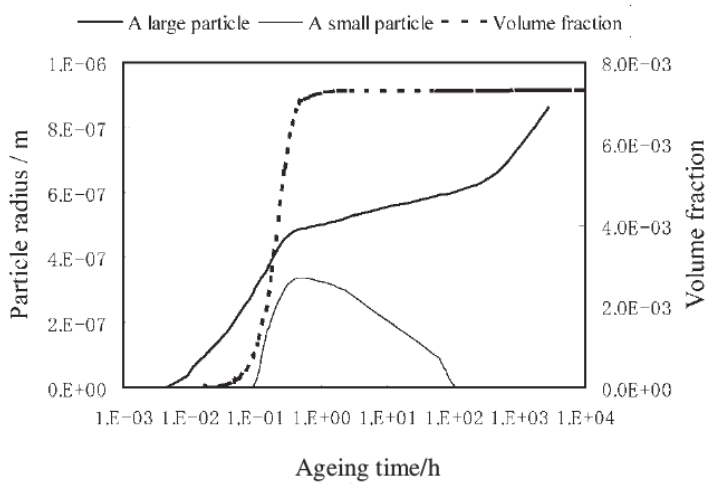
Volume fraction

- Precipitation sequence verified
- Increases and saturates after some time
  $\rightarrow$ Simultaneous dissolution of smaller particles + coarsening of the larger particles.



Precipitate sizes

- Mean radius increases and stabilizes after some time
- Larger particle: radii increases $\rightarrow$ Coarsening
- Smaller particle: radii decreases $\rightarrow$ Dissolution
- The number density of precipitates, decreasing during coarsening.



Summary

- Fe-Nb-C system considered
- Parameters varied: N_0 and σ.
- Close agreement with experimental data.
- Interfacial energy 15 times stronger impact than number of nucleation sites.
- Larger particle: radii increases $\rightarrow$ Coarsening
- Smaller particle: radii decreases $\rightarrow$ Dissolution