Carburization behavior of steels in high temperature sodium

M. Romedenne, F. Rouillard, D. Hamon, D. Monceau

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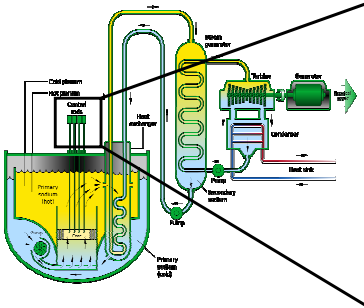
Marie Romedenne[a], Fabien Rouillard[a], Didier Hamon[b], Daniel Monceau[c]

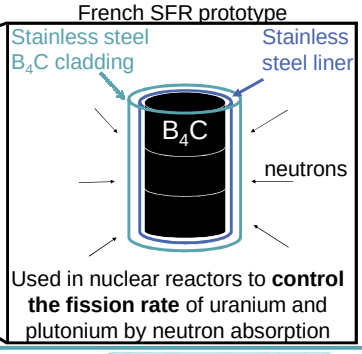
[a]Den-Service de la Corrosion et du Comportement des Matériaux dans leur Environnement (SCCME), CEA,
[b]Den-Service de Recherches Métallurgiques Appliquées (SRMA), CEA,
Université Paris-Saclay, F-91191, Gif-sur-Yvette, France
[c]CIRIMAT, Université de Toulouse, CNRS, INPT, UPS, ENSIACET 4, allée Emile Monso BP-44362 31030 Toulouse cedex 4, France,

Scope and Issue

Sodium-cooled fast reactor (SFR)



Control rod concept in next French SFR prototype



Used in nuclear reactors to **control the fission rate** of uranium and plutonium by neutron absorption

Feedbacks from former SFR:
Mechanical rupture

Induced by Carburization ✓ — Induced by Boriding ?

Conservative lifetime models based on the carburization kinetics of stainless steels have been proposed in countries having developed SFRs. All these previous studies proposed that the mechanical properties were highly degraded over a critical carbon concentration lying between 0.2 and 0.4 wt.% [1-3]. In order to **optimize the control rod lifetime** in the reactor, the **carburization mechanisms and kinetics have to be described accurately.**

[1] J.L. Krankota. *Journal of Engineering Materials and Technology*, **98(1)**, 9 (1976).
[2] A. W. Thorley and M. R. Hobdell. *Carbon in sodium: A review of work in the UK* (UKAEA Harwell 1984).
[3] L. Brunel. *Proposition d'une loi envelope de carburation* (CEA 1984).

Experimental procedure

Carburization experiment in Na

- a_c **= 1** to maximize carburization
- **T = 600 °C** near service temperature
- **t = 0 to 5000 h**
- Sample **thickness = 1 mm**

- Steels tested : **γ 17Cr10Ni – 316L**
  γ 14Cr14Ni0.4Ti – AIM1
  α 9Cr – EM10

Collected data

1. **Kinetics** of carbon mass gain
2. Carburization induced **microstructure**
3. Carbon profiling by **EPMA = f(t)**

Objectives

Determination of an **apparent carbon diffusion coefficient (D_{app})** for technological use from:

A $$C(X,t) = \mathrm{erfc}\left(\frac{X}{2\sqrt{D_{app}t}}\right)(C^S - C_0) + C_0$$

Determination of a **carburization model** for extrapolation purpose on other steel grades from:

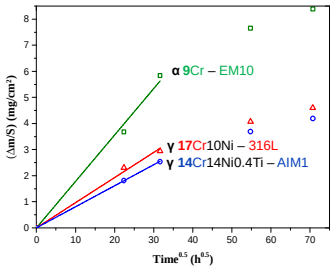
B Wagner's carburization model [4]
Young *et al.*'s carburization model [5]

[4] C. Wagner. *Z. Elektrochem*, **63**, 772.782 (1959).
[5] D. Young, P. Huczkowski, T. Olszewski, T. Hüttel, L. Singheiser, W.J. Quadakkers. *Corrosion Science*, **88**, 161 (2014).

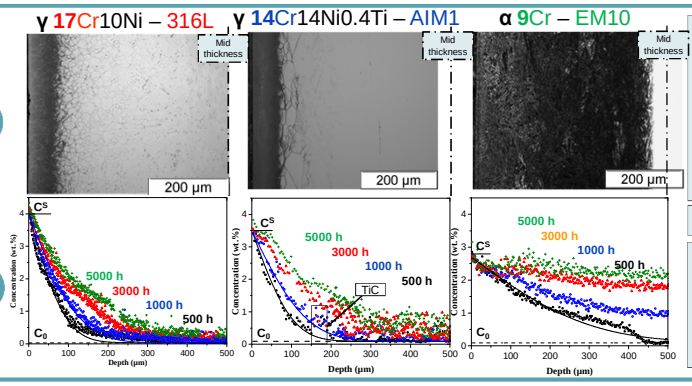
Kinetic study

Parabolic kinetics until 1000 h
(semi-infinite media only valid for exposure times of 500 h and 1000 h)

1



2 3



Cross section images by optical microscopy showing:
Intragranular carburization zone with or without **Intergranular** carburization zone

C^S constant with time

A
D_{app} = 1.4 10^{-11} cm².s^{-1}
D_{app} = 3.2 10^{-11} cm².s^{-1}
D_{app} = 1.7 10^{-10} cm².s^{-1}

Carburization model

Wagner's diffusion model:

All Cr precipitate to form carbides
Only carbon diffuses which implies: $C^S_M D_C(\gamma) >> C^0_{Cr} D_{Cr}(\gamma)$

For γ 14Cr14Ni0.4Ti – AIM1
C^S_M x $D_C(\gamma)$ >> C^0_{Cr} x $D_{Cr}(\gamma)$
3.810^{-3} x $5.6\ 10^{-10} = 10^{-12}$ >> $14 \times 5.0\ 10^{-17} = 10^{-16}$ cm².s^{-1}

$$D_c(\gamma \text{ or } \alpha) = \frac{k_p^c \nu C^0_{Cr}}{C^S_M}$$

k_p^c : Intragranular carburization rate constant from 2
ν : Carbide CrC_ν with $\nu = 3/7$
C^0_{Cr} : Chromium content in the steel
C^S_M : Carbon content in the matrix calculated with ThermoCalc (TCFE8)

B
$D_c(\gamma)$ = 1.8 10^{-8} cm².s^{-1}
$D_c(\gamma)$ = 2.9 10^{-9} cm².s^{-1}
= 30 to 50 times the carbon diffusion coefficient in austenite given in the literature $D_c(\gamma) = 5.6\ 10^{-10}$ cm².s^{-1} [6]
$D_c(\alpha)$ = 6.7 10^{-7} cm².s^{-1}
= 3 times the carbon diffusion coefficient in ferrite given in the literature $D_c(\alpha) = 2.2\ 10^{-7}$ cm².s^{-1} [7]

- From Wagner's model of carburization, $D_c(\gamma,\alpha)$ should be overestimated compared to literature values in order to fit the experimental carburization kinetics
- The fact that not all Cr form carbides may explain this discrepancy

[6] J. Agren. *Scripta Metallurgica*, **20**, 1507 (1986).
[7] A. W. Bowen, G. M. Leak. *Metallurgical Transactions*, **1**, 1695 (1970).

Young *et al.*'s carburization model:

Not all Cr precipitate
Normal diffusion of solute carbon within the metal phase coupled with rapid carbide precipitation and equilibrium partitioning of carbon between the metal and the precipitates phases

$$\frac{\partial C_M}{\partial t} = D_C \frac{\partial^2 C_M}{\partial x^2} - \frac{\partial C^P}{\partial t}$$
$$C^P \approx C^{TOT} - C_M \approx \beta C_M$$
$$\frac{\partial C^{TOT}}{\partial t} = \frac{D_C}{1+\beta}\frac{\partial^2 C^{TOT}}{\partial x^2}$$

C^P : Carbon content in carbide precipitates determined with ThermoCalc (TCFE8)
C_M : Carbon content in the matrix calculated with ThermoCalc (TCFE8) **neglected**
β : Partitioning coefficient **supposed constant considering only one carbide M_7C_3**
C^{TOT} : Total carbon content in the steel from 3
$\frac{D_C}{1+\beta} = D_{app}$: Apparent carbon diffusion coefficient

B
$D_c(\gamma)$ = 5.6 10^{-10} cm².s^{-1}
$D_c(\gamma)$ = 1.2 10^{-9} cm².s^{-1}
= 1 to 2 times the carbon diffusion coefficient in austenite given in the literature $D_c(\gamma) = 5.6\ 10^{-10}$ cm².s^{-1} [6]
$D_c(\alpha)$ = 2.7 10^{-7} cm².s^{-1}
= 1.2 times the carbon diffusion coefficient in ferrite given in the literature $D_c(\alpha) = 2.2\ 10^{-7}$ cm².s^{-1} [7]

- Young *et al.*'s carburization model well described the observed kinetics
- Slight discrepancy for AIM1: effect of strong carbide former TiC on β ?

Conclusions

- C^S at equilibrium with a_c = 1 can be estimated from EPMA profiles
- Parabolic carburization kinetics in strong carburizing Na (a_c =1)
- **Faster carbon diffusion** in **ferritic and low Cr steel** (but lower carbon absorption power)
- Carburization well described using Young *et al.* diffusion model

Prospects

- **The apparent diffusion coefficient, D_{app}, which has technological interest, can be predicted whatever steel grades by the expression: $D_{app} = \frac{D_C}{1+\beta}$**
- Characterization of carbides within the steels
- Experiments in reactor's conditions (B_4C)