Use of ion irradiations to help the design of advanced austenitic steels

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Abstract

CEA develops new austenitic and ODS alloys to limit the swelling and withstand very high doses. In this study, 10 Austenitic Stainless Steels with different content of phosphorus, nickel, silicon, titanium and niobium were elaborated and irradiated with iron ions at 600°C in several metallurgical conditions. Different effects on void swelling were observed by Transmission Electron Microscopy (TEM). The presence of dislocations, nano-precipitates and solutes in the matrix modify the size and the density of the cavities which appear during the irradiation. Results help to design new alloys optimized regarding the swelling resistance. Titanium in solid solution and as nano-carbides limits the swelling and a nickel enrichment (15wt% -> 25wt%) decreases cavity size but increases their density. In this irradiation conditions, dislocations are efficient recombination sites for punctual defects to limit the swelling.

Key words: Austenitic steels, ion irradiations, nano-carbides, dislocations, cavity, swelling.

Introduction

Austenitic steels are used for Sodim Fast Reactor (SFR) as cladding materials. They exhibit good corrosion resistance and excellent creep properties between 400°C and 700°C but are limited in dose (dpa) due to their swelling under irradiation [1, 2]. Currently in France, the most optimized steel is a 15Cr-15Ni titanium stabilized, called AIM1. Around this material, a generic study is conducted to identify new tracks to understand and improve the 15Cr/15Ni alloys. Swelling depends on various microstructural properties such as the dislocation density, the shape and the nature of precipitates or the chemical elements in solid solution. Their influences in the voids formation and growth are complex. The objective of this study is to appreciate the role of these metallurgical parameters on the voids formation mechanisms to help to develop improved austenitic alloys.

Numerous model steels have been produced. They are composed of ten grades with chemical variations in Ti, Nb, Ni, and P compared to a conventional 15/15 Ti alloy. Besides, in order to isolate different contributions in swelling, each alloy has been elaborated in various specific Metallurgical States (MS). They consist in different cold working and heat treatments (annealing and/or aging). To simulate neutron irradiation, selected samples were irradiated at 600°C up to 150 dpa with 2MeV Fe^{2+} in the JANNuS facility in CEA Saclay (France). The resulting microstructures are analyzed by Transmission Electron Microscopy.

Materials and methods:

Material manufacturing

10 model alloys were designed by CEA and elaborated by OCAS in Gent as thin plates of 500 microns in thickness in different metallurgical conditions. The following diagram presents the elaborated alloys.

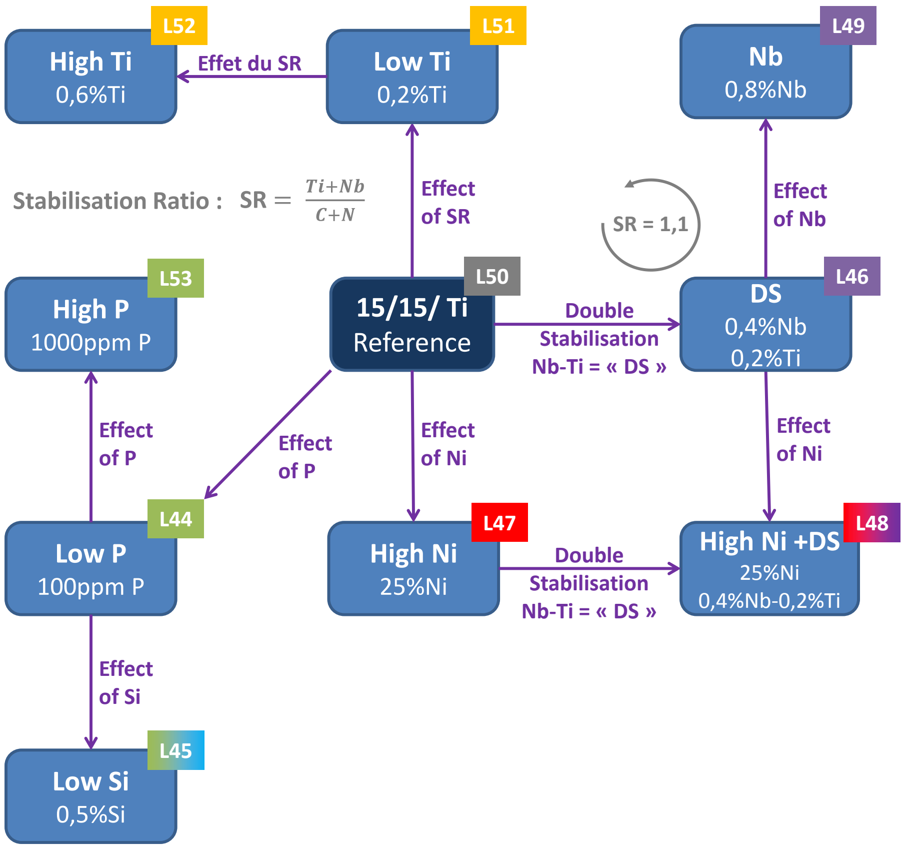


FIG. 1: Diagram of the elaborated alloys to study the effect of titanium, niobium, nickel and phosphorus.

The reference material is a standard austenitic steel Fe 15Cr-15 Ni. Its chemical composition and the one of the other steels are given in table 1. They were measured by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES). From this reference alloy, different steels were designed in order to assess the effect of an increase in the titanium content, the effect of a niobium addition (with and without titanium), the effect of an increase in the nickel content and the addition of a high amount of phosphorus.

Wt %	Cr	Ni	Ti	Nb	C	N	P	Si
L50	14.3	16	0.42	0.059	0.095	0.005	0.4	0.8
L51	14.3	15.8	0.19	0.005	0.085	0.0053	0.038	0.81
L52	14.6	15.9	0.58	0.0063	0.086	0.0026	0.04	0.81
L53	14.4	15.9	0.44	0.0048	0.088	0.0051	0.087	0.757
L44	14.4	15.9	0.44	0.0071	0.092	0.0038	0.012	0.86
L45	14.7	15.9	0.42	0.0066	0.09	0.0043	0.011	0.51
L46	14.3	16	0.21	0.43	0.09	0.0058	0.033	0.8
L47	14.4	25.1	0.42	0.013	0.09	0.0034	0.039	0.81
L48	14.3	25.2	0.2	0.42	0.091	0.0059	0.039	0.81
L49	14.4	15.9	0.0087	0.9	0.058	0.02	0.039	0.82

TABLE I: Chemical composition (wt%) of the reference material 15/15 Ti alloy and the model alloys.

In order to isolate the contribution of different metallurgical parameters on the cavity formation under ion irradiation, model alloys were elaborated in several metallurgical states. The fabrication process for each alloy has been optimized to obtain a grain size between 20 and 60µm. The different metallurgical states are the followings:

- M1 = Solution Annealed (SA, dislocation free)

- M2 = SA + 20% Cold Worked –CW = SA with a dense dislocation network = microstructure of industrial tubes

- M3’ = SA + ageing 24h at 800°C (to precipitate all the phases as large phases and create a solute depleted matrix)

- M6 = SA + CW + ageing at 650°C to induce the nanoprecipitation on dislocations of titanium or niobium carbides.

Irradiation conditions

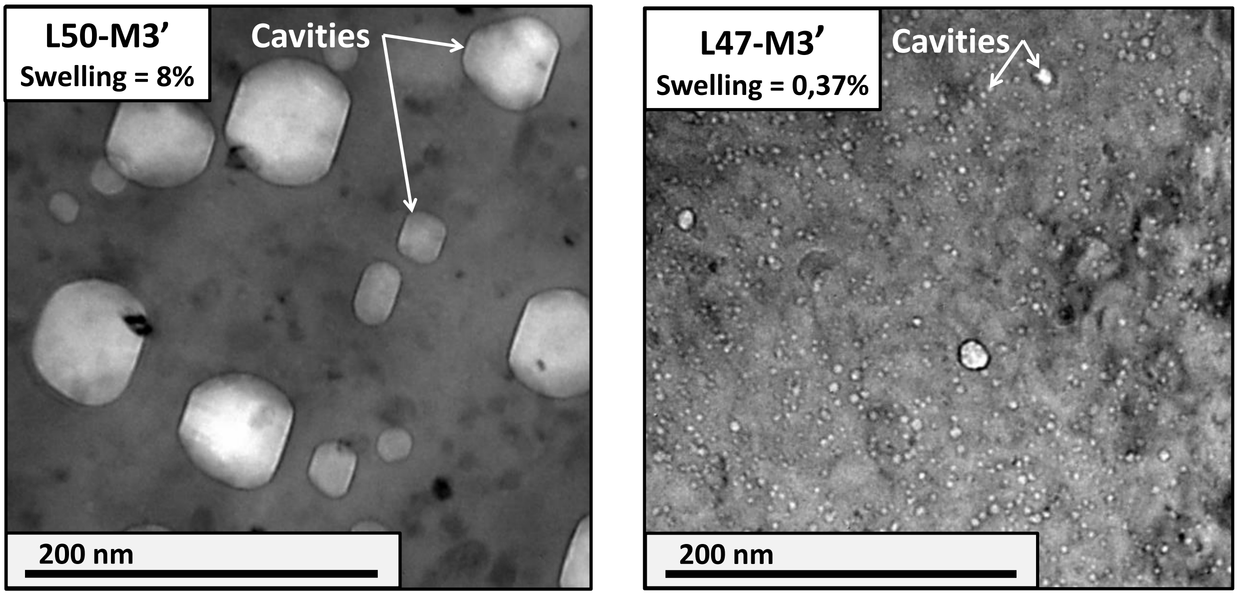
The neutron irradiation was simulated with a 2 MeV Fe^{2+} ions irradiation on 19 pre-polished thin foils. The mean flux was close to 4.10^{12} ions.$cm^{-2}s^{-1}$ and the irradiation time close to 21 hours at 600/620°C for a dose between 150 and 180 dpa. After the irradiation, the irradiated area was protected; the thin foils were electrolytically thinned to get a small hole. The protection on the irradiated surface is then removed and samples are characterized by Transmission Electron Microscopy. Thus, areas characterized by TEM are the irradiated surfaces on a thickness of 100 to 200 nm.

Results and Discussion

1. *Influence of the nickel content*

To study the influence of the nickel content, different samples, in the M3’ state, were irradiated. This metallurgical condition allows studying the response of the matrix without elements like titanium or niobium in solid solution and without dislocations. It allows to highlight the intrinsic influence of the nickel on the swelling resistance.

The results are presented in figure 2.



Fe-14Cr 16Ni alloy *Fe-14Cr 25Ni alloy*

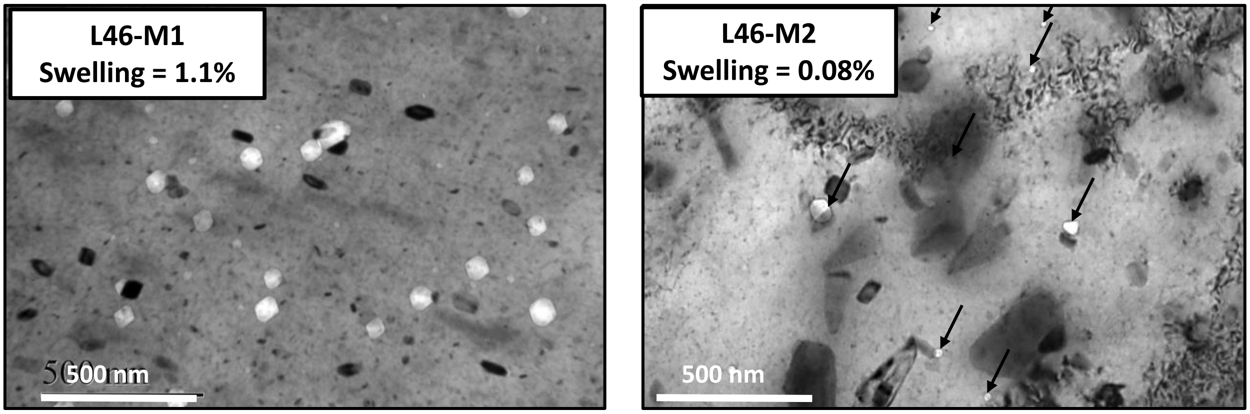
FIG. 2: TEM micrographs of the alloys Fe 14Cr 16Ni and Fe-14Cr 25 Ni irradiated 150 dpa at 650°C.

The two alloys followed the same thermal cycle. The difference between the two samples before irradiation is the amount of Ni in the matrix. Ni is known to increase the incubation dose for swelling [4, 5, 6]. In this experiment, Ni decreases the cavities mean size but increases their density. Different assumptions are proposed in the literature to explain the effect of Ni. The high Ni-vacancy binding (Ev-Ni= 0.26eV) could help the formation of Ni-v clusters. Hence, these complexes would decrease vacancies mobility, act as recombination sites for punctual defects or as nucleation sites for cavities. In previous work reported in [7], on neutron irradiated materials, the sharp swelling drop with nickel up to 35%Ni is explained by a drop of voids density. Garner claims that this density reduction is caused by an increase of vacancy mobility with nickel [4]. This shows the complexity of the phenomenon [8] despite nickel is usually recognized to decrease the swelling.

2. *Influence of the cold working*

This effect was studied using the L46 alloy, Fe- 14Cr-16Ni 0.2Ti 0.4Nb, in the two metallurgical states: solution annealed and solution annealed + cold worked to introduce dislocations. The micrographs are presented in figure 3.

This alloy contains some titanium in solid solution and do not swell a lot. Nevertheless, the introduction of a dense dislocations network reduces clearly the swelling. Dislocations are often considered as recombination sites for punctual defects and they are well known to reduce the swelling under neutron irradiation. Industrial tubes profit from this metallurgical state which appears as the optimized microstructure. In this experiment, the ion irradiations reproduce well this experimental feature.



Fe-14Cr 16Ni 0.2Ti 0.4Nb alloy SA   *Fe-14Cr 16Ni 0.2Ti 0.4Nb alloy SA + CW*

FIG. 3: TEM micrographs of the alloys Fe 14Cr 16Ni 0.2Ti 0.4 Nb irradiated 150 dpa at 600°C. In 46-M2 cavities are arrowed in black.

3. *Influence of the nano-titanium and nano-niobium carbides*

In the as-received state, cladding tubes for SFR reactors are solution annealed and cold worked. In service, many nano-carbides precipitate under irradiation. To simulate partially this evolution, the alloys (L46, L48, L50, L51, L52), stabilized with titanium and niobium were aged at 650°C during 50 hours (M6 state) before ion irradiations. After ageing, the microstructure was characterized by TEM and by Small Angle Neutron Scattering [9]. A dense precipitation of nano -titanium carbides and nano niobium carbides was observed on the dislocation network. In average, their size in diameter was below 5nm for a volume fraction between 0.15 and 0.3 %. According to atom probe measurements, after this heat treatment, only few hundreds ppm of titanium remain in solid solution.

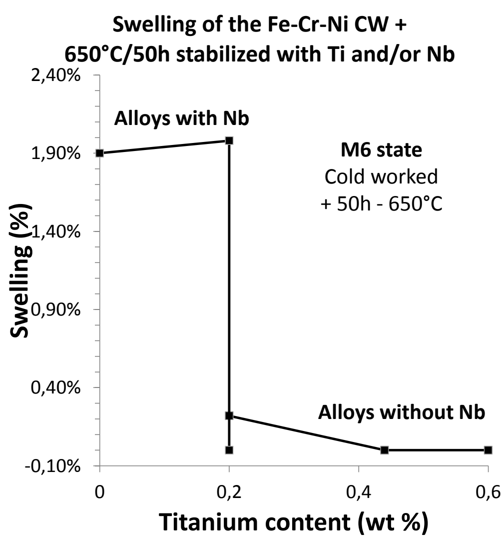


FIG. 4: Swelling of different alloys stabilized with titanium and niobium after ageing and irradiation at 600°C – 150 dpa.

After irradiation, as soon as the alloy contains some titanium, the swelling dropped dramatically. The benefit of titanium to reduce the swelling has been already noticed. It seems even after precipitation, it still contribute effectively to limit the swelling.

Conclusion

CEA develops new austenitic and ODS alloys to limit the swelling and withstand very high doses. 10 Austenitic Stainless Steels with different content of phosphorus, nickel, silicon, titanium and niobium were elaborated and irradiated with iron ions at 600°C in several metallurgical conditions. It is confirmed that a nickel enrichment (15wt% -> 25wt%) decreases the swelling. The presence of a dislocation network reduces the irradiation swelling. Titanium in solid solution but also after precipitation as nano-phases helps also to reduce the swelling. These types of ion irradiations appear powerful to compare different model alloys, to classify their swelling resistance as a function of their microstructures and chemical compositions and to help the design of optimized alloys. Additional irradiations are forecast to understand the temperature effects, the influence of the Ti/Nb ratio or to study the effect of phosphorus.

References

[1] P. Yvon and F. Carré, “Structural materials challenges for advanced reactor systems,” *J. Nucl. Mater.*, vol. 385, no. 2, pp. 217–222, 2009.

[2] M. Le Flem, M. Blat-Yrieix, V. Garat, J.L. Séran, “French R&D on materials for the core components of Sodium", paper presented at Int. Conf. Fast Reactors and Related Fuel Cycles: Safe Technologies and Sustainable Scenarios (FR13), Paris, 2013Fast Reactors.

[3] P. DUBUISSON, “Core Structural Materials – feedback experience from Phénix Design Manufacturing and Irradiation behaviour of Fast Reactor Fuel” IAEA-TECDOC 1689, 235-247 (2013)

[4] F. A. GARNER, “Recent insights on the swelling and creep of irradiated austenitic alloys” Journal of Nuclear Materials, 123, 459-471 (1984).

[5] J.L. SERAN and al., “Behaviour under neutron irradiation of the 15-15Ti and EM10 steels used as standard materials of the Phénix fuel subassembly,” Effects of radiation on materials :15th International Symposium ASTM STP 1125, 1209-1233, Philadelphia, (1992).

[6] T. MUROGA and F. Garner, “Microstructural investigation of swelling dependence on nickel content in fast neutron-irradiated Fe-Cr-Ni austenitic ternaries,” Journal of Nuclear Materials, 179, 546-549 (1991).

[7] T. MUROGA and F. Garner, “Microstructural investigation of swelling dependence on nickel content in fast neutron-irradiated Fe-Cr-Ni austenitic ternaries,” Journal of Nuclear Materials, 179, 546-549 (1991).

[8] B. Rouxel et al. “Influence of the Austenitic Stainless Steel Microstructure on the Void Swelling under Ion Irradiation,” EPJ Nuclear Sci. Technol.Volume 2, 2016.

[9] B. Rouxel, PhD, “Développement d'aciers austénitiques avancés résistants au gonflement sous irradiation,” Université Lille 1, Dec 2016.