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DUBUISSON P. - LEVY V. - SERAN J.L. - GILBON D. -
LE NAOUR L. - DIDOUT D.

CEA Centre d'Etudes Nucléaires de Saclay, 91 - Gif-sur-Yvette (FR).
Dept. de Technologie

EFFET DU Ge, Sn ET Sb SUR LA RESISTANCE AU GONFLEMENT D'ALLIAGES AUSTENITIQUES IRRADIES PAR DES ELECTRONS DE 1 MeV

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The effect of new solute elements namely Ge, Sn and Sb on the void swelling resistance of austenitic alloys irradiated with 1 MeV electrons has been studied. Except for tin in Ti-modified 316, all solute improve the swelling resistance of base alloys. Tin addition shifts the swelling peak of 316 S.S. to high temperature. In fact, these solute additions have the same qualitative effect on the swelling components : they enhance the void density and decrease strongly void growth rate. This effect is opposite to the one of usual swelling inhibitors such as Si or Ti which decrease the void density. We have explained this influence on the void nucleation and void growth by introducing a strong interaction between vacancies and solute atoms in a void growth model.

INTRODUCTION

1. Usual swelling inhibitor elements such as C, Si, Mo or Ti have been studied extensively in austenitic steels. Nevertheless other elements which are generally unspecified, can have an unsuspected effect on the swelling resistance of austenitic steels and could explain a part of the swelling variability observed in reactor irradiations.

2. The purpose of this paper is to describe the effect of Ge and Sn on the swelling behaviour of three austenitic alloys : a "pure" Fe-15Cr-20Ni alloy and two commercial steels, a 316 and a Ti-modified 316. The effect of Sb has also been investigated in the 316 S.S.. All the experiments were performed by simulation with 1 MeV electrons in high voltage electronic microscope (HVEM). This technique has the advantage of a direct observation of the damage process during the irradiation.

EXPERIMENTAL

3. Materials. In order to observe the sole effect of solute addition on swelling the different alloys (Fe-15Cr-20Ni alloys, Ti-mod.316 or 316 steels) were prepared by the same process of manufacturing. The Fe-15Cr-20Ni alloys are prepared from high purity elements Fe, Cr, Ni and solute element by melting in an induction furnace. Steels were prepared from 316 S.S. or Ti-mod.316 by addition of solute (Ge, Sn or Sb) and remelting in an arc furnace. They were then annealed at 1250°C for 5 hours to homogenize the composition of the steels. All the alloys are reduced to sheet, 1mm thick, by rolling and followed by a argon quenching after 10 minutes at 1150°C. Chemical compositions of the base alloys are listed in table 1. The content of different solutes that we have studied are given in table 2.

4. The specimens in the solution annealed state are mechanically thinned to about 80 µm thick and then punched out to 3 mm diameter discs. Thin foils specimens for HVEM observation are finally prepared by a twin jet electropolishing technique.

Table 1. Chemical compositions of base-alloys (wt %)

	Fe-15Cr-20Ni	316S.S.	Ti-modified 316
C	0.005	0.054	0.057
Cr	15.4	16.8	16.88
Ni	20.2	13.2	13.13
Mo	≤ 0.05	2.12	2.25
Mn	≤ 0.03	1.4	1.4
Si	≤ 0.02	0.55	0.33
Ti	-	0.003	0.25
Fe	bal.	bal.	bal.

Table 2. Solute additions. Terms in bracket are weight percentage.

Fe-15Cr-20Ni	Ge (0.4) Sn (0.6)
316 S.S.	Ge (0.3) Sn (0.02-0.1-0.5) Sb (0.5)
Ti-mod.316	Ge (0.7) Sn (0.5)

5. Irradiation. The electron irradiation and in situ observation are carried out in the HVEM of C.E.N. Saclay using a beam of 1 MeV electrons with a center area intensity of ∼ 1,5 10^{20} electrons $cm^{-2}s^{-1}$. This beam produces displacements in alloys at a rate close to 5,5 10^{-3} dpa s^{-1}, assuming a displacement cross-section of 40 barns (ref. 1). The irradiated area has always an orientation close to (110). The influence of the nature of the minor element on swelling is investigated at 500°C ; this temperature lies between the temperatures of fuel pins and wrappers maximum dose rate. In the case of tin addition, which exhibits the largest effect, we have investigated the influence of irradiation temperature in the range of 500 to 600°C and, at 550°C, the effect of solute concentration on the swelling of 316 stainless steel.

RESULTS

6. Dose dependence. The plots of the parameters of swelling (void swelling, void number density, average void volume) versus irradiation dose show that the different alloys irradiated in different conditions have the same behaviour. Swelling varies linearly with dose, the linear swelling regime sets up rapidly, after a dose of few dpa (< 5 dpa). Void number density saturates as soon as voids are measured (5-10 dpa), void swelling and average void volume increase linearly with dose. The 316 steels irradiated at 500°C give an example of such variations with dose (see Fig. 1-3).

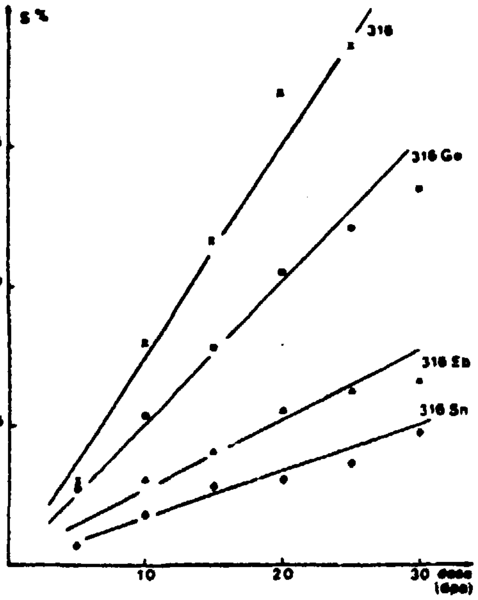

Fig. 1. Swelling versus dose in 316 steels irradiated at 500°C

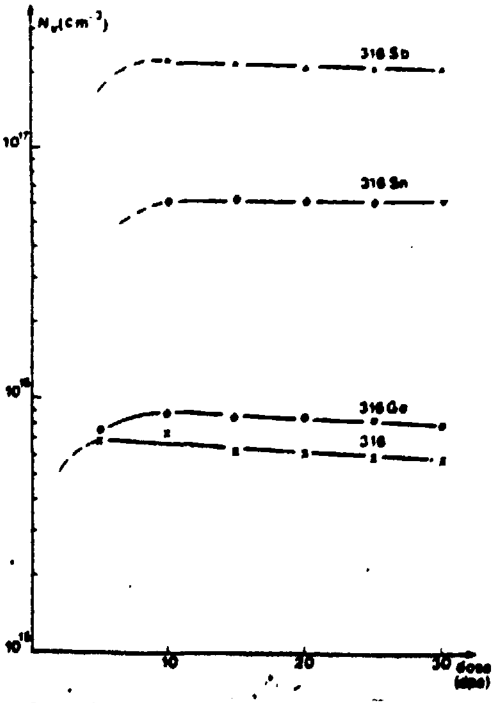

Fig. 2. Void densities versus dose in 316 steels irradiated at 500°C

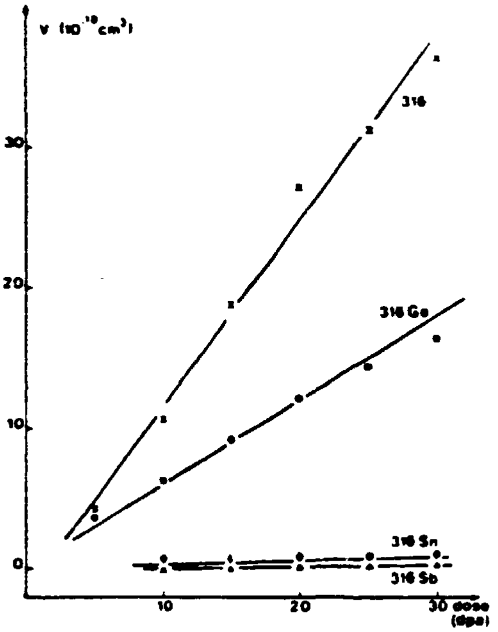

Fig. 3. Average void volume versus dose in 316 steels irradiated at 500°C

7. In the results given here after, all irradiations will be defined by the maximum void density, the linear void growth rate, the linear swelling rate and the incubation dose. It is defined as the value measured by extrapolation of the linear swelling line to zero swelling. These results are reported in tables 3-5. All incubation dose values are below 4 dpa.

Table 3. Expérimental results of alloys irradiated at 500°C

Alloy	$\dot{S}$	N_V max.	$\dot{V}$	Δ
Fe-15Cr-20Ni	0,85	8 10^{15}	1,3	0
Fe-15Cr-20Ni-0.4Ge	0.36	2 10^{16}	0.17	0
Fe-15Cr-20Ni-0.6Sn	0.11	3.7 10^{16}	0.03	0
316	0,81	7,4 10^{15}	1,4	0,5
316-0,3Ge	0,49	8,8 10^{15}	0,58	0
316-0,5Sn	0,15	6,3 10^{16}	0,02	0
316-0,5Sb	0,26	2,3 10^{17}	0,01	0
Ti-mod.316	0,033	7,9 10^{14}	0,37	1,9
Ti-mod.316-0,7Ge	0,016	9,7 10^{14}	0,18	0
Ti-mod.316-0,5Sn	0,195	1,3 10^{17}	0,016	0

$\dot{S}$ = Swelling rate (% dpa^{-1})
N_V max. = Maximum void density (cm^{-3})
$\dot{V}$ = void growth rate (10^{-18}cm^{3}dpa^{-1})
Δ = Incubation dose (dpa)

The incubation dose variations are not significant. Nevertheless, it seems that incubation dose varies with temperature and decreases for solute additions (Ge, Sn or Sb).

Table 4. Experimental results of alloys irradiated at 550°C

Alloy	$\dot{S}$	N_V max.	$\dot{V}$	Δ
315	1.16	$4.1\ 10^{15}$	3.9	1.7
316-0.02Sn	0.93	$3.3\ 10^{15}$	3.02	0.7
316-0.1 Sn	0.70	$1.1\ 10^{16}$	0.74	0
316-0.5 Sn	0.3	$1.9\ 10^{16}$	0.2	0

Table 5. Experimental results of alloys irradiated at 600 °C

Alloy	$\dot{S}$	N_V max.	$\dot{V}$	Δ
316	0.53	$1.4\ 10^{14}$	52.8	3.3
316-0.5Sn	0.89	$2.7\ 10^{15}$	6.4	0.9

8. Influence of the nature of minor element. This effect was investigated at 500°C on the three base alloys, Fe - 15Cr - 20Ni, 316 and Ti-modified 316. All the solutes tested in this work, germanium tin or antimony improve the swelling resistance of the base alloys except for tin in Ti-modified 316 (see table 3). In Fe-15Cr-20Ni alloy and 316 S.S. the largest swelling reduction is obtained for tin addition, the swelling rate is reduced by a factor 8.

9. The swelling reduction of 316 S.S., see figure 2-4, is due to a large population of small voids. This effect on the swelling parameters is also observed in the other base alloys, the Fe - 15Cr - 20Ni alloy and the Ti-modified 316 (see table 3) : Ge, Sn and Sb enhance the void density and decrease the void growth rate of base alloys. The effect of Ge, Sn or Sb on the swelling parameters seems to be qualitatively independent of the nature of base alloys. On the other hand, the magnitude of the effect depends not only of the solute element but also of the base alloy. The largest effect is observed for antimony addition in 316 stainless steel: the void growth rate is reduced by a factor close to 100 and the void density is increased by a factor 30.

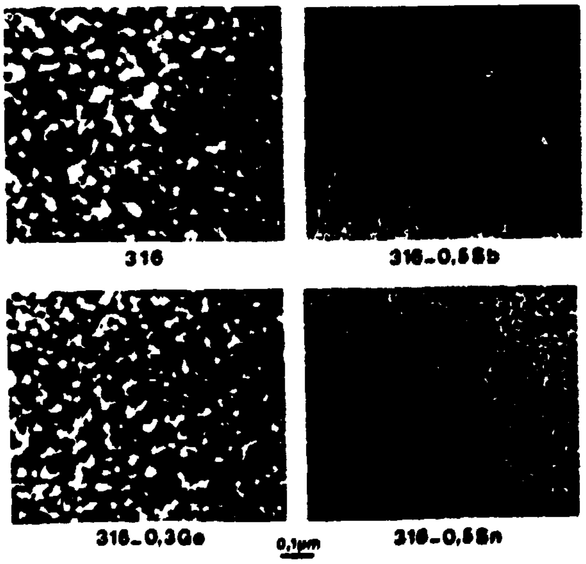

Fig.4. Irradiated area of 316 steels (20dpa-500°C)

Tin effect on swelling of 316 stainless steel.

10. Temperature dependence of swelling. Both steels, 316 S.S. and 316-0.5 Sn have been irradiated in the range of 500 to 600°C. Micrography of the irradiated area of both steels after 20 dpa are given in figure 5. For both steels, void size decrease with temperature and with tin addition. Void densities decrease with an increase of temperature (see fig.6), this evolution becomes more pronounced at higher temperature, especially for 316 S.S.. On the other hand, the void growth rate increases with temperature. Whatever irradiation temperature, Sn addition increases the void density and decreases the void growth rate.

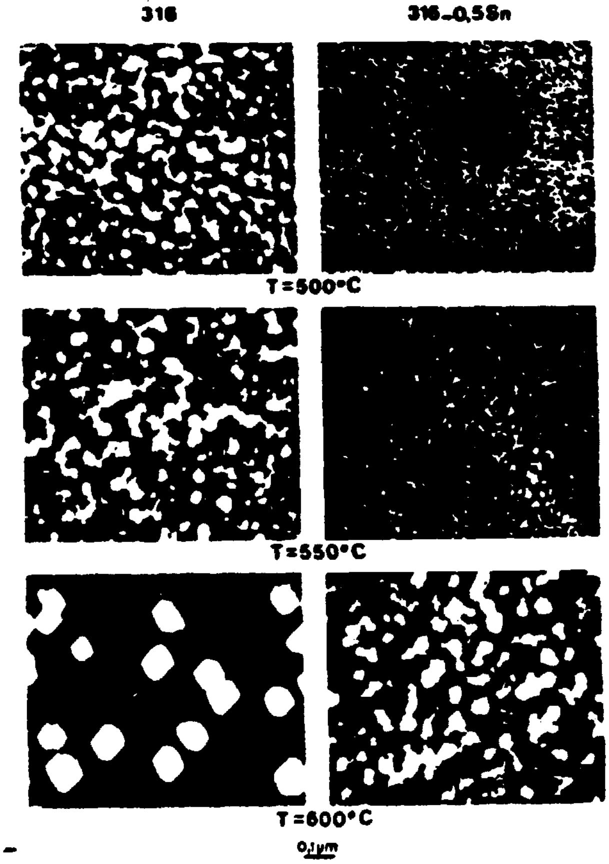

Fig. 5. Irradiated area of 316 and 316 Sn steels at 20 dpa.

Therefore, the swelling rate curves of both steels show a maximum as a function of temperature (see fig. 7). The maximum swelling of 316 stainless steels is at close to 550°C. For 316-0.5Sn steel, the peak swelling temperature is above 600°C. At this last temperature, tin addition (0.5% wt) increases the swelling rate of 316 S.S.

11. Dependence of swelling on tin concentration. Figure 8 shows that the swelling rate decreases with an increase of tin concentration.

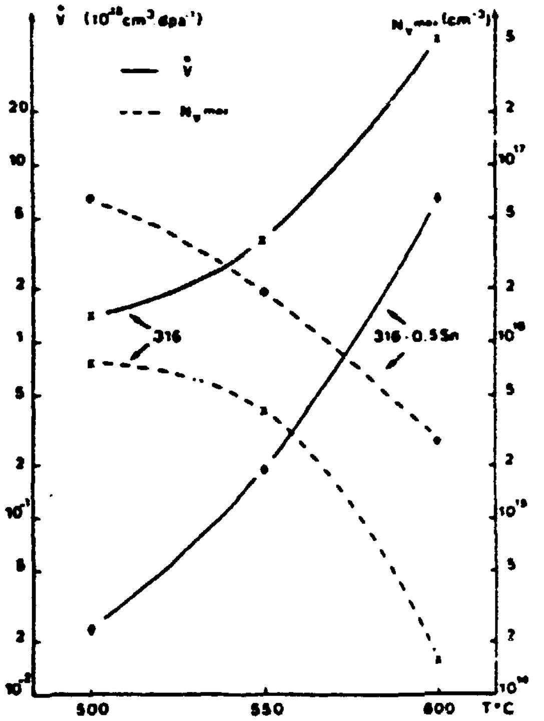

Fig. 6. Temperature dependence of void growth rate ($\dot{V}$) and maximum void density ($N_V$max.) of 316 and 316-0.5 Sn.

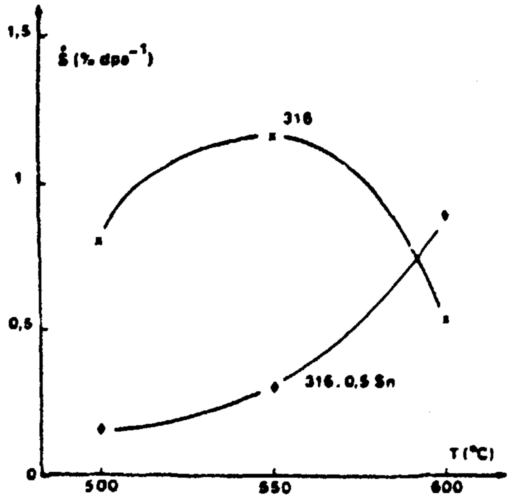

Fig. 7. Temperature dependence of swelling rate ($\dot{S}$)

This reduction is mainly due, once again, to a large effect of tin addition on the void growth rate (see fig. 9). The void density increases with tin concentration.

DISCUSSION

12. To our knowledge, the influence of Ge, Sn or Sb on swelling of austenitic alloys has never been studied. Therefore, no comparison between our results and litterature is possible.

This work so shows the existence of new swelling inhibitor elements but it is not the most prominent result. Indeed, the effect of Ge, Sn or Sb on swelling resistance is opposite to the influence of usual swelling inhibitors such as Si or Ti which mainly decrease the void density (refs 2-4), they enhance the void density. The swelling decrease is obtained by a large void growth reduction.

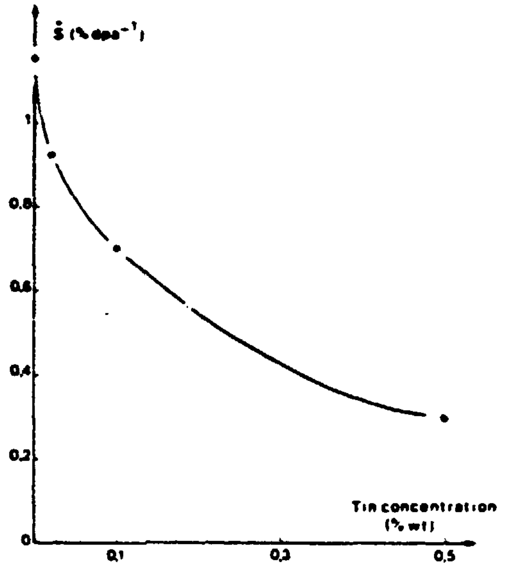

Fig. 8. Tin concentration dependence of swelling rate.

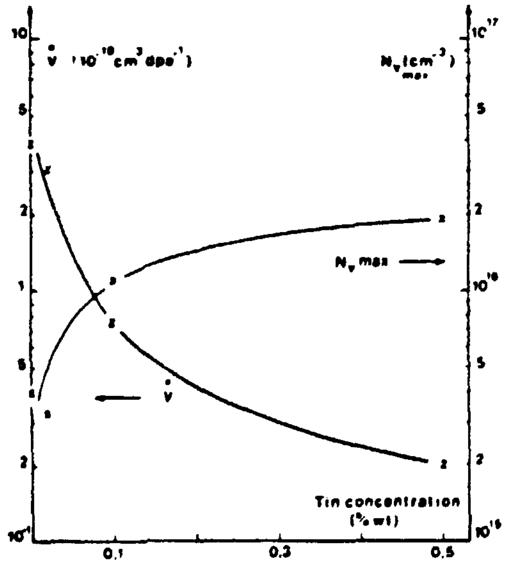

Fig. 9. Tin concentration dependence of void growth rate (V) and maximum void density (N_V max.)

Nevertheless these elements have already been studied in fcc pure metals irradiated by 1 MeV electrons. Thus in nickel, A. Barbu (ref.5) and T. N Guy (ref.6) show that Ge and Sb additions enhance the void density. M. Kiritani also shows that voids not observed in pure gold, are formed abundantly in dilute Au Ge, Au Sn and Au Sb alloys (ref.7). In fcc pure metals, this influence of Ge, Sn and Sb on the behaviour of pure metals irradiated is attributed to a strong vacancy-solute atom binding.

13. Our experimental result may be attributed to the vacancy trapping of oversize Ge, Sn or Sb atoms. Indeed, an increase of void density can not explained by a usual interaction between gas and solute atoms which decreases the void nucleation (ref.8). The addition of Ge, Sn or Sb atoms does not seem modify the dislocation microstructure of 316 S.S. (ref.9).

14. To explain the effect of these additions on void nucleation, we suggest to invoque the same mechanism as void nucleation in pure metals such as Ni, Au or Al (refs.5 - 7, 10), a strong interaction between vacancies and solute atoms. This interaction forms vacancies-solutes complexes which are the void embryons. This void nucleation process can be enhanced by the solute segregation to vacancy clusters (ref.11). The formation of vacancy cluster surrounded by oversize solute atoms decreases the free energy of vancancy cluster formation. The void nucleation rate consequently increase.

15. Two mechanisms can be considered to explain the large decrease of void growth rate. Owing to the large void densities, the first mechanism is a strong loss of point defects on the void sinks to the detriment of dislocation sinks which are responsible of swelling. On the other hand, to explain the void nucleation, we have introduced a vacancy solute interaction. This point defect trapping also reduces void growth rate by enhancing point defect recombinaison.

16. In order to determine the mechanism by which Ge, Sn and Sb atoms occur, we compare our experimental results with calculations performed in a simple void growth model. This model is based on the theory of chemical reaction rates, and has been described in detail by L.K. Mansur (ref.12). The programm used calculated the growth rate of an ideal void of radius r, placed on a structurally homogeneous material.The point defect sinks considered are dislocation lines (Nd) and voids (N_V). A dislocation interstitial bias factor (ε) characterizes the dislocation preference for interstitials over vacancies.

In order to visualize the effect of vacancy trapping, L.K. Mansur (ref.13) suggests that the diffusivity of the entire population of vacancies, trapped (C_V') plus free (C_V) may be characterized by an effective diffusion coefficient D_V^{ef} although only free vancancies are moving and these with the usual diffusivity D_V. So, by *definition, we have :*

$$D_V C_V = D_V^{ef}(C_V + C_V') = D_V^{ef} C_V^{ef} \qquad (1)$$

In conditions of quasi-steady state, the defect rate equations are :

- for the trapped plus free vacancies

$$G - R^{ef} C_V^{ef} C_i - C_V^{ef} D_V^{ef} (N_d + 4\pi r N_V) = 0 \qquad (2a)$$

- for the interstitials (C_i)

$$G - R^{ef} C_V^{ef} C_i - C_i D_i (N_d(1+\varepsilon) + 4\pi r N_V) = 0 \qquad (2b)$$

Where G is the defect production rate, $R^{ef} C_V^{ef} C_i$ the defect loss rate by mutual recombinaison. R^{ef} is the recombinaison coefficient for point defects. $C_V^{ef} D_V^{ef} (N_d + 4\pi r N_V)$, $C_i D_i (N_d(1+\varepsilon) + 4\pi r N_V)$ are the defect loss rate to the fixed sinks, dislocation lines and voids. D_i is the diffusivity of the interstitials.

If vacancies are trapped by free traps and if trapped vacancies are mainly eliminated by vacancy detrapping and not by mutual recombinaison with interstitials, the effective diffusion coefficient can be written :

$$D_V^{ef} = \frac{D_V}{1 + \tau_V C_t \chi_V} \qquad (3)$$

where C_t is the traps concentration, χ_V the trap capture coefficient for vacancies and τ_V the average time spent by a vacancy at a trap. It is defined by

$$\tau_V = \frac{b^2}{D_V} \exp(E_V^b / kT) \qquad (4)$$

where E_V^b is the binding energy of the vacancy at the trap, T the absolute temperature, k the Boltzmann's constant and b a constant in order of an atomic distance.

These equations are coupled to the following equation for the growth rate of a void of radius r:

$$\frac{dr}{dt} = \frac{\Omega}{r} (D_V^{ef} C_V^{ef} - D_i C_i - D_V^{ef} C_V^e(r)) \qquad (5)$$

where Ω is atomic volume and $C_V^e(r)$ the thermal equilibrium concentration of vacancies at voids of radius r.

17. The values of the parameters used in this calculation are reported in table 6. Irradiation condition parameters (temperature, dose rate) are the one chosen for each experiment. For dislocation densities, for which these are no results in the present study, we have used values of M.J. Makin (ref.16) for 316 S.S. and this of G.P. Walters (ref.17) for Fe-15Cr-20Ni alloys. As Ti atoms interact with dislocations, we have chosen for Ti-modified 316 dislocation density a higher value than for 316 S.S., of 5 10^{11} cm^{-2}.

Table 6. Parameters used in the void growth model (ref. 14, 15, 18)

Parameters		316 S.S. and Ti-modified 316	Fe-15Cr-20Ni alloys
E_i^m	(eV)	0.3	0.92
E_v^m	(eV)	1.3	1.32
H_v^f	(eV)	1.6	1.86
D_i^o	($cm^2 s^{-1}$)	10^{-3}	10^{-3}
D_v^o	($cm^2 s^{-1}$)	0.6	0.6
S_v^f	(eV/K)	1.5k	1.5k
r_c	(nm)	0.15	0.15
γ	($erg\ cm^{-2}$)	2000	2000

r_c = recombinaison radius

18. The dislocation bias factors (ε) resulted from the fit of the computed values to the experimental results of the three base alloys.

We then computed the void growth rate of Ge, Sn or Sb modified alloys and, if necessary, introduced binding energy to fit to the experimental result.

The computed results are reported in table 7 for irradiation performed at 500°C and on fig.10 and 11 for tin effect.

Table 7. Binding energy to consider to obtain experimental results.

base alloys	addition (%wt)	E_V^b (eV)
316 S.S.	Ge (0.3)	0.33
	Sn (0.5)	0.53
	Sb (0.5)	0.35
Ti-mod. 316	Ge (0.7)	0.37
	Sn (0.5)	0.55
Fe-15Cr-20Ni	Ge (0.4)	0.42
	Sn (0.6)	0.60

These simple calculations show that the increase by solute additions of the void density decrease the void growth rate but not enough to obtain the experimental results. A vacancy trapping must be taken into account. Vacancy trapping energy depends on the nature of solute addition. It seems that vacancy trapping energy is also a fonction of the nature of base alloys.

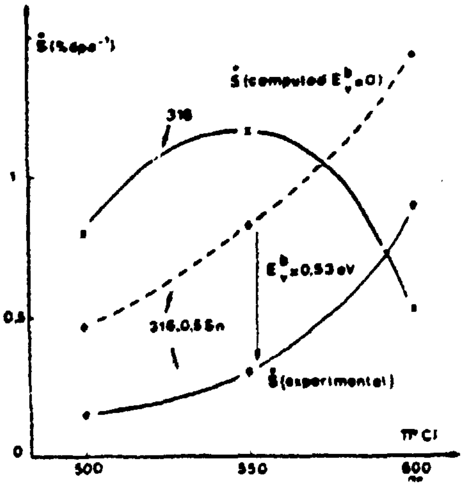

Fig.10. Experimental and computed swelling rate versus temperature

We can see on figure 10 that only the increase of void density is responsible of the shift of the swelling peak of tin modified 316 to high temperature.

CONCLUSION

19. In this work we have studied the effect of Ge, Sn or Sb on the swelling of three austenitic alloys irradiated by 1 MeV electrons in HVEM. At 500°C,all solutes improve the swelling resistance of base alloys except for tin in Ti-modified 316. In fact Ge, Sn and Sb have the same qualitative effect on the swelling components : they enhance the void density and decrease their void growth rate. Tin addition shifts the swelling peak of 316 stainless steel to high temperature. By the use of a void growth model we can explain by a strong interaction between vacancies and solute atoms the effect of Ge, Sn or Sb on the void nucleation and the void growth.

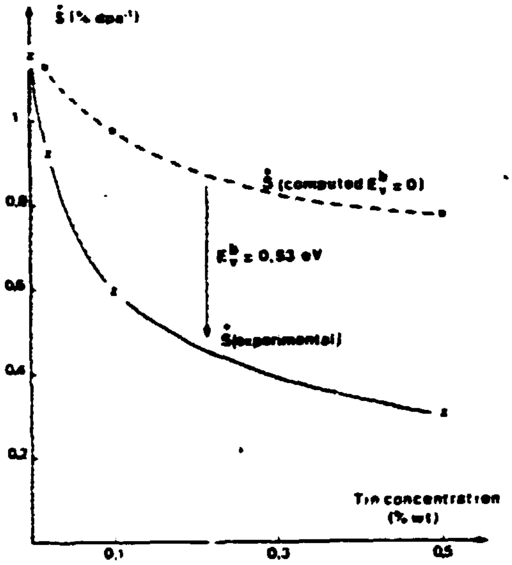

Fig.11. Experimental and computed swelling rate versus tin concentration.

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