Ab Initio Study of Tin Segregation in Zirconium at the $\Sigma 17(0\overline{3}37)$ Tilt Grain Boundary

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Zircaloy-2 and zircaloy-4 contain alloying elements that improve their mechanical properties and corrosion resistance. However, the segregation of these alloying elements affects considerably these properties. In this work, the steps of constructing a symmetrical tilt grain boundary in hcp structure are described and the segregation energy of Sn in the symmetric tilt grain boundary $\Sigma 17[\theta = 49.71^{\circ}/[2110], (0\bar{3}37)]$ in Zr is also calculated using the first principles *ab initio* and the ABINIT calculation code. Among five selected pseudopotentials, the optimization and convergence calculations for the bulk hcp Zr lattice show that the most optimal pseudopotentials are GGA–PBE–HGH and GGA–PBE–Troullier Martins (TM) and a good agreement was found with previous theoretical and experimental data. The segregation energy calculations show that the segregation of Sn at the sites of symmetric tilt grain boundary plane is unfavourable, while it is favourable at the sites of the first plane parallel to the grain boundary plane. However, for the other planes, the segregation is unfavourable. From an energetic point of view, it is not appropriate for the Sn to replace the Zr atom in the studied grain boundary, which was demonstrated by the charge density maps.

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1. Introduction

The fuel rod cladding represents the first barrier for radioactive products confinement. The use of zirconium alloys for the cladding fuel rod of various reactors is related to their lower neutron absorption, corrosion resistance, good mechanical and thermal properties, compatibility with fuel and sufficient resistance to neutron irradiation (swelling, embrittlement, etc.) [1]. During the reactor operation, the alloy is subjected to various degradation phenomenons like intergranular segregation, that may affect considerably the material characteristics and threaten the structural integrity of the fuel rod cladding.

The segregation is a local enrichment phenomenon of the solute resulting from its redistribution between the bulk and certain sites of the crystal lattice defects (dislocations, surfaces, interfaces), during thermal and mechanical treatment. This interaction between punctual, linear or planar defects leads to a reduction in the free enthalpy of the system and a relaxation of the defects. Intergranular segregation considerably modifies the behavior of grain boundaries whose concentration of solute elements can reach high levels even if these elements are in very limited quantities in the crystals. For all polycrystalline materials, the consequences of intergranular segregation on structural and functional properties are considerable: embrittlement or consolidation, intergranular corrosion and modification of electrical properties [2]. Several studies have been carried out on crystal defects of metals having the hexagonal close-packed structure such as Mg, Ti, and Zr [3], particularly on the atomic scale, by *ab initio* calculations [4–10] or by molecular dynamics [11, 12].

In this work, we are interested in studying the bulk hcp Zr lattice and the segregation of Sn as an alloving element for zircaloy-2 and zircaloy-4 at the symmetrical tilt grain boundary in Zr with a high angle of coincidence $\Sigma 17[\theta = 49.71^{\circ}/[2\overline{11}0], (0\overline{3}37)]$. The tin has a hardening effect in solution, in cold and in hot, and thus allows an improvement of thermal creep characteristics [13]. This element was selected for its effect on the corrosion resistance and mechanical properties. The intergranular segregation of this element leads to the grains depletion by this element and the enrichment of the grain boundaries, leading to the degradation of the corrosion resistance properties. The energetic segregation and the site preference of Sn in a Zr GB, have been also investigated using a first-principles method and the ABINIT calculation code [14–16].

The convergence and optimization of the crystal parameters of Zr with hcp crystal structure have been calculated. The construction steps of the supercell containing the symmetrical tilt grain boundary $\Sigma 17[\theta = 49.71^{\circ}/[2110], (0\bar{3}37)]$ and its relaxation to equilibrium are given. In order to investigate the intergranular segregation phenomenon, the Zr atom is substituted by the Sn atom in the relaxed supercell and the segregation energies of this element have been calculated at the grain boundary and at different atomic sites.

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2. Computational methodology

2.1. Convergence and optimization

In the present work, and within the density functional theory (DFT), the norm-conserving pseudopotentials [17] have been used with generalized gradient approximations (GGA) [18, 19] and local density approximations (LDA) [20] for the exchange-correlation functional and various parameterizations and valence electrons configurations.

The zirconium electronic configuration is: $1s^22s^22p^63s^23p^63d^{10}4s^24p^64d^25s^2$. Two kinds of pseudopotentials were considered for zirconium: the first one with 4 electrons is noted as Zr_4 ($4d^25s^2$) and the second one with 12 electrons is noted as Zr_12 ($4s^24p^64d^25s^2$).

2.1.1. Adjustable parameters

The convergence and the optimization are based on the variation of the total energy of bulk hcp Zr lattice as a function of the following parameters:

- Discretization of the Brillouin zone (ngkpt) which was performed by the Monkhorst–Pack algorithm [21];
- Kinetic energy cut-off (ecut);
- The temperature of smearing (tsmear) according to: cold smearing (Marzari [22, 23]) or the Hermite–Gauss smearing (Methfessel and Paxton [24]).

For these parameters, the following values were used: tsmear : 0.001, 0.005, 0.01, 0.02, 0.03, 0.04, 0.05 Ha ngkpt : $2 \times 2 \times 1$ (nkpt 4), $3 \times 3 \times 2$ (nkpt 18), $4 \times 4 \times 3$ (nkpt 48), $5 \times 5 \times 3$ (nkpt 75), $6 \times 6 \times 4$ (nkpt 144), $8 \times 8 \times 6$ (nkpt 384), $10 \times 10 \times 6$ (nkpt 600), $12 \times 12 \times 7$ (nkpt 1008), $14 \times 14 \times 9$ (nkpt 1764), $16 \times 16 \times 10$ (nkpt 2560).

The nkpt parameter is the number of k-points. These points are used to sample the Brillouin zone.

ecut : 30, 40, 50, 60, 70, 80, 90, 100, 120, 140 Ha

The crystal parameters for the Zr primitive cell are: a = b = 6.1 [bohr], c = 9.7 [bohr]. The calculation has been done using three nested loops: the first for tsmear, the second for ngkpt and the third for ecut.

The objective of calculating the total energy for the bulk hexagonal close-packed structure using the different pseudopotentials is to choose the best values of the convergence parameters (tsmear, ngkpt, and ecut).

For each value of tsmear, we calculated the difference between etotal (ngkpt $16 \times 16 \times 10$) and etotal (ngkpt = $i \times i \times k$, i = 2,3,4,5,6,8,10,12,14 and 16, k = 1,2,3,4,6,7,9and 10) and we choose the values of the convergence parameters tsmear, ngkpt, and ecut so that the energy difference is in the order of 1 meV.

The calculation results showing the convergence for each type of pseudopotential are given in Table I.

Figure 1 shows the total energy convergence of the bulk hcp Zr lattice as a function of the kinetic energy cut-off (ecut) for the pseudopotential GGA–PBE–HGH, as an example among other pseudopotentials.

Values of ngkpt, tsmear and ecut which ensure convergence for the pseudopotentials tested.

Pseudopotentials	ecut [Ha]	tsmear [Ha]	ngkpt
GGA-PBE-TM	70	0.04	$8 \times 8 \times 6$
GGA-PBE-HGH	100	0.04	$8 \times 8 \times 6$
LDA-TM	60	0.04	$8 \times 8 \times 6$
LDA-HGH-40zr.4.hgh	70	0.03	$8 \times 8 \times 6$
LDA-HGH-40zr.12.hgh	60	0.02	$8 \times 8 \times 6$



Fig. 1. Total energy convergence of bulk hcp Zr lattice for increasing kinetic energy cut-off (ecut) : (a) as a function of the k-points (ngkpt), (b) ngkp set at $8 \times$ 8×6 . Calculations performed for the pseudopotential GGA-PBE-HGH with the tsmear set at 0.04 H.

This convergence has been shown in Fig. 1a for different values of ngkpt. Figure 1b shows the choice of ecut optimum value for ngkpt $8 \times 8 \times 6$. The choice of ecut value is based on the difference between the total energy for a value of ecut (j) and that for the previous value ecut (i), this difference must be less than 1 meV. In Fig. 1b, ecut optimum set at 100 [Ha].

The convergence test of the calculations with respect to the temperature of smearing (tsmear) and simultaneously with respect to the sampling of k-points (ngkpt), indicate that tsmear is set at 0.04 H for the pseudopotential GGA–PBE–HGH. For higher ngkpt and ecut, more precise results from the calculation are obtained. Due to the high computation cost for these parameters, it is necessary to balance between them. For this reason, we choose ngkpt set at $8 \times 8 \times 6$ and ecut set at 100 H.

2.1.2. Structural optimization

-6.035

-6.040

-6.045

-6.050

-6.055

-6.060

-6.065

-6.070

-7.395

-7.400

-7.405

-7.410

-7.415

-7.420

-7.425

-7.430

-7.435

260

Total Energy (Hartree)

260

Fotal Energy (Hartree)

The structural optimization of the Zr primitive cell is done by the variation of the total energy as a function of the volume by modifying the crystal parameters a and cor by modifying the ratio (c/a). Both methods are used in this work, but we retained the results obtained by the first method.

For each pseudopotential, the total energies of the Zr primitive cell are calculated with the optimized values of ecut, tsmear and ngkpt, by modifying the values of the crystal parameters a and c; $a = a_0 \pm \Delta a$, $5.7 \leq a_0 \leq 6.6$ [bohr], $\Delta a = 0.1$ [bohr], $c = c_0 \pm \Delta c$, $9.2 \leq c_0 \leq 10.1$ [bohr] and $\Delta c = 0.1$ [bohr].

The results for the different pseudopotentials show the variation of etotal as a function of the volume (V) of Zr (hcp) primitive cell for each value of c. Figure 2 shows these results for two pseudopotentials: GGA–PBE–TM and LDA–TM.

2.1.3. Calculation of the equilibrium crystal parameter a_0

According to the curves of Fig. 2, the value of the crystalline parameter c_0 , for each pseudopotential, is chosen as the corresponding total energy is minimal.

After identifying the value of the crystal parameter c_0 , the etotal is calculated and plotted as a function of the volume (V) for different values of a ($a = a_0 \pm \Delta a$). The curve is adjusted according to the polynomial Eq. (1) where A, B, and C are constants

$$E(V) = AV^2 + BV + C \tag{1}$$

The volume corresponding to the minimum energy (V_0) is calculated by the zero derivation of the total energy with respect to volume (red curve after the fit in Fig. 3):

 $dE(V)/dV|_{V=V_0} = 0, \text{ thus: } V_0 = -B/2A.$ (2) For the hexagonal close-packed structure: $V_0 = (\sqrt{3}/2)a_0^2c_0$, therefore $a_0 = \sqrt{(V_0/c_0)(2/\sqrt{3})}.$

The minimum energy for each pseudopotential is searched, this minimum is the vertex of the parabola curve. For the GGA–PBE–TM pseudopotential and after the fitting of the parabolic curve; $V_0 = 322.95$ bohr³, with $c_0 = c8 = 9.9$ bohr, so $a_0 = 6.14$ bohr (Fig. 3).



Fig. 2. Total energy as a function of hcp Zr primitive cell volume for GGA–PBE–TM and LDA–TM pseudopotentials.



Fig. 3. Optimization of the crystal parameter a for GGA–PBE–TM pseudopotential ($a_0 = 6.14$ bohr) and LDA–TM pseudopotential ($a_0 = 6.20$ bohr).

2.1.4. Optimization of crystal parameter c

In order to optimize our structure, the same calculation is done. Initially, we have fixed the parameter $(a = a_0)$ and varied the parameter c $(c = c_0 \pm \Delta c)$ (c = 9.2-10.2 bohr, $\Delta c = 0.1$ bohr).

The calculation results are represented by the curves etotal = f(V). The fit of each curve provides the new value of c_0 which corresponds to the minimum of the total energy (Fig. 4).



Fig. 4. Optimization of the crystal parameter c for GGA–PBE–TM pseudopotential ($c_0 = 9.84$ bohr) and LDA–TM pseudopotential ($c_0 = 9.93$ bohr).

2.1.5. Calculation of the bulk modulus B_0

To calculate the bulk modulus of Zr (hcp), the variation of etotal is plotted as a function of the primitive cell volume V (Fig. 5) and then, these curves are fitted according to the Birch–Murnaghan equation of state [25]:

$$E(V) = E_0 + \frac{9V_0B_0}{16} \left\{ \left[\left(\frac{V_0}{V} \right)^{\frac{2}{3}} - 1 \right]^3 B_1 \right] + \left[\left(\frac{V_0}{V} \right)^{\frac{2}{3}} - 1 \right]^2 \left[6 - 4 \left(\frac{V_0}{V} \right)^{\frac{2}{3}} \right] \right\}.$$

We have four parameters to determine: E_0 , V_0 , B_0 , and B_1 .



Fig. 5. Calculation of the bulk modulus (B_0) and parameter (B_1) for GGA–PBE–TM and LDA–TM pseudopotentials.

After identifying of the crystal parameters which correspond to the minimum total energy for each pseudopotential, (a_0, c_0) , the bulk modulus (B_0) and (B_1) , the best pseudopotential can now be chosen by comparing these parameters by the *ab initio* calculation and the experimental values [26].

The comparison between the different pseudopotentials shows that the best agreement corresponds to the GGA– PBE–HGH and GGA-TM pseudopotentials, as indicated in Table II. For the first pseudopotential, the calculated value of the crystalline parameter a is identical to the experimental one, with 0.08% of deviation. For the crystal parameter c, there is a small difference between the calculated and the experimental data (0.74%) and the bulk modulus B_0 is near the experimental value (3.43%).

For the GGA-TM pseudopotential, the deviation from the experimental data of the crystalline parameter a is negligible (0.55%) and for the crystalline parameter c, the deviation is 1.35%. The bulk modulus is 111.21 GPa near the experimental value with a difference of 14.65%.

2.2. Atomistic construction of the symmetric tilt grain boundary $[\theta = 49.71^{\circ}/[2\overline{110}], (0\overline{3}37)]$

In order to construct the symmetric tilt grain boundary $[\theta = 49.71^{\circ}/[2\overline{11}0], (0\overline{3}37)]$, we have based ourselves on



Fig. 6. Projection of the conventional cell of the hcp structure on the (0001) basal plane. Atoms in black and in deep blue: atoms at the vertices belonging to the $(2\overline{110})$ parallel planes. Atoms in gray and in light blue: projection of the atoms situated in the centers of the primitive cells of hcp lattice and belonging to the $(2\overline{110})$ parallel planes.



Fig. 7. (a) Representation of the $(2\overline{110})$ plane in the conventional cell of hcp structure, (b) projection of two $(2\overline{110})$ planes of the hcp structure. The atoms in black colour correspond to $x = 0 \times a_1$ and the atoms in blue colour correspond to $x = \frac{1}{2} \times a_1$.



Fig. 8. Atom's coordinates in the $(2\overline{110})$ plane of the hcp structure.

the hcp zirconium conventional cell (Fig. 6), and drawn the $(2\overline{110})$ plane (Fig. 7). The Cartesian coordinates of the atoms of $(2\overline{110})$ plane are shown in Fig. 8.

The $(2\overline{110})$ plane is rotated by an angle $\theta/2 = 24.85^{\circ}$ about the $[2\overline{110}]$ axis, where, the rotation by the angle θ gives a coincidence-site lattice (CSL) (Fig. 9a). The produced supercell contains two successive planes, each of



Fig. 9. (a) CSL, (b) projection of the first grain after the rotation along the $[2\overline{110}]$ axis, it contains two successive atomic planes (34 atoms $\times 2$). The plane presented in the figure is the $(2\overline{110})$ one.



Fig. 10. Projection along the $[2\overline{110}]$ axis of the supercell containing the grain boundary. (a) The supercell containing two successive atomic planes in the $[2\overline{110}]$ direction, the plane presented in the figure is the $(2\overline{110})$ plane, the $(0\overline{337})$ boundary plane is perpendicular to the figure plane. (b) The grain boundary is formed by repeated structural units in red that represent particular arrangements of a limited number of atoms.

them containing 34 atoms. The dimensions of the supercell which forms the first grain are: $a = a_0 = 6.109$ bohr, $b = 2\sqrt{3a_0}/\cos\theta = 23.322$ bohr and $c = 7c_0/\cos\theta =$ 75.613 bohr, Fig. 9b.

To form the grain boundary, we have duplicated the first grain, where x' = x, y' = y, and z' = -z.

The new supercell containing 134 atoms and its dimensions along the three axes are: a = 6.109 bohr, b = 23.322 bohr and $c = 75.613 \times 2 = 151.227$ bohr. This supercell contains the symmetrical tilt grain boundary [$\theta = 49.7146^{\circ}/[2\overline{110}], (0\overline{337})$] (Fig. 10).

The extension of the supercell in the $[0\overline{3}37]$ direction perpendicular to the boundary plane and in the opposite direction is limited to the distance between an atom of the plane and its image (Fig. 10a).

The extension of the supercell in the $[02\overline{2}1]$ direction parallel to the boundary plane is a periodic function of what is called the structural units. After the duplication of the supercell towards the $[02\overline{2}1]$ direction, the structural units were formed as illustrated in Fig. 10b.

2.2.1. Interfacial energy

To minimize the computation time required to calculate the supercell interfacial energy, we have replaced the supercell of 134 atoms by another containing only 60 atoms and containing the grain boundary plane. In order to not affecting the results afterwards, we have based ourselves on the important assumption of the periodic boundary conditions [12]. The grain boundary plane is the x-y plane. Periodic boundary conditions are adopted in the x and y directions. The regions along the z direction serve as a flexible boundary in this direction. We have chosen only the z direction [0–337] for the cut of the supercell by choosing the grain boundary plane as a symmetry plane, and we have kept the atomic configuration along x and y axes ([2–1–10] and [02–21]). In addition, for interfacial and segregation energies, the calculation is based on the difference between the supercell energies with the same number of atoms.

The interfacial energy γ_{GB} is defined by the following formula [27]:

$$\gamma_{GB} = \frac{E_{GB}(N \text{ atomes}) - (N/2) \times E(\text{Zr}_{hcp})}{2 \times a_{SC} \times b_{SC}}, \qquad (4)$$

where E_{GB} is the supercell total energy of N atoms containing the grain boundary and $E(\text{Zr}_{hcp})$ is the total energy of the primitive cells with N atoms. In which the primitive cell for the hcp structure contains two atoms. The crystal parameters of the grain boundary surface after relaxation a_{SC} and b_{SC} are respectively: 6.17 bohr and 23.58 bohr.

TABLE II

Comparison between calculated and experimental [26] data of the crystal parameters values and the bulk modulus.

	Experimental (at 4 K)	GGA-PBE-HGH	GGA-TM	LDA-TM	LDA-GGH-4	LDA-GGH-12
1 8 1		0.000	0.0450	0.0001	2 1 2 2 5	2.1.02.1
a [A]	3.23	3.2327	3.2478	3.2831	3.1207	3.1634
$\Delta a/a_{exp}$		(0.08%)	(0.55%)	(1.64%)	(3.38%)	(2.06%)
c [Å]	5.15	5.1880	5.2196	5.2538	5.0274	5.0822
$\Delta c/c_{exp}$		(0.74%)	(1.35%)	(2.01%)	(2.38 %)	(1.32%)
c/a	1.5944	1.6048	1.6071	1.6002	1.6189	1.6066
$\Delta(c/a)/(c/a)_{exp}$		(0.65%)	(0.8%)	(0.36%)	(1.54%)	(0.77%)
B_0 [GPa]	97	100.33	111.21	110.03	105.33	111.50
$\Delta B_0/B_{0exp}$		(3.43%)	(14.65%)	(13.43%)	(8.59%)	(14.95%)
		•			•	

TABLE III

Typical values of the interfacial energy for some metals and alloys $[mJ/m^2]$ [27, 28].

hcp metals	$\{10\overline{1}2\}$ twin grain boundaries [27]	fcc and bcc metals or alloys	Free surfaces $(T = T_f)$ [28]	Grain boundaries [28]
Υ	364.8	Al	$1080 \ (660 ^{\circ}\text{C})$	$324 (450 ^{\circ}\text{C})$
$_{\rm Hf}$	449.1	Ag	1136 (961 °C)	$375 \ (950 ^{\circ}\text{C})$
\mathbf{Zr}	253.8	Au	1400 (1063 °C)	$378 \ (1000 \ ^{\circ}C)$
Tl	43.0	Cu	1710 (1083 °C)	$615 (925 ^{\circ}\text{C})$
Ti	317.4	stainless steel	2088 (1421 °C)	835
Mg	129.5	W	2634 (3410 °C)	1080 (2000 °C)

 T_f : melting temperature of the material

In the denominator of Eq. (4), there are two surfaces having the same type, that were reflected by the number N = 2.

The calculations show that the interfacial energy for this supercell is 358.6 MJ/m^2 , which is close to some metals and alloys values, as indicated in Table III.

2.2.2. Relaxation of the supercell

Before starting the calculation of the segregation energies of Sn at the symmetric tilt grain boundary [$\theta = 49.7146^{\circ}/[2\overline{110}], (0\overline{337})$], the supercell is relaxed until reaching the minimum energy with new atomic coordinates and new crystal parameters. Minimizing the total energy is achieved only by optimizing the volume and by controlling the ions displacement using the Broyden– Fletcher–Goldfarb–Shanno minimization (BFGS). The GGA–PBE–TM pseudopotential has been chosen for Zr and Sn [18, 19]. The applied plane-wave cutoff energy is 20 Ha and the Brillouin zone discretization is $2 \times 1 \times 1$. The computed total energies are converged within 10^{-7} Ha. The new crystal parameters of this supercell, after relaxation are: 6.307, 24.079, and 68.881 bohr.

2.3. Segregation of Sn at the $\Sigma 17$ symmetrical tilt grain boundary

With the assumption of an infinitely diluted solution, the segregation energy of a solute atom located at site i, ΔE_i^{seg} , is calculated by the following formula [6, 11]:

$$\Delta E_i^{seg} = E_i^{tot}(\text{solute}) - E_b^{tot}(\text{solute}), \tag{5}$$

where E_i^{tot} (solute) [respectively E_b^{tot} (solute)] is the total energy of the relaxed system with a solute atom located at the intergranular site *i* [respectively located at a bulk site].

If the segregation energy is negative, the intergranular site i is favourable to segregation. The total energy was calculated for the relaxed supercell containing the grain boundary and formed by 59 Zr atoms. The Zr atom located in a site i is replaced by an atom of Sn. The calculation is repeated for non-equivalent sites in this system: intergranular site and sites in the parallel planes to the boundary plane. As illustrated in Fig. 11, the sites and



Fig. 11. Projection along the axis $[2\overline{11}0]$ of the supercell containing two successive atomic planes. Selected sites for segregation are indicated in the figure.

their symmetry equivalence are as the following: GB and 30, 1 and 31, 2 and 32, 3 and 33, 4 and 34, 5 and 35, 10 and 40, and so on. The GB site is a site in the boundary plane, the site 1 is in the first plane parallel to the boundary plane and the site 2 is in the second plane parallel to the boundary plane, the following sites are sites in atomic planes more distant. The site 29 corresponds to a site in the bulk.

The supercell projection along the axis $[2\overline{110}]$ is given in Fig. 11. It contains two $(2\overline{110})$ successive atomic planes and the $(0\overline{3}37)$ boundary plane which is perpendicular to the figure plane. The black atoms correspond to $x = 0 \times a_1$ and the blue atoms correspond to $x = \frac{1}{2} \times a_1$. Selected sites for segregation are illustrated in the figure.

3. Results and discussion

3.1. Segregation energies

To calculate the segregation energies of Sn at the $\Sigma 17$ grain boundary and at the different atomic sites in the supercell, we began by the relaxed supercell as an initial configuration of input data, and we substituted the Zr atom with the Sn atom in the various atomic sites: in the grain boundary, in the sites of the planes near and far from the boundary, and in the bulk. For each calculation of the supercell total energy, the supercell containing the Sn atom in the selected site was relaxed again. Equation (5) is applied to calculate the segregation energies for each site. Table IV shows the segregation energies of Sn at the different atomic sites of the supercell.

TABLE IV

Segregation energies of Sn for different atomic sites.

Sites	ΔE_i^{seg} [meV]
GB	373.44
1	-110.03
2	240.72
3	176.80
4	187.72
5	203.91
6	149.55
7	197.57
8	271.55
9	191.42
10	213.15
29 (bulk)	0

The results of the segregation energies calculation of the Sn at the various atomic sites in the supercell are illustrated in Fig. 12. It is clear that for the site (GB) of the grain boundary plane, the segregation energy eseg is 373.44 meV with a positive value, so the segregation is unfavourable (Fig. 12). For the site (1) of the first plane parallel to the boundary plane, the segregation energy is eseg= -110.03 meV, so the segregation is favourable. However, for the other sites, the segregation energies



Fig. 12. Variation of the segregation energy with the distance to the $(0\overline{3}37)$ grain boundary plane for the Zr (Sn) alloy. Plane GB is the grain boundary one, the planes $\pm 1, \pm 2...$, are the first, second, etc., planes parallel to the grain boundary plane.

are positive (Table IV). This implies that energetically it is not appropriate for Sn atom to replace a Zr atom, i.e. the segregation is unfavourable. Therefore, the site (1) of the first plane parallel to the boundary plane for the Sn atom at the Zr supercell is more stable than other sites.

3.2. Charge density maps

The relationship between segregation and electronic structure remains relatively little studied and qualitative. In metal systems, the presence of a solute at the grain boundary induces changes in the chemical bonds, in terms of binding states or non-binding states occupancy, of the covalent or ionic type, which leads to an effect on the intergranular consolidation or embrittlement.

Using the utility cut3d of ABINIT, the data of planar charge density maps are extracted and plotted for the supercell containing the grain boundary for the following configurations:

- 1. The supercell containing only Zr atoms and the symmetric tilt grain boundary $[\theta = 49.71^{\circ}/[2\overline{11}0], (0\overline{3}37)]$ after relaxation,
- 2. Sn atom situated in the grain boundary plane (site GB),
- 3. Sn atom situated in the first plane parallel to the boundary plane (site 1),
- 4. Sn atom situated in the site 10,
- 5. Sn atom situated in the bulk, far from the grain boundary (site 29).

Figure 13 shows sections of the electron charge density maps for each atomic configuration of the supercell containing the grain boundary. These sections are illustrated for two $(2\overline{11}0)$ parallel planes with x coordinates is equal to 0 for the first plane and is equal to $\frac{1}{2}a$ for the second plane.

The sites denoted in this figure are the same as in Fig. 11. The yellow colour indicates an increase in the electronic density, the blue colour a decrease of the electronic density.

When the Sn atom is situated at the grain boundary (Fig. 13b) and at the bulk (Fig. 13e), the charge density demonstrates that there is a low interaction between the Sn atom and its nearest neighbor Zr atoms.

If the Sn atom is in the first plane parallel to the boundary plane (Fig. 13c), the charge density is modified with respect to the supercell without Sn atom (Fig. 13a).

When Sn atom is in site 10, Fig. 13d shows a small perturbation of the charge density around the Sn atom.

The distances between Sn and its first nearest neighbor (1 NN) at different sites have been calculated. It is found that the Sn–Zr (1 NN) distances for Sn at the different sites are in the range of 5.46–6.07 bohr.

The analysis of the electronic charge density distribution shows that there is a strong interaction between the Sn atom in the site 1 and its first nearest neighbor Zr atom in the site 31, this interaction is described by the overlap between the electronic charge densities of these atoms, and by the atomic distance: 5.46 bohr, which represents the minimum value of 1 NN. This implies that it is possible for Sn to replace a Zr atom in this site, contrary to other sites which are energetically unfavourable for Sn to replace a Zr atom, particularly, the site of the grain boundary.

4. Conclusion

This work is a contribution to study the intergranular segregation of Sn in Zr. The steps of constructing the symmetric tilt grain boundary $\Sigma 17 [\theta] =$ $49.71^{\circ}/[2\overline{110}], (0\overline{3}37)$ in Zr with hcp structure are described, and the segregation energies are calculated for Sn at the grain boundary by *ab initio* calculations. We started with optimization and convergence calculations on Zr with the hcp crystal structure, the results showed that the GGA-PBE-HGH and the GGA-PBE-TM pseudopotentials are the optimal pseudopotentials and there is a good agreement with theoretical and experimental results. After the relaxation of the supercell containing the $\Sigma 17$ symmetric tilt grain boundary, the Zr atom is substituted by the Sn atom in the grain boundary and in different atomic sites, and calculated the segregation energies of this solute in those different sites. The results for the segregation energy showed that the segregation of Sn at the grain boundary sites is unfavourable, but it is favourable for the sites of the first plane parallel to the grain boundary plane. For the sites of the other planes parallel to the boundary plane, the segregation is unfavourable. The charge density maps showed that here is an overlap between the electronic charge densities of the

Sn atom situated in the site 1 of the first plane parallel to the gain boundary plane and its 1 NN Zr atom, this implies that it is possible for Sn to replace a Zr atom in this site, contrary to other sites which are energetically unfavourable for Sn to replace a Zr atom. This work could be interestingly extended to investigate the segregation at this grain boundary of the other alloying element Fe, Cr, and Ni of zircaloy 2 and 4.



Fig. 13. Charge density maps in the $(2\overline{11}0)$ plane for different configurations of the relaxed supercell containing the symmetric tilt grain boundary [$\theta = 49.7146^{\circ}/[2\overline{11}0]$, ($0\overline{3}37$)]. (a) Without Sn, (b) Sn atom situated in the grain boundary plane, (c) Sn atom situated in the first plane parallel to the boundary plane, (d) Sn atom situated in the site 10 and (e) Sn atom situated in the bulk far from the grain boundary plane (site 29).

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