Free software for general prediction of surface and interface segregation: SurfSeg - updated

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Abstract

The updated functions of a free software for general prediction of surface and interface segregation, SurfSeg, is reported. So far, only surface segregation of underlayer element on the top film surface was implemented in SurfSeg. With the current update, Surface segregation (bulk), Interface segregation (film), and Interface segregation (bulk) have become available. The mathematical formula for each type of prediction have been provided in the article. Dump screens of the software for operating the predictions, input of an element for prediction and the display of the predicted results are given.

Keywords: segregation, diffusion, mixing enthalpy, surface energy, bulk modulus

1. Introduction

It is often observed that a minor component or impurity element segregates on the surface, or an underlayer element segregates on the surface of the top film layer. [1-6]. Segregation phenomena at the surface and interface are of great importance in many industrial fields including electronic devices and magnetic films. Surface segregation phenomena can be utilized to improve device performance [7] or can be the cause of problems in diffusion barriers [8]. Heating is one of the frequently used processes in materials preparation, which often causes diffusion of atoms. These segregation behaviors are accompanied with the diffusion of atoms, however, either segregation occurs or not does not necessarily depend on the values of diffusion coefficient. Segregation behavior depends on species of materials.

We have studied surface segregation phenomena in various metal–metal layered systems [9-20] and developed a general method to predict if surface segregation of underlayer metals occurs in layered structures ("Surface segregation (film)"). [21]. The prediction method of the surface segregation was implemented as a software called SurfSeg and released in April 2009 [22-23]. Moreover, we discussed diffusion behaviors in three-element systems, film A – film B – substrate C and applied the principle of surface segregation to the segregation behavior of A at the interface between B and C [24]. In the current updated version of SurfSeg, the interface segregation of A in three-element systems, film A – film B – substrate C is also implemented ("Interface segregation (film)"). In addition, the prediction of surface and interface segregation of minor elements in alloys have been implemented with this update.

In this article, previously available function is briefly reviewed and updated functions and their scientific principles of the prediction are reported.

2. Overview

The new front page after running SurfSeg is shown in Fig. 1, where the three colored enclosures are only for this article but not displayed during the software operation. The mode at the most left side, "Surface segregation (film)" is the mode available in the previous version. Other modes, "Surface segregation (bulk)", "Interface segregation (film)", and "Interface segregation (bulk)" are added in the current updated version. In the following, the principles of the prediction for the added modes are explained briefly as well as the mode implemented in the previous version.

2.1 Previous version

The previous version functions only for surface segregation in films, where the prediction is made if an element of the underlayer segregates on the surface of the top layer or not. For this mode, an input screen of elements shown in Fig. 2(a) appears. When elements of the film and the underlayer (noted as substrate) are chosen from the right-side periodic table, "chose annealing condition" brinks and a user should choose annealing condition for segregation prediction as shown in Fig. 2(b). Clicking "Calculate" button after the choice of annealing condition gives the result of prediction by a picture as in Fig. 2(b), together with the calculated adsorption energy values used for the prediction. In some cases, where reference data of diffusion coefficient is available, annealing temperature to observe the predicted segregation is also estimated under the assumption that the film thickness is 1 micrometer and annealing time is 1800 s. The way how the predicted results are shown as pictures is explained in ref [25].

2.2. Added three modes in the updated version

The added three modes became effective in Fig. 1, where the modes enclosed by red, blue and green lines were gray before the update. “Surface segregation (bulk)” mode, enclosed by red line, is to predict if a solute element in alloys segregates on the surface of the alloy or not. “Interface segregation (film)” mode, enclosed by blue line, is to predict if a top layer element segregates at the interface between the layer just below the top layer (underlayer) and the layer below the under layer (noted as substrate). “Interface segregation (bulk)” mode, enclosed by green line, is to predict segregation of a solute element in alloy (either bulk or film) at the interface between the alloy and the underlayer of the alloy (noted as substrate). The principles of the predictions are described for each model in the successive sections.

3. Surface segregation (bulk)

When “Surface segregation (bulk)” in the front page is chosen, input screen as shown in Fig. 3(a) appears, where a solute element and solvent element can be selected from the right-side periodic table. The choice of either solute or solvent is done by clicking radio button next to “A (solute)” or “B (solvent)”.

The prediction is made by calculating the segregation energy of solute element A, ΔH^{A}_{seg} by the following equation [26],

$$\Delta H^{A}_{seg} = \Delta H(mix) + \Delta H(surface) + \Delta H(strain) = \frac{f\Delta H^{A}_{sol}}{3RT} - \frac{g\left(\gamma_A^{s,0} - \gamma_B^{s,0}\right)V_A^{\frac{2}{3}}}{3RT} + \frac{0.42\overline{KV_m}\delta^2}{RT} \quad \cdots \quad (1)$$

where

$$f = 0.71, \qquad g = 4.0 \times 10^8, \qquad \delta = 2\frac{V_A^{1/3} - V_B^{1/3}}{V_A^{1/3} + V_B^{1/3}}, \qquad \overline{KV_m} = \frac{K_A V_A + K_B V_B}{2}$$

Here, ΔH^{A}_{sol} is the enthalpy of solution of element A in B (or mixing enthalpy of A in B) and a value of ΔH^{A}_{sol} is calculated as described in ref. 27. $\gamma^{s,0}_{M}$ (M=A or B) is the surface energy of element M, $V^{2/3}_{M}$ is molar volume of element M, and K_M is the bulk modulus of element M. Values of $\gamma^{s,0}_{M}$, $V^{2/3}_{M}$, and K_M are listed in Table 1 together with other values used for ΔH^{A}_{sol} calculation, where the values of $\gamma^{s,0}_{M}$ and $V^{2/3}_{M}$ are the same of those used to calculate ΔH^{A}_{sol} in ref. 27-31. Most values of K_M in Table 1 are taken from ref. 32.

The first term in eq. (1) is the contribution of heat of solution (if energy stabilization by mixing is large, segregation is not preferred), the second term comes from surface energy (surface of B decreases with the segregation of A) and the third term is the

contribution of size mismatch (size mismatch tends to induce surface segregation because of strain release by segregation). T = 298 K is used for calculating ΔH^{A}_{seg} in the system.

If the calculated value of ΔH^{A}_{seg} is positive, solute element A is predicted to segregate and no segregation of A is predicted if ΔH^{A}_{seg} is negative. Fig. 3(b) shows an example of a dump screen displaying the prediction result. The values of the three terms and ΔH^{A}_{seg} in [J/mol] unit are also displayed for users' convenience. Please note that the unit of energy (J/mol) is different from that used in "Surface segregation (film)" (kJ/mol).

4. Interface segregation (film)

By choosing "Interface segregation (film)" on the front page in Fig. 1, a screen for elements input appears. When elements A, B and C are chosen from the periodic table in the same way described in section 3, the input form of the activation energy of diffusion appears as shown in the broken red lines in Fig. 4 (a). A user should input values of each activation energy required. Because the activation energies are very important to judge whether interface segregation occurs without a significant interface reaction, the prediction is impossible without the input of these values. For users who cannot input these values, return button is provided to go back to the front page.

After the input of these activation energy values, clicking calculate button conducts the judgement whether the input values satisfy the following order or not [24].

$$\mathrm{AinC} \leq (\mathrm{AinB}) \cdot 0.65 < \mathrm{BinC},\ \mathrm{CinB}$$

If this order is not satisfied, an interface reaction either between A and B or B and C occurs, which prevents interface segregation of A at the interface between B and C. In this case, the massage "Interface diffusion dominates." appears. If the above order is satisfied, clicking calculate button then conducts the judgement whether interface segregation occurs or not by the same way used for the prediction of "Surface segregation (film)". When segregation of A on B is predicted (although colors in this mode is vice versa of "Surface segregation (film)" mode), the interface segregation of A at the interface between B and C is predicted. The predicted results are shown as a picture such like shown in Fig. 4(b).

5. Interface segregation (bulk)

When "Interface segregation (bulk)" on the front page in Fig. 1 is chosen, input screen as shown in Fig. 5(a) appears, where a solute element A, solvent element B and substrate element C can be selected from the right-side periodic table. After choosing elements A, B, and C, clicking calculate button gives the predicted result as a picture

and the values of segregation energy terms in [J/mol] unit used for the prediction, as shown in Fig. 5(b). Here, the prediction is performed by following equation [33],

$$\Delta H^{seg} = \Delta H_1^{seg} + \Delta H_2^{seg} + \Delta H_3^{seg}$$
$$= -\frac{1}{3}\Delta H_{AinB}^{sol} + 1.33 \times 10^8 \left(\gamma_{CA}^{chem} - \gamma_{CB}^{chem}\right) V_A^{\frac{2}{3}} + 1.33 \times 10^8 \left(0.15\gamma_A^0 - 0.15\gamma_B^0\right) V_A^{\frac{2}{3}} \quad \cdots \quad (2)$$

$$\gamma_{CA}^{chem} = \gamma_{AC}^{chem} = 2.5 \times 10^{-9} \times \frac{\Delta H_{AinC}^{sol}}{V_A^{\frac{2}{3}}}$$

$$\gamma_{CB}^{chem} = \gamma_{BC}^{chem} = 2.5 \times 10^{-9} \times \frac{\Delta H_{BinC}^{sol}}{V_B^{\frac{2}{3}}}$$

where $\Delta H^{sol}{}_{AinB}$ is the heat of solution for alloys (solute A in solvent B).

The first term of eq. (2) represents that A atoms in the interface layer are less completely surrounded by B neighbors than A atoms in the bulk film. Segregation of A at the interface with C rather than dissolved in B causes the decrease of the number of A atoms completely surrounded by B, resulting in the decrease of energy stabilization by the heat of solution of A in B. The second term (chemical term) reflects the change in interfacial energy when A atoms are replacing B atoms in the interface layer excluding the effect of misfit dislocations. The third term represents the effect of misfit dislocation, which is approximated by the large-angle grain boundary energy between two elements [33].

When ΔH^{seg} is negative, segregation is predicted. Please note that the sign of ΔH^{seg} for segregation is opposite compared to the case of "Surface segregation (bulk)" in eq. (1). This is because the author adopted the equations in each of the reference papers. Please note also that the unit of ΔH^{seg} for "Interface segregation (bulk)" (J/mol) is different from the unit of the adsorption energy used for the prediction in "Interface segregation (film)" (kJ/mol).

6. Conclusion

A software to predict surface and interface segregation in alloys or layered materials, which is the update of the previously released SurfSeg for the surface segregation of an underlayer element on the top layer, is reported. Newly added functions are the prediction of (1) surface segregation in bulk alloys, (2) interface segregation of a top layer element between the underlayer film and the substrate, and (3) interface

segregation of a solute element in an alloy between the alloy film and the substrate. The principles of these segregation predictions, equations used for the predictions, and values used to calculate equations for each element are provided. To demonstrate the software functions, dump screens of the software for each function are also shown. The software is web-base and available for registered users (free of charge for registration).

References

[1] C.L. White, R.A. Padgett, C.T. Liu and S.M. Yalisove : Scripta Metallurgica 18, 1417 (1984).

[2] M. Es-Souni and A. Mosser : Scripta Metallurgica 22, 1469 (1988).

[3] J. Oudar : Materials Science and Engineering 42, 101 (1980).

[4] K. Muraki, S. Fukatsu, Y. Shiraki and R. Ito : Appl. Phys. Lett. 61, 557 (1992).

[5] M. Tvrdy, R. Seidl, L. Hyspecka and K. Mazanec : Scripta Metallurgica 19, 1199 (1985).

[6] A. Hiraki, E. Lugujjo and J.W. Mayer : J. Appl. Phys. 43, 3643 (1972)

[7] S. Tsukimoto, T. Morita, M. Moriyama, K. Ito, and M. Murakami: J. Electron. Mater. 34, 592 (2005).

[8] K. Holloway, P. M. Fryer, C. Cabral, Jr., J. M. E. Harper, P. J. Bailey, and K. H. Kelleher: J. Appl. Phys. 71, 5433 (1992).

[9] M. Yoshitake and K. Yoshihara: Nihon Kinzoku Gakkaishi 54, 1013 (1990) [in Japanese].

[10] M. Yoshitake and K. Yoshihara: Nihon Kinzoku Gakkaishi 54, 778 (1990) [in Japanese].

[11] M. Yoshitake and K. Yoshihara: Nihon Kinzoku Gakkaishi 55, 727 (1991) [in Japanese].

[12] M. Yoshitake and K. Yoshihara: Nihon Kinzoku Gakkaishi 55, 773 (1991) [in Japanese].

[13] M. Yoshitake and K. Yoshihara: Surf. Interface Anal. 18, 509 (1992).

[14] M. Yoshitake and K. Yoshihara: Nihon Kinzoku Gakkaishi 56, 89 (1992) [in Japanese].

[15] M. Yoshitake and K. Yoshihara: Nihon Kinzoku Gakkaishi 58, 768 (1994) [in Japanese].

[16] M. Yoshitake and K. Yoshihara: J. Surf. Anal. 2, 368 (1996) [in Japanese].

[17] M. Yoshitake and K. Yoshihara: Vacuum 51, 369 (1998).

[18] M. Yoshitake and K. Yoshihara: Nihon Kinzoku Gakkaishi 63, 252 (1999) [in

Japanese].
[19] A. Y. Reddy, M. Yoshitake, and K. Yoshihara: Jpn. J. Appl. Phys. 39, 4447 (2000).
[20] M. Yoshitake, Y. Aparna, and K. Yoshihara: Surf. Interface Anal. 30, 337 (2000).
[21] M. Yoshitake, Y. Aparna, and K. Yoshihara: J. Vac. Sci. Technol. A19, 1432 (2001).
[22] http://surfseg.nims.go.jp/
[23] M. Yoshitake: Kinzoku 81, 1075 (2011) [in Japanese].
[24] M. Yoshitake, Y.-R. Aparna, and K. Yoshihara: J. Vac. Sci. Technol. A19, 2612 (2001).
[25] M. Yoshitake: J. Surf. Sci. Soc. Jpn. 34, 340 (2013) [in Japanese].
[26] A.R. Miedema, Zeitschrift fur Metallkunde, 69, H7, 455 (1978).
[27] M. Yoshitake and K. Yoshihara, J. Jpn. Inst. Met. 58, 768 (1994).
[28] R. Boom, F.R. de Boer and A.R. Miedema, J. Less-Common Metals 45, 237 (1976).
[29] R. Boom, F.R. de Boer and A.R. Miedema, J. Less-Common Metals 46, 271 (1976).
[30] A.R. Miedema, F.R. de Boer and R. Boom, J. LessCommon Metals 41, 283 (1975).
[31] A.R. Miedema, F.R. de Boer and R. Boom, J. LessCommon Metals 46, 67 (1976).
[32]
https://www.schoolmykids.com/learn/periodic-table/bulk-modulus-of-all-the-elements
[33] J. Gerkema and A.R. Miedema, Surface Science 124, 351 (1983).

Table 1 List of values used for calculating equations used for the predictions.

	n^(1/3)	V^(2/3)	ϕ	γ	ΔHvap	K
unit		cm^2	V	x10^4 (J/cm^2)	kJ/mol	GPa
				=J/m^2		
Li	0.98	5.5	2.85	0.53	158	11
Be	1.6	2.9	4.2	1.9	320	130
Na	0.82	8.3	2.7	0.26	107	6.3
Mg	1.17	5.8	3.45	0.79	145	45
Al	1.39	4.6	4.2	1.2	327	76
Si	1.5	4.2	4.7	1.29	415	100
K	0.65	12.8	2.25	0.15	90	3.1
Ca	0.91	8.8	2.55	0.49	178	17
Sc	1.27	6.1	3.25	1.2	376	57
Ti	1.47	4.8	3.65	2.05	464	110
V	1.64	4.1	4.25	2.6	511	160
Cr	1.73	3.7	4.65	2.4	395	160
Mn	1.61	3.8	4.45	1.6	283	120
Fe	1.77	3.7	4.93	2.55	413	170
Co	1.75	3.5	5.1	2.55	427	180
Ni	1.75	3.5	5.2	2.45	428	180
Cu	1.47	3.7	4.55	1.85	336	140
Zn	1.32	4.4	4.1	1.02	130	70
Ga	1.31	5.2	4.1	0.83	271	56
Ge	1.37	4.6	4.55	1.03	346	75.8
As	1.44	5.2	4.8	1	301	22
Rb	0.6	14.6	2.1	0.12	82	2.5
Sr	0.84	10.2	2.4	0.43	180	12
Y	1.21	7.3	3.2	1.1	424	41
Zr	1.39	5.8	3.4	1.95	607	51.5
Nb	1.62	4.9	4	2.7	718	170
Mo	1.77	4.4	4.65	2.95	657	230
Tc	1.81	4.2	5.3	3.05	660	281
Ru	1.83	4.1	5.4	3.05	650	220
Rh	1.76	4.1	5.4	2.75	551	380
Pd	1.67	4.3	5.45	2.1	376	180
Ag	1.39	4.7	4.45	1.25	283	100
Cd	1.24	5.5	4.05	0.78	112	42
In	1.17	6.3	3.9	0.69	243	35.3
Sn	1.24	6.4	4.15	0.71	301	58
Sb	1.26	6.6	4.4	0.68	264	42
Cs	0.55	16.8	1.95	0.095	78	1.6
Ba	0.81	11.3	2.32	0.37	183	9.6
Hf	1.43	5.6	3.55	2.2	619	110
Ta	1.63	4.9	4.05	3.05	781	200
W	1.81	4.5	4.8	3.3	848	310
Re	1.86	4.3	5.4	3.65	774	370
Os	1.85	4.2	5.4	3.5	788	462
Ir	1.83	4.2	5.55	3.1	669	320
Pt	1.78	4.4	5.65	2.55	564	230
Au	1.57	4.7	5.15	1.55	368	220
Hg	1.24	5.8	4.2	0.61	60	25
Tl	1.12	6.6	3.9	0.61	182	43
Pb	1.15	6.9	4.1	0.61	196	46
Bi	1.16	7.2	4.15	0.55	210	31
La	1.09	8	3.05	0.9	432	28
Th	1.28	7.3	3.3	-	-	-
U	1.58	5.6	4.05	-	-	-
Pu	1.44	5.2	3.8	-	-	-

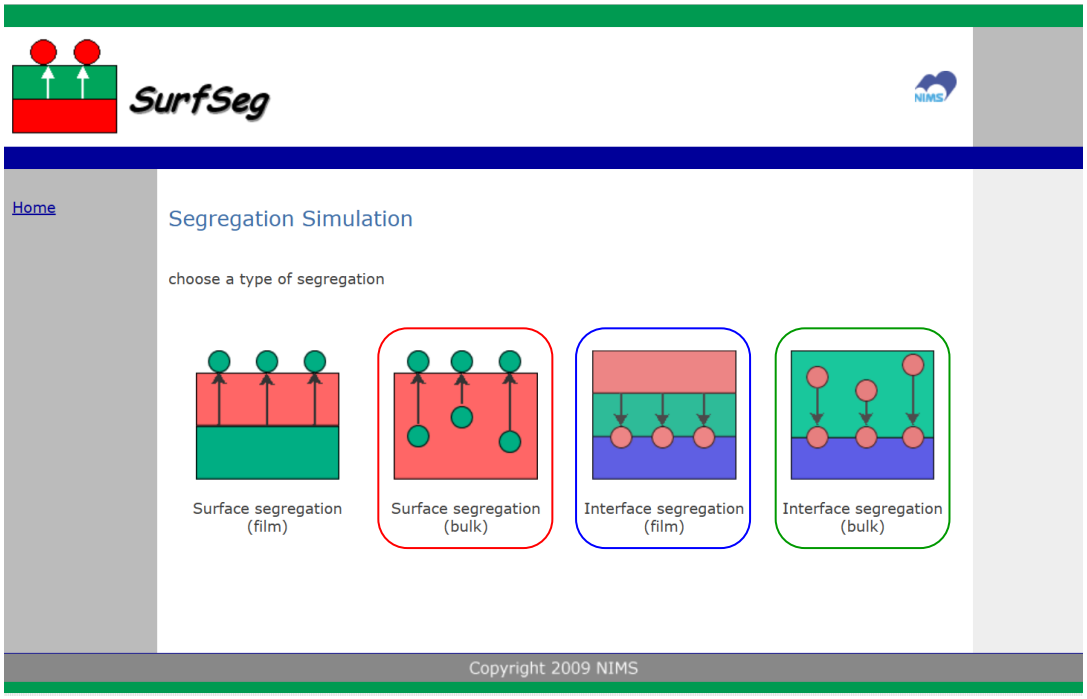


Fig.1 Picture of the dump screen of the newly updated front page of SurfSeg after running, where three red, blue and green enclosures (updated modes) are added to the dump screen.

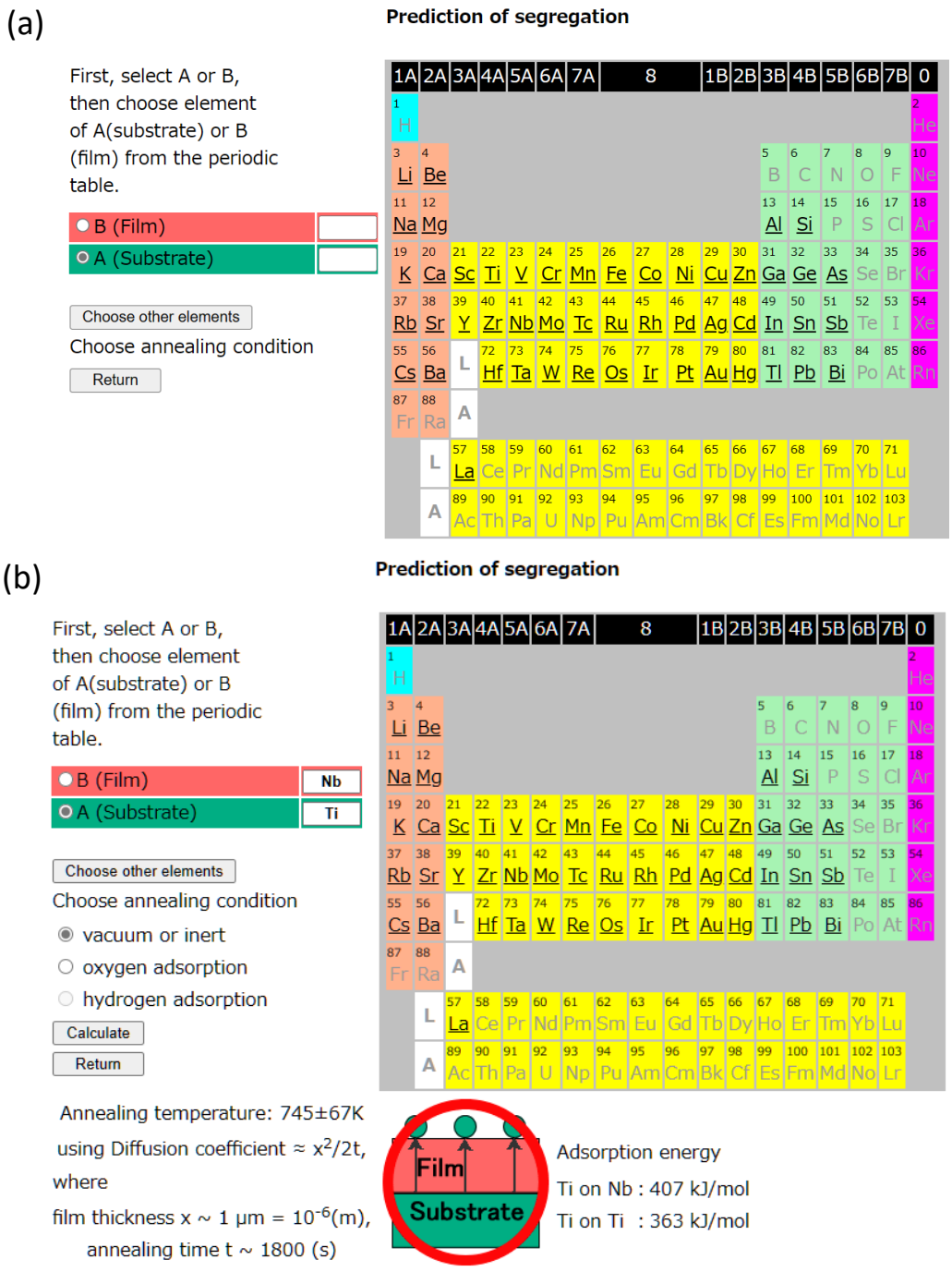
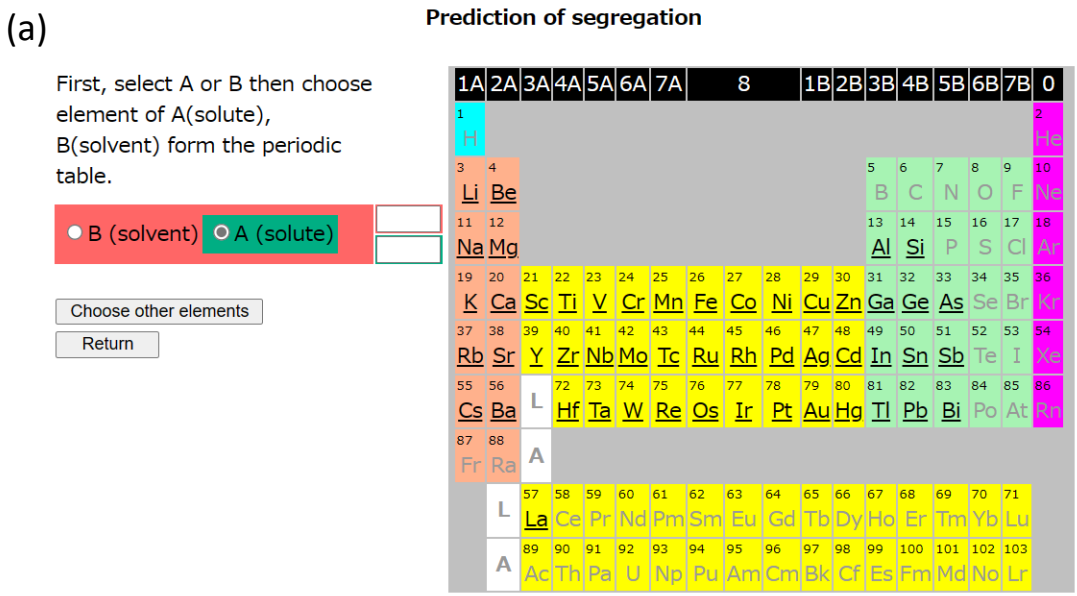
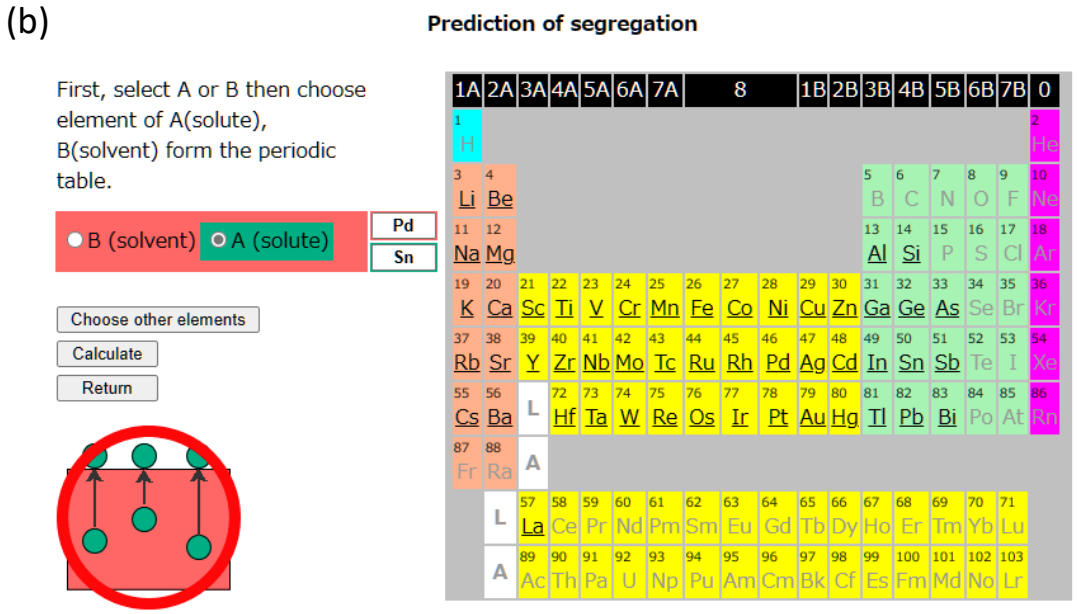


Fig.2 Input screen of elements, the film and the underlayer (noted as substrate) from the right-side periodic table, which appears after "Surface segregation (bulk)" in the front page (Fig. 1) is chosen (a). The screen of prediction result display after choosing annealing condition for segregation prediction and clicking "Calculate" button (b).





$$\Delta H_{seg}^{A} = \Delta H(\text{mix}) + \Delta H(\text{surface}) + \Delta H(\text{strain})$$

$$= -15.924434376 + 47.875 + 8.49$$

$$= 40.441$$

Fig.3 Input screen of a solute element and solvent element from the right-side periodic table, which appears when “Surface segregation (bulk)” in the front page (Fig. 1) is chosen (a). The screen of prediction result display after clicking “Calculate” button (b). Calculated values of three terms (J/mol) used for the prediction are also shown.

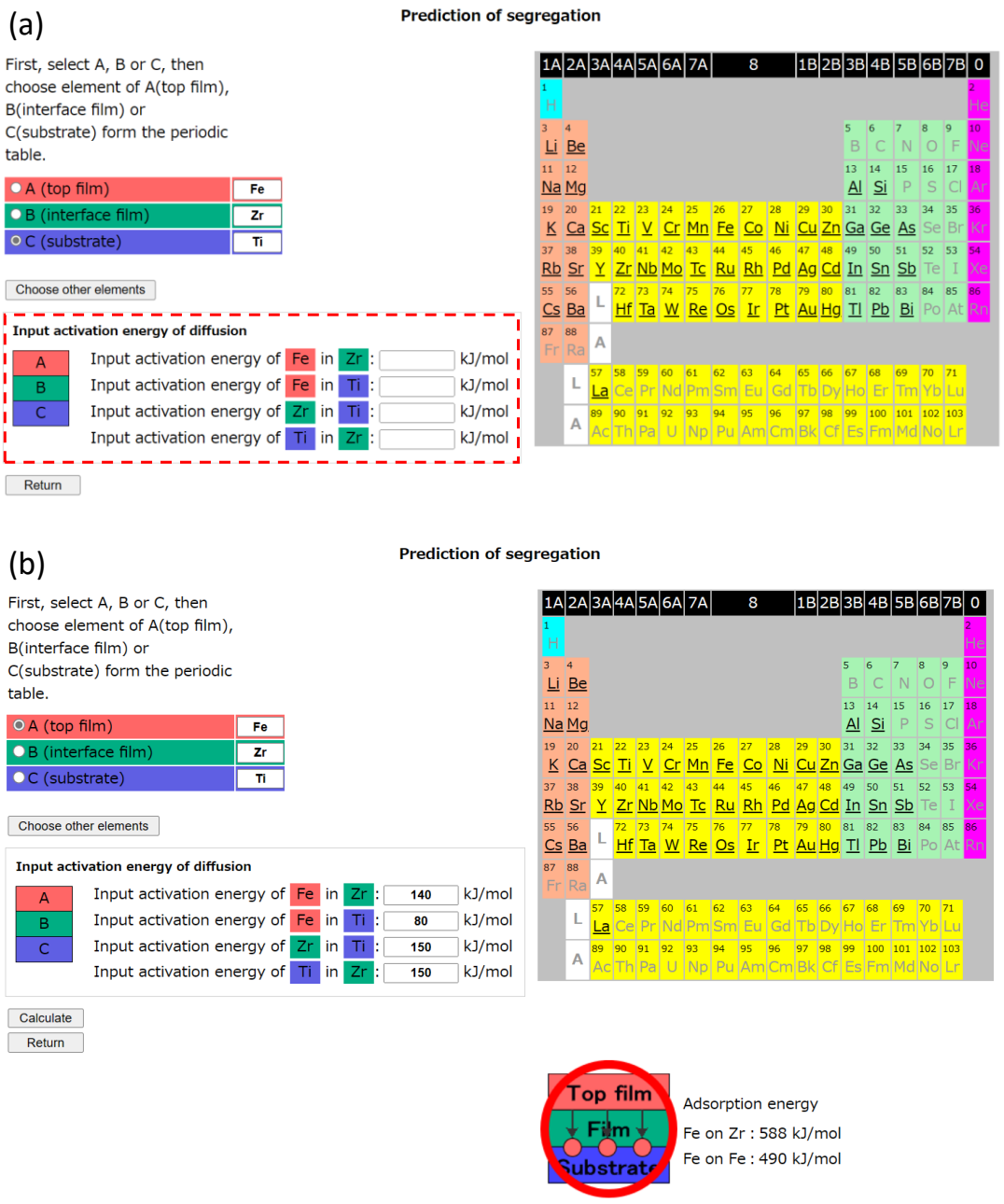


Fig.4 Dump screen for activation energy input, which appears after choosing "Interface segregation (film)" in the front page (Fig. 1) and choosing element A, B and C from the periodic table (a). Screen of the result display after the activation energies input and the click of "Calculate" button (b).

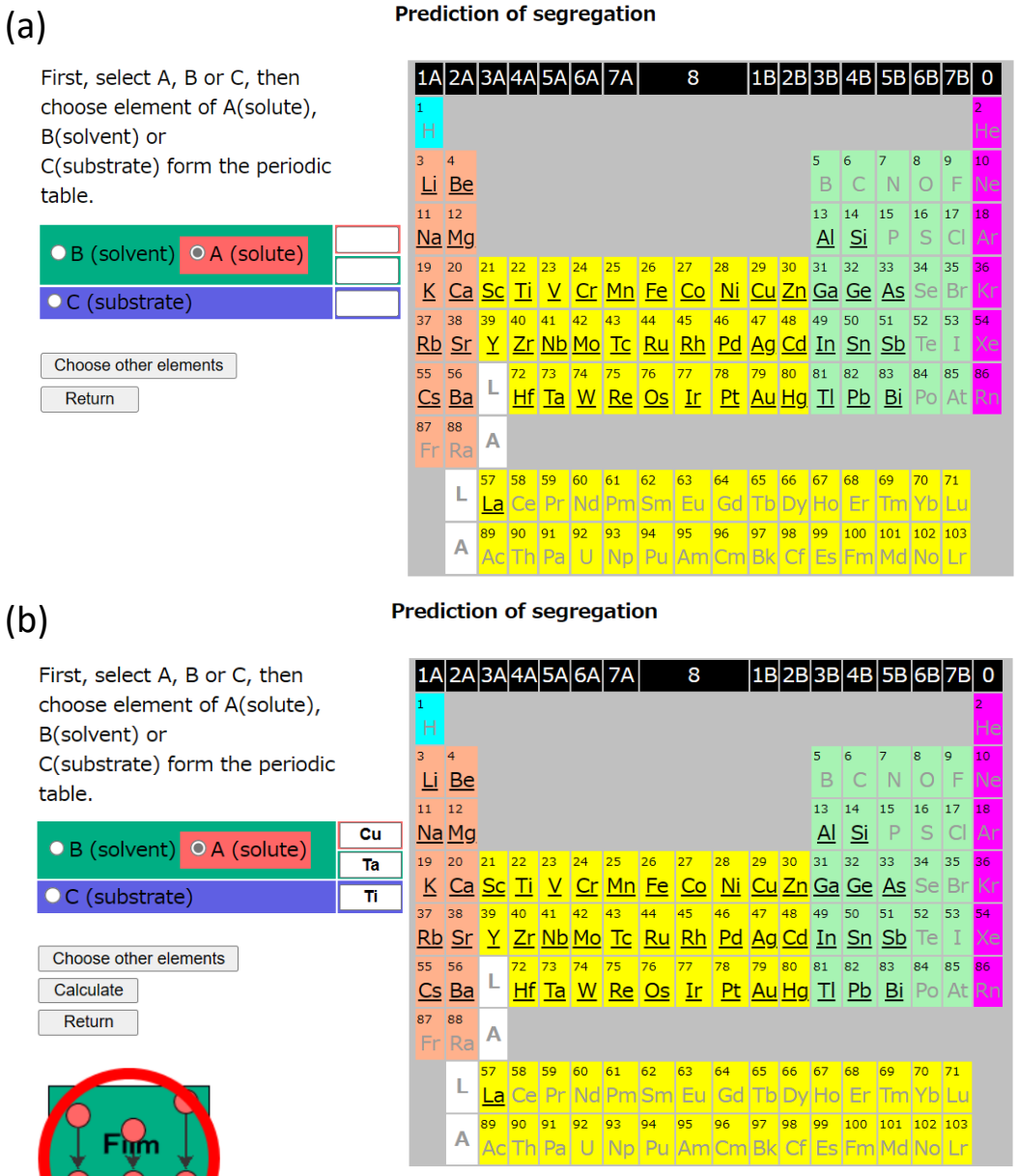


Fig.5 Input screen of element A, B and C from the periodic table after choosing "Interface segregation (bulk)" on the front page (Fig. 1) (a). Screen of the results display after clicking "Calculate" button (b). Calculated values of three terms (J/mol) used for the prediction are also shown.