**Supplementary Materials**

**Forming mechanism of equilibrium and non-equilibrium metallurgical phases in dissimilar materials: Illustrated with aluminum/steel (Al-Fe) joints**

Shun-Li Shanga,\*, Hui Suna, Bo Panb, Adam M. Krajewskia, Yi Wanga, Mihaela Banu,c

Jingjing Lib, Zi-Kui Liua

a Department of Materials Science and Engineering, Pennsylvania State University, University Park, PA 16802, USA

b Department of Industrial and Manufacturing Engineering, Pennsylvania State University, University Park, PA 16802, USA

c Department of Mechanical Engineering, University of Michigan, Ann Arbor, MI 48109, USA

\*E-mail: sus26@psu.edu

Table S 1. Details of DFT calculations together with the predicted equilibrium properties (*V*0, *B*0, *B’*, and ΔH0 with respect to FCC Al and BCC Fe) by Eq. 6. Experimental data in the literature (except ΔH0, *cf.* Figure 3) are also shown when available. The “structures” refer to those used in the Materials Project (mp) database 1, this work, etc. *x*Fe indicates mole fraction of Fe; *C*ij and TC indicate elastic constants and thermochemical properties by Eq. 3, respectively, predicted in the present work (Yes, Y) or not (empty). Atoms and numbers in the parentheses indicate atoms in the supercells and *k*-point meshes used in the DFT, *C*ij, and phonon calculations. Spin MM indicates the spin moment at the equilibrium volume.

|  |  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Name | Structures | Spacegroup | *x*Fe | *C*ij | TC | Atoms (*k*-mesh): DFT/*C*ij | Atoms (*k*-mesh): Phonon  | Spin MM(μB/atom) | *V0*(Å3/atom) | *B*0(GPa) | *B’* | ΔH0 in kJ/mol-atom |
| FCC Al | mp-134 | $$Fm\overbar{3}m$$ | 0.000 | Y | Y | 4 (27×27×27) | 32 (777) | 0.00 | 16.49616.58a | 77.879.4a | 4.43 | 0.00 |
| Al6Fe | mp-570001 | $$Cmcm$$ | 0.143 | Y | Y | 28 (565) | 28 (565) | 0.00 | 15.07315.16b | 105.2 | 4.38 | -19.17 |
| Al9Fe2 | mp-1191778 | $$P2\_{1}/c$$ | 0.182 |  |  | 22 (765) | 88 (223) | 0.00 | 15.353 | 93.6 | 5.49 | -23.23 |
| Al13Fe4 | Ref. 2 | $$C2/m$$ | 0.235 | Y | Y | 102 (122) | 102 (122) | 0.00 | 14.38914.60c | 121.4 | 4.40 | -31.55 |
| Al3Fe | mp-984873 | $$P6\_{3}/mmc$$ | 0.250 |  | Y | 8 (131313) | 64 (444) | 0.10 | 13.658 | 125.1 | 4.48 | -15.28 |
| Al5Fe2 (1) d | This work | $$Cmcm$$ | 0.250 |  | Y | 16 (865) | 64 (324) | 0.03 | 14.004 | 120.4 | 4.81 | -23.95 |
| Al5Fe2 (2) d | This work | $$Cmcm$$ | 0.250 |  | Y | 16 (865) | 64 (324) | 0.03 | 14.005 | 120.3 | 4.73 | -23.95 |
| Al5Fe2 (3) d | This work | $$Cmcm$$ | 0.267 |  | Y | 15 (1286) | 60 (324) | 0.04 | 14.261 | 119.2 | 4.57 | -22.95 |
| Al5Fe2 (4) d | This work | $$Cmcm$$ | 0.267 |  | Y | 15 (1286) | 60 (324) | 0.05 | 14.260 | 119.3 | 4.61 | -22.95 |
| Al5Fe2 (5) d | This work | $$Cmcm$$ | 0.286 | Y | Y | 14 (1065) | 56 (424) | 0.00 | 13.963 | 126.8 | 4.30 | -29.95 |
| Al5Fe2 (6) e | By USPEX | $$C2/m$$ | 0.286 | Y | Y | 14 (1165) | 56 (424) | 0.00 | 13.62613.63 f | 132.4 | 4.23 | -32.22 |
| Al5Fe2 (m1) g | Model1 3 | $$Cmcm$$ | 0.276 |  |  | 29 (565) |  | 0.00 | 13.948 | 125.4 | 4.47 | -30.85 |
| Al5Fe2 (m2) g | Model2 3 | $$Cmcm$$ | 0.286 |  |  | 28 (565) |  | 0.00 | 14.426 | 120.1 | 4.25 | -28.80 |
| Al5Fe2 (m3) g | Model3 3 | $$Cmcm$$ | 0.286 |  |  | 14 (7812) |  | 0.00 | 14.298 | 122.4 | 4.60 | -23.99 |
| Al5Fe2 (m5) g | Model5 3 | $$Cmcm$$ | 0.286 |  |  | 28 (565) |  | 0.00 | 14.360 | 122.9 | 4.24 | -27.38 |
| Al2Fe (MoSi2)  | MoSi2-type(mp-2592) | $$I4/mmm$$ | 0.333 | Y | Y | 6 (20207) | 54 (555) | 0.00 | 12.80313.01h | 147.2 | 4.42 | -34.63 |
| Al2Fe (1)i | This work | $$P\overbar{1}$$ | 0.333 | Y | Y | 57 (432) | 57 (432) | 0.27 | 13.62013.83j | 125.6 | 4.82 | -31.36 |
| Al2Fe (2) i | This work | $$P\overbar{1}$$ | 0.342 | Y | Y | 38 (543) | 38 (543) | 0.29 | 13.57813.83j | 125.6 | 5.11 | -31.09 |
| Al12Fe7 | mp-1214901 | $$P\overbar{1}$$ | 0.368 |  | Y | 19 (864) | 76 (222) | 0.44 | 13.531 | 123.8 | 4.14 | -30.72 |
| Al8Fe5 (D82) | mp-1193259 | $$I\overbar{4}3m$$ | 0.385 | Y | Y | 52 (555) | 52 (555) | 0.59 | 13.18313.906k | 138.0 | 4.14 | -27.30 |
| AlFe (B2) | mp-2658 | $$Pm\overbar{3}m$$ | 0.500 | Y | Y | 2 (313131) | 54 (444) | 0.35 | 11.89612.317k | 174.3 | 4.43 | -31.79 |
| AlFe (Hex) | mp-985578 | $$P6/mmm$$ | 0.500 |  | Y | 2 (282813) | 36 (554) | 1.21 | 14.938 | 90.7 | 4.59 | 45.17 |
| AlFe2 (Hex) | mp-985579 | $$P6/mmm$$ | 0.667 |  | Y | 3 (171724) | 36 (555) | 1.48 | 12.654 | 143.9 | 3.56 | -13.03 |
| AlFe2 (Cubic) | mp-31184 | $$Fd\overbar{3}m$$ | 0.667 |  | Y | 24 (777) | 192 (111) | 1.10 | 12.559 | 129.6 | 5.26 | -9.85 |
| AlFe3 (L12) | mp-1183162 | $$Pm\overbar{3}m$$ | 0.750 | Y | Y | 4 (212121) | 108 (222) | 1.72 | 12.206 | 169.1 | 3.89 | -19.10 |
| AlFe3 (D03) | mp-2018 | $$Fm\overbar{3}m$$ | 0.750 | Y | Y | 16 (999) | 128 (111) | 1.48 | 11.86412.14m | 164.1 | 5.74 | -19.02 |
| AlFe3 (Orth) | mp-1228919 | $$Cmmm$$ | 0.750 |  | Y | 8 (16126) | 48 (333) | 1.60 | 12.139 | 149.9 | 5.38 | -8.29 |
| AlFe4 | mp-1228952 | $$Fmmm$$ | 0.800 |  | Y | 20 (1292) | 120 (231) | 1.76 | 12.047 | 157.4 | 4.61 | -6.09 |
| BCC Fe | mp-13 | $$Im\overbar{3}m$$ | 1.000 | Y | Y | 2 (313131) | 54 (555) | 2.23 | 11.43811.84a | 188.5173.1a | 5.89 | 0.00 |

a Experimental data of pure elements collected by Shang et al. 4; where the bulk moduli were calculated from elastic constants *C*ij at 0 K or 4.2 K.

b Measured data 5.

c Determined by single crystal X-ray diffraction 2.

d All possible Al5Fe2 configurations were generated by the ATAT code 6 using the 24-atom supercell with Al partially in Wyckoff sites 4b (occupation of 0.32) and 8f (occupation of 0.24) of space group $Cmcm$ 7. Only one or two of the low energy configurations were used herein after DFT calculations for each composition.

e Starting from the configuration of Al5Fe2 (5), the USPEX method 8 was used to find the lowest energy configuration; see the relaxed structure in VASP POSCAR formation in **Table S 2**.

f Measured data of Al5Fe2 7.

g Suggested low energy configurations of Al5Fe2 by Vinokur et al. 3.

h Measured data of tetragonal Al2Fe which was synthesized at 7.5 GPa and 873 K 9.

i Based on one of the Wyckoff sites, 2i of $P\overbar{1}$, is occupied by both Fe (occupation of 0.705) and Al (occupation of 0.705) 10, the ATAT code 6 in terms of the 38- and 57-atom supercells of Al2Fe was used to build all possible configurations, and only the low configurations were used herein.

j Measured data of Al2Fe 10.

k Measured data at 1120 °C for Al8Fe5 and room temperature for AlFe (B2) 11.

m Based on the measured lattice parameter of 5.791Å 12.

Table S 2. Predicted low energy configuration of Al5Fe2 by the USPEX method [48]; showing in the POSCAR format used by VASP.

|  |
| --- |
| Al5Fe2 obtained from USPEX  1.00000000000000 3.9856825100556255 0.0180139195117352 -0.0119959383759500 -2.0223150583039149 6.3609873531164363 -0.1236273035337276 0.0309977658533041 -1.8398680209679523 7.4966967430280356 Al Fe 10 4Direct 0.3957394519960999 0.4091982017268107 0.2399459199414556 0.9778201474046904 0.5733094819459010 0.7894016211923789 0.6007990938587022 0.8193711169069814 0.7272403546970154 0.3741398967557212 0.3659567715349421 0.8905644993630734 0.7931962793206077 0.2041882284349636 0.4876203816651489 0.7853874596828249 0.1884574927561469 0.0291626674869105 0.9931096244929684 0.6040178111125385 0.4407466632656956 0.5855374362993363 0.7886233363379547 0.0758845690733351 0.2043975531648467 0.0266110548503117 0.6260544053994812 0.1829370190242693 0.9835634314595856 0.2767080212576478 0.4026563358045122 0.4230849778281406 0.5685866454611316 0.9815066050839097 0.5805820997532304 0.1100919446767003 0.5971753624837085 0.8120861753909097 0.4065897199004853 0.1759887346277932 0.9696118199616005 0.9480645866195526 |

Table S 3. Predicted elastic properties (GPa or dimensionless) of the Al-Fe IMCs, including single crystal elastic constants *C*ij and the calculated aggregate properties in Hill approach (H) 13 of bulk modulus (*B*H), shear modulus (*G*H), *B*H/*G*H ratio, Poisson’s ratio (νH), and anisotropy index *A*U (*A*U = 0 for locally isotropic single crystals); see details of the methodology by Shang et al.4 It shows that Al8Fe5 is very close to an isotropic crystal, while AlFe3 (L12) shows extremely anisotropic.

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Materials | *C*ij matrix (only the upper values) | *B*H | *G*H | *B*H/*G*H | νH | *A*U |
| Al(FCC, Cubic)a | $$\left[\begin{matrix}98.3&67.6&67.6&0&0&0\\&98.3&67.6&0&0&0\\&&98.3&0&0&0\\&&&25.7&0&0\\&&&&25.7&0\\&&&&&25.7\end{matrix}\right]$$ | 77.877.8b | 20.9 | 3.728 | 0.377 | 0.329 |
| Al6Fe(Orth.) | $$\left[\begin{matrix}240.4&43.3&68.8&0&0&0\\&185.2&82.8&0&0&0\\&&149.3&0&0&0\\&&&56.8&0&0\\&&&&32.6&0\\&&&&&65.7\end{matrix}\right]$$ | 106.6105.2b | 53.0 | 2.013 | 0.287 | 0.694 |
| Al13Fe4(Mono.)  | $$\left[\begin{matrix}241.6&93.4&65.8&0&-1.7&0\\&216.9&51.3&0&10.2&0\\&&254.3&0&-7.6&0\\&&&69.2&0&1.0\\&&&&78.4&0\\&&&&&80.5\end{matrix}\right]$$ | 125.6121.4b | 76.7 | 1.639 | 0.247 | 0.163 |
| Al5Fe2 (5)(Based on orth.) | $$\left[\begin{matrix}220.6&82.5&100.0&0&0&0\\&237.3&48.4&0&0&0\\&&277.3&0&0&0\\&&&83.6&0&0\\&&&&102.2&0\\&&&&&92.6\end{matrix}\right]$$ | 132.6126.8b | 87.8 | 1.509 | 0.229 | 0.177 |
| Al5Fe2 (6)(by USPEX, mono.) | $$\left[\begin{matrix}275.9&107.0&64.7&17.5&-6.5&0\\&253.8&47.3&0&-7.2&0\\&&274.4&-21.6&-6.6&0\\&&&53.5&0&0\\&&&&79.2&-7.0\\&&&&&116.2\end{matrix}\right]$$ | 137.0132.4b | 83.7 | 1.638 | 0.247 | 0.664 |
| Al2Fe (MoSi2-type,tetr.)  | $$\left[\begin{matrix}274.5&89.9&110.6&0&0&0\\&274.5&110.6&0&0&0\\&&223.1&0&0&0\\&&&168.9&0&0\\&&&&168.9&0\\&&&&&130.7\end{matrix}\right]$$ | 154.7147.2b | 115.8 | 1.336 | 0.201 | 0.812 |
| Al2Fe (1)(Triclinic) | $$\left[\begin{matrix}243.9&79.1&72.4&0.0&-13.2&0.0\\&258.7&85.5&4.6&8.9&2.0\\&&256.8&-8.4&10.1&1.6\\&&&77.4&11.7&-4.2\\&&&&85.1&-4.1\\&&&&&85.3\end{matrix}\right]$$ | 136.9125.6b | 83.3 | 1.643 | 0.247 | 0.134 |
| Al2Fe (2)(Triclinic) | $$\left[\begin{matrix}241.6&75.6&72.5&0.0&-14.3&0.6\\&248.4&88.3&6.9&9.1&1.6\\&&247.1&-10.1&7.1&5.5\\&&&75.3&11.5&-4.9\\&&&&83.2&-3.6\\&&&&&79.5\end{matrix}\right]$$ | 134.3125.6b | 79.8 | 1.682 | 0.252 | 0.147 |
| Al8Fe5 (D82, cubic) | $$\left[\begin{matrix}241.1&92.1&92.1&0&0&0\\&241.1&92.1&0&0&0\\&&241.1&0&0&0\\&&&72.6&0&0\\&&&&72.6&0\\&&&&&72.6\end{matrix}\right]$$ | 141.8138.0b | 73.3 | 1.933 | 0.279 | 0.001 |
| AlFe (B2, cubic) | $$\left[\begin{matrix}265.6&143.3&143.3&0&0&0\\&265.6&143.3&0&0&0\\&&265.6&0&0&0\\&&&145.0&0&0\\&&&&145.0&0\\&&&&&145.0\end{matrix}\right]$$ | 184.0174.3b | 93.6 | 1.795 | 0.265 | 0.951 |
| AlFe3 (L12, cubic | $$\left[\begin{matrix}204.5&180.1&180.1&0&0&0\\&204.5&180.1&0&0&0\\&&204.5&0&0&0\\&&&135.5&0&0\\&&&&135.5&0\\&&&&&135.5\end{matrix}\right]$$ | 188.3169.1b | 56.5 | 3.330 | 0.367 | 11.040 |
| AlFe3 (D03, cubic) | $$\left[\begin{matrix}240.3&175.7&175.7&0&0&0\\&240.3&175.7&0&0&0\\&&240.3&0&0&0\\&&&147.4&0&0\\&&&&147.4&0\\&&&&&147.4\end{matrix}\right]$$ | 197.2164.1b | 81.0 | 2.433 | 0.321 | 3.343 |
| Fe(BCC, cubic)a | $$\left[\begin{matrix}260.7&140.5&140.5&0&0&0\\&260.7&140.5&0&0&0\\&&260.7&0&0&0\\&&&89.8&0&0\\&&&&89.8&0\\&&&&&89.8\end{matrix}\right]$$ | 180.6173.1b | 76.5 | 2.362 | 0.315 | 0.196 |

aMeasured elastic constants for Al at 0 K (*C*11 =114.3, *C*12 = 61.9 GPa, and *C*44 = 31.6 GPa) and Fe at 4.2 K (*C*11 =243.1, *C*12 = 138.1 GPa, and *C*44 = 121.9 GPa) 13.

b Predicted value by EOS fitting, see **Table S 1**.

**References of Supplementary Material:**

1. Jain, A. *et al.* Commentary: The Materials Project: A materials genome approach to accelerating materials innovation. *APL Mater.* **1**, 011002 (2013).

2. Popčević, P. *et al.* Anisotropic physical properties of the Al13Fe4 complex intermetallic and its ternary derivative Al13(Fe,Ni)4. *Phys. Rev. B* **81**, 184203 (2010).

3. Vinokur, A. I., Hilleke, K. P. & Fredrickson, D. C. Principles of weakly ordered domains in intermetallics: The cooperative effects of atomic packing and electronics in Fe2Al5. *Acta Crystallogr. Sect. A Found. Adv.* **75**, 297–306 (2019).

4. Shang, S. L. *et al.* First-principles calculations of pure elements: Equations of state and elastic stiffness constants. *Comput. Mater. Sci.* **48**, 813–826 (2010).

5. Aliravci, C. A. & Pekgüleryüz, M. Ö. Calculation of phase diagrams for the metastable Al-Fe phases forming in direct-chill (DC)-cast aluminum alloy ingots. *Calphad* **22**, 147–155 (1998).

6. van de Walle, A. *et al.* Efficient stochastic generation of special quasirandom structures. *Calphad* **42**, 13–18 (2013).

7. Burkhardt, U., Grin, Y., Ellner, M., Peters, K. & IUCr. Structure refinement of the iron–aluminium phase with the approximate composition Fe2Al5. *Acta Crystallogr. Sect. B Struct. Sci.* **50**, 313–316 (1994).

8. Lyakhov, A. O., Oganov, A. R., Stokes, H. T. & Zhu, Q. New developments in evolutionary structure prediction algorithm USPEX. *Comput. Phys. Commun.* **184**, 1172–1182 (2013).

9. Tobita, K. *et al.* Phase stability and thermoelectric properties of semiconductor-like tetragonal FeAl2. *Sci. Technol. Adv. Mater.* **20**, 937–948 (2019).

10. Chumak, I., Richter, K. W. & Ehrenberg, H. Redetermination of iron dialuminide, FeAl 2. *Acta Crystallogr. Sect. C Cryst. Struct. Commun.* **66**, i87–i88 (2010).

11. Stein, F., Vogel, S. C., Eumann, M. & Palm, M. Determination of the crystal structure of the ε phase in the Fe-Al system by high-temperature neutron diffraction. *Intermetallics* **18**, 150–156 (2010).

12. Nishino, Y. *et al.* Semiconductorlike Behavior of Electrical Resistivity in Heusler-type Fe2VAl Compound. *Phys. Rev. Lett.* **79**, 1909–1912 (1997).

13. Simmons, G. & Wang, H. *Single crystal elastic constants and calculated aggregate properties: A handbook*. (M.I.T. Press, 1971).