Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Towards Tuning the Modality of Hierarchical Macro-Nanoporous Metals by Controlling the Dealloying Kinetics of Close-to-Eutectic Alloys

Supplementary Information

Alex Aziz[a], Javier Carrasco[a], and Yaroslav Grosu[a,b,*]

a. Centre for Cooperative Research on Alternative Energies (CIC energiGUNE), Basque Research and Technology Alliance (BRTA), Alava Technology Park, Albert Einstein 48, 01510 Vitoria-Gasteiz, Spain, Email: ygrosu@cicenergigune.com

b. Institute of Chemistry, University of Silesia in Katowice, 40-006 Katowice, Poland

Table S1. Structural parameters, experiment versus DFT results at the PBE-D2 level of theory

	Experiment					Theory		
	Space group	*a* (Å)	*b* (Å)	*c* (Å)	Ref	*a* (Å)	*b* (Å)	*c* (Å)
Cu	Fm-3m	3.5942(32)			[1]	3.6264		
Mg	P63/mmc	3.2093		5.2103	[2]	3.1067		4.9679
Cu_2Mg	Fd-3m	7.0210			[3]	7.0157		
$CuMg_2$	Fddd	5.2622(3)	9.0207(6)	18.310(1)	[4]	5.1975	8.9120	18.3005
CuMgZn *	Fd-3m	7.1690			[5]	7.1305		
	$P4_122$					5.0399		7.1364
$Mg_{21}Zn_{25}$	R-3C	25.7758		8.7624	[6]	25.2428		8.5316

*Symmetry of the lowest energy substituted configuration is reduced to the tetragonal $P4_122$ space group. However, simulations were performed without imposing symmetry, keeping the structure consistent with the parent unit-cell.

Table S2. Energy per atom of the reoriented bulk unit cell for Cu and various Mg surfaces. The energy of the conventional bulk unit-cell was calculated to be -4.145 and -1.831 eV per atom for Cu and Mg respectfully at the PBE-D2 level of theory

Cu		Mg			
Surface	Energy eV / atom	Surface	Energy eV / atom	Surface	Energy eV / atom
(1, 0, 0)	-4.145	(0, 0, 0, 1)	-1.831	(3, 1, -4, 0)	-1.831
(1, 1, 0)	-4.145	(1, 0, -1, 1)	-1.831	(3, 1, -4, 1)	-1.830
(1, 1, 1)	-4.145	(1, 0, -1, 3)	-1.831	(3, 1, -4, 2)	-1.830
(2, 1, 0)	-4.145	(1, 0, -1, 0)	-1.831	(3, 1, -4, 3)	-1.831
(2, 1, 1)	-4.145	(1, 0, -1, 2)	-1.831	(3, 2, -5, 0)	-1.831
(2, 2, 1)	-4.145	(1, 0, -1, 3)	-1.831	(3, 2, -5, 1)	-1.831
(3, 1, 0)	-4.145	(1, 1, -2, 0)	-1.831	(3, 2, -5, 2)	-1.831
(3, 1, 1)	-4.145	(1, 1, -2, 1)	-1.831	(3, 2, -5, 3)	-1.831
(3, 2, 0)	-4.144	(2, 0, -2, 1)	-1.831	(3, 3, -6, 1)	-1.831
(3, 2, 1)	-4.144	(2, 0, -2, 3)	-1.831	(3, 3, -6, 2)	-1.830
(3, 2, 2)	-4.144	(2, -1, -1, 3)	-1.831	(2, -1, -1, 3)	-1.831
(3, 3, 1)	-4.144	(2, -1, -1, 2)	-1.831	(3, -1, -2, 3)	-1.831
(3, 3, 2)	-4.144	(2, 2, -4, 1)	-1.831	(3, -1, -2, 0)	-1.831
		(2, 2, -4, 3)	-1.831	(3, -1, -2, 1)	-1.830
		(3, 0, -3, 1)	-1.831	(2, -1, -1, 2)	-1.831
		(3, 0, -3, 2)	-1.831	(3, -1, -2, 2)	-1.830

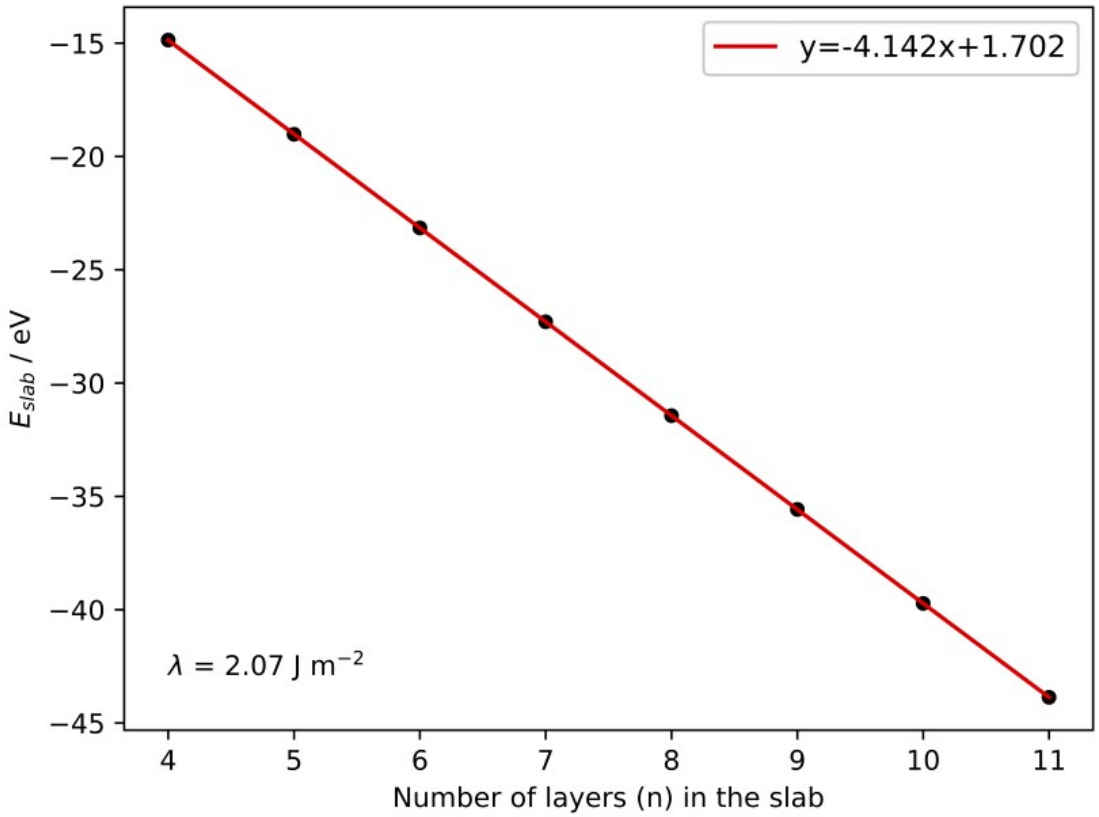

Fig. S1. Convergence of the Cu 100 surface with the linear fitting method. The bulk energy of -4.142 eV is calculated as the gradient of the line and within 3 meV per atom to that of the bulk energy using a dense *k*-mesh. The surface energy is within 0.03 J m^{-2} compared to that obtained using the conventional bulk unit-cell.

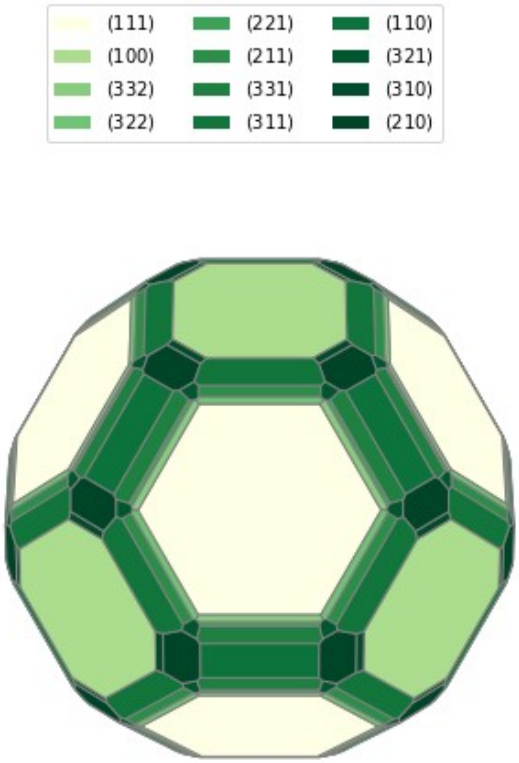

Fig. S2. Calculated Wulff shape for Cu up to a maximum Miller index of three. Generated using Pymatgen.[7]

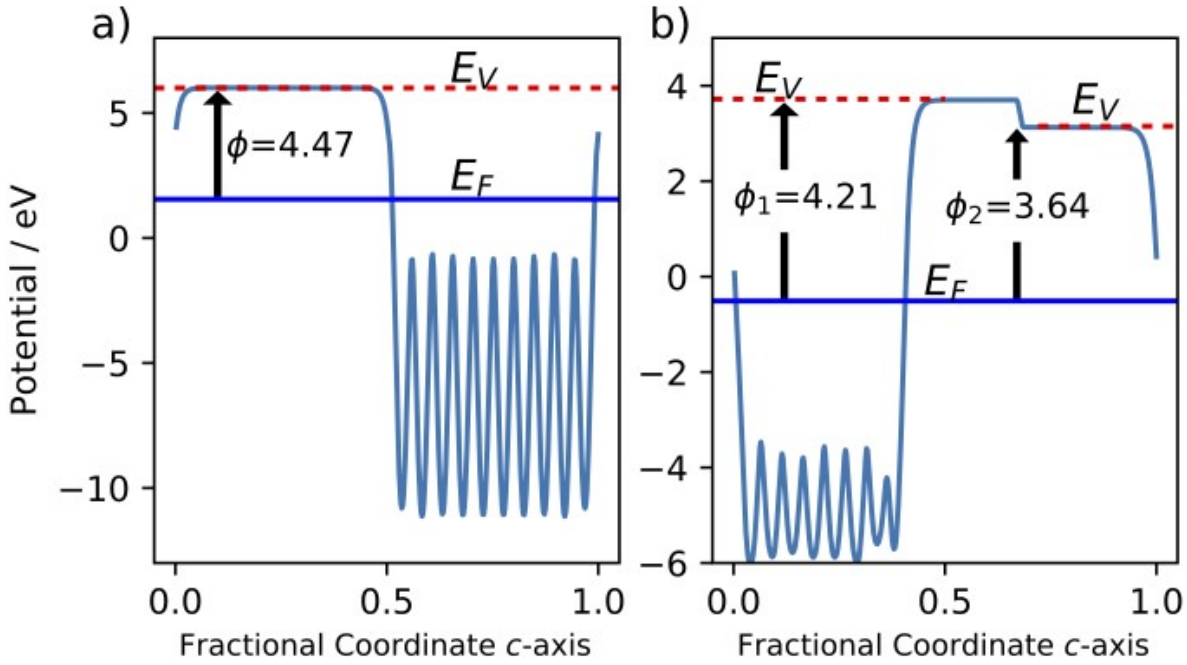

Fig. S3. Planar-averaged electrostatic potential of a) the Cu (100) surface and b) the CuMgZn (100) surface showing 2 work functions due to its asymmetric termination. Cu Zn termination exhibits a workfunction of 4.21 eV and Cu Mg termination exhibits a workfunction of 3.64 eV.

References

(1) Shkvarina, E. G.; Titov, A. A.; Shkvarin, A. S.; Plaisier, J. R.; Gigli, L.; Titov, A. N. Thermal Stability of the Layered Modification of $Cu_{0.5}ZrTe_2$ in the Temperature Range 25–900 °C. *Acta Crystallogr. Sect. C Struct. Chem.* **2018**, *74* (9), 1020–1025. https://doi.org/10.1107/S2053229618009841.

(2) Straumanis, M. E. The Precision Determination of Lattice Constants by the Powder and Rotating Crystal Methods and Applications. *J. Appl. Phys.* **1949**, *20* (8), 726–734. https://doi.org/10.1063/1.1698520.

(3) Friauf, J. B. The Crystal Structures of Two Intermetallic Compounds. *J. Am. Chem. Soc.* **1927**, *49* (12), 3107–3114. https://doi.org/10.1021/ja01411a017.

(4) Braga, M. H.; Ferreira, J. J. A.; Siewenie, J.; Proffen, T.; Vogel, S. C.; Daemen, L. L. Neutron Powder Diffraction and First-Principles Computational Studies of $CuLi_xMg_{2-x}$ ($X\cong0.08$), $CuMg_2$, and Cu_2Mg. *J. Solid State Chem.* **2010**, *183* (1), 10–19. https://doi.org/https://doi.org/10.1016/j.jssc.2009.09.010.

(5) Ellner, M.; Predel, B. Neutronenbeugungsuntersuchungen an Ternären Laves-Phasen Vom $MgCu_2$-Typ. *J. Solid State Chem.* **1979**, *30* (2), 209–221. https://doi.org/10.1016/0022-4596(79)90103-8.

(6) Černý, R.; Renaudin, G. The Intermetallic Compound Mg21Zn25. *Acta Crystallogr. Sect. C* **2002**, *58* (11), i154–i155. https://doi.org/https://doi.org/10.1107/S0108270102018103.

(7) Ong, S. P.; Richards, W. D.; Jain, A.; Hautier, G.; Kocher, M.; Cholia, S.; Gunter, D.; Chevrier, V. L.; Persson, K. A.; Ceder, G. Python Materials Genomics (Pymatgen): A Robust, Open-Source Python Library for Materials Analysis. *Comput. Mater. Sci.* **2013**, *68*, 314–319. https://doi.org/10.1016/j.commatsci.2012.10.028.