Supplementary Information

Determination of Bulk and Surface Atomic Arrangement in Ni-Zn Gamma Brass Phase at Different Ni to Zn Ratios

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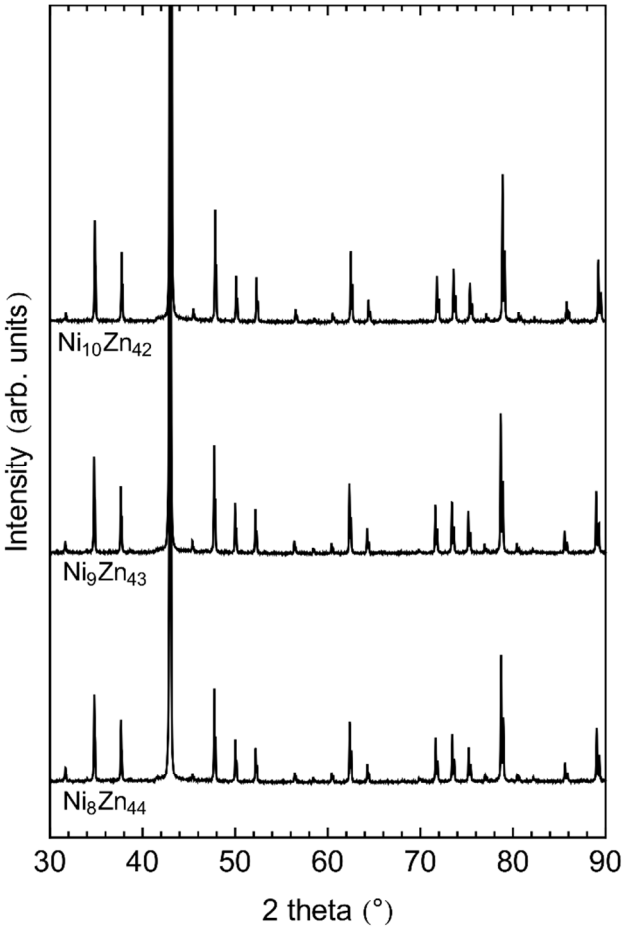

Figure S1. Powder X-ray diffraction patterns for annealed (500°C, 7 days) Ni_8Zn_{44}, Ni_9Zn_{43}, and $Ni_{10}Zn_{42}$.

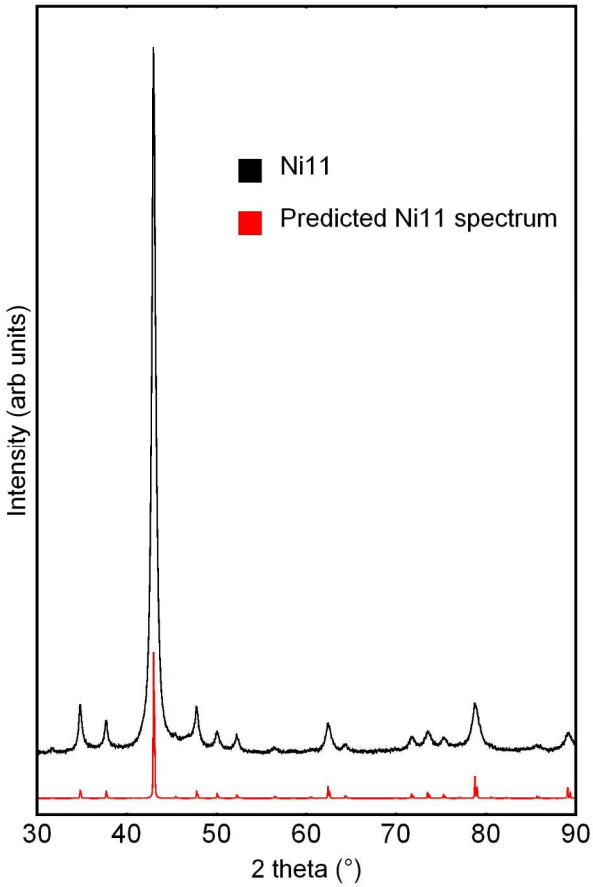

Figure S2. XRD spectrum of as-prepared $Ni_{11}Zn_{41}$.

Table S1. Chemical composition of Ni-Zn γ-brass samples.

Nominal Composition	ICP Determined Composition
Ni_8Zn_{44}	$Ni_{8\pm0.09}Zn_{44\pm0.09}$
Ni_9Zn_{43}	$Ni_{9.2\pm0.13}Zn_{42.8\pm0.13}$
$Ni_{10}Zn_{42}$	$Ni_{10\pm0.14}Zn_{42\pm0.14}$
$Ni_{11}Zn_{41}$	$Ni_{10.8\pm0.04}Zn_{41.2\pm0.04}$

S1. Details of the Rietveld Refinement of Neutron Diffraction Data

In order to verify the location of Ni atoms in the Ni_8Zn_{44} structure, the neutron diffraction data were refined with four different models, each placing the Ni in one of the four sites in the unit cell. For the purpose of this comparison, the occupancies (SOFs) were fixed to match the nominal composition, while other atomic parameters were allowed to freely refine. The results, presented in Table S2 clearly indicate that the Ni prefers the OT site, as the goodness of fit is significantly better than if the Ni is located in any other site. As a further check, the Ni occupancy was then allowed to refine, as shown in Table S3. With the Ni placed on the OT site, the Ni occupancy refined to a value near 1, resulting in an overall composition consistent with that determined by ICP (Table S1). With the Ni placed in any other site, the Ni occupancy refined to abnormally low values, resulting in overall compositions that are far from the experimentally determined values.

Having located the initial eight Ni atoms on the OT site, the location of the additional Ni atoms in Ni_9Zn_{43} and $Ni_{10}Zn_{42}$ was determined by further refinements of the neutron diffraction data with three different models, one each placing the additional Ni in each of the IT, OH or CO sites. As before, the occupancies (SOFs) were fixed to match the nominal composition, while other atomic parameters were allowed to freely refine. For both compositions, the results indicate that the additional Ni prefers the OH site, as the best fits to the experimental data are obtained with that model (Tables S4 and S6). The difference is subtler than with the Ni_8Zn_{44} refinements, which is as expected, since changing the placement of only 1 or 2 atoms will have less of an effect on a diffraction pattern than changing the placement of 8 atoms. To further verify this finding, the Ni occupancy was then allowed to refine, as shown in Tables S5 and S7 constraining the total occupancy of the Ni/Zn shared site to be 1. For both the Ni_9Zn_{43} and $Ni_{10}Zn_{42}$ data, the Ni occupancies refined to effectively zero when placed on the IT or CO site, and the resulting overall compositions are far from the values determined by ICP. With the additional Ni placed on the OH site, however, the refined Ni occupancies are reasonable, and the resulting overall compositions are much closer to the experimentally determined values.

Table S2. Rietveld refinement residuals for Ni_8Zn_{44} with compositions fixed at nominal amount.

Ni Site	χ^2	R_{wp}	$R_{F\hat{}2}$
OT	2.917	0.0357	0.1779
IT	23.62	0.1016	0.3514
OH	7.293	0.0565	0.2464
CO	12.67	0.0744	0.2687

Table S3. Rietveld refinement of SOF of Ni in Ni_8Zn_{44} with all other SOF=1 (Zn).

Ni Site	χ^2	Ni SOF	Refined Composition
OT	2.915	0.98±0.01	$Ni_{7.9}Zn_{44}$
IT	6.642	0.391±0.006	$Ni_{3.1}Zn_{44}$
OH	7.125	0.554±0.009	$Ni_{6.7}Zn_{44}$
CO	5.931	0.019±0.004	$Ni_{0.46}Zn_{44}$

Table S4. Rietveld refinement residuals for Ni_9Zn_{43} while keeping compositions fixed at the nominal amount.

Excess Ni Site	χ^2	R_{wp}	$R_{F\hat{}2}$
IT	5.707	0.0350	0.1333
OH	5.401	0.0340	0.1295
CO	5.595	0.0346	0.1315

Table S5. Rietveld refinement of SOF of shared site in Ni_9Zn_{43} with all other SOF=1 (Zn).

Excess Ni Site	χ^2	**Ni SOF**	**Refined Composition**
IT	5.533	-0.02±0.01	$Ni_{7.9}Zn_{44.1}$
OH	5.380	0.14±0.02	$Ni_{9.7}Zn_{44.3}$
CO	5.931	-0.03±0.01	$Ni_{7.3}Zn_{44.7}$

Table S6. Rietveld refinement residuals for $Ni_{10}Zn_{42}$ while keeping compositions fixed at the nominal amount.

Excess Ni Site	χ^2	R_{wp}	$R_{F\hat{}2}$
IT	2.548	0.0332	0.1870
OH	2.303	0.0316	0.1766
CO	2.440	0.0325	0.1832

Table S7. Rietveld refinement of SOF of shared site in $Ni_{10}Zn_{42}$ with all other SOF=1 (Zn).

Excess Ni Site	χ^2	**Ni SOF**	**Refined Composition**
IT	2.387	-0.01±0.02	$Ni_{7.9}Zn_{44.1}$
OH	2.301	0.21±0.02	$Ni_{10.5}Zn_{41.5}$
CO	2.379	-0.04±0.01	$Ni_{6.9}Zn_{45.1}$

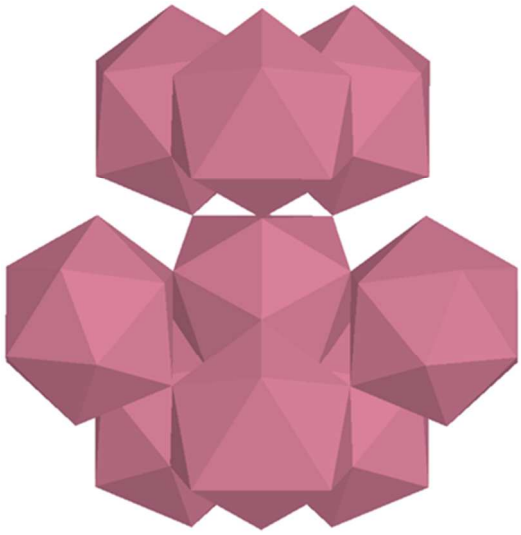

Figure S3. Stacking pattern of icosahedrons centered on the OT positions in the structure of Ni_8Zn_{44}. Ni atoms are at the centers and Zn atoms are at the vertices of the icosahedrons. Each icosahedron shares 6 vertices and 3 faces with neighboring icosahedra.

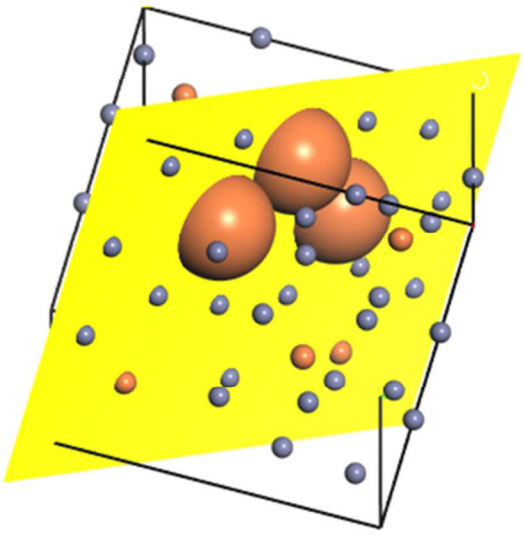

Figure S4. The trimer containing (1 -1 0) surface in the Ni_9Zn_{43} unit cell is marked in yellow. The Ni atoms forming the trimer have been enlarged for easier visualization.

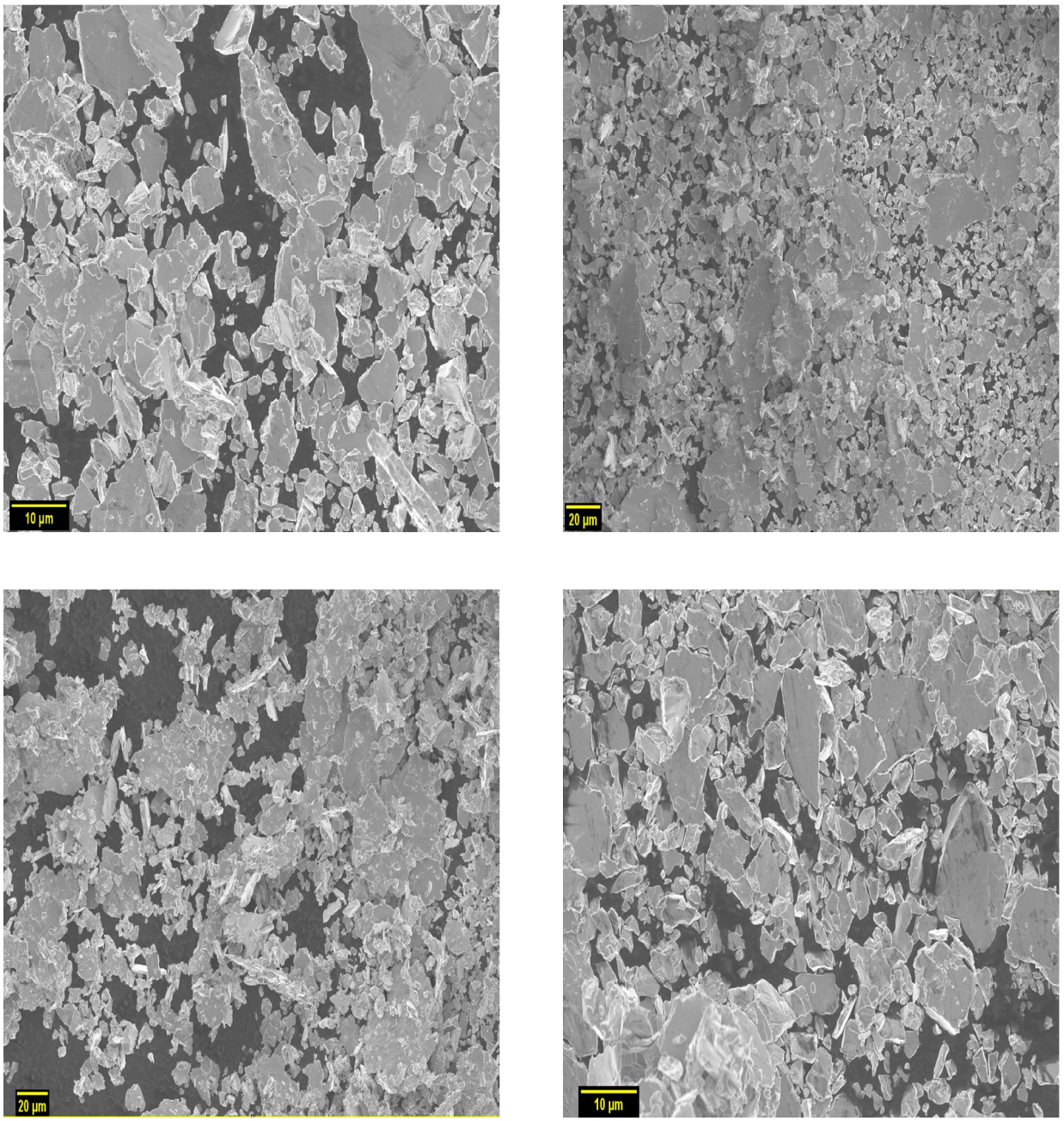

Figure S5. SEM images of (A) Ni_8Zn_{44}, (B) Ni_9Zn_{43}, (C) $Ni_{10}Zn_{42}$ and (D) $Ni_{11}Zn_{41}$.

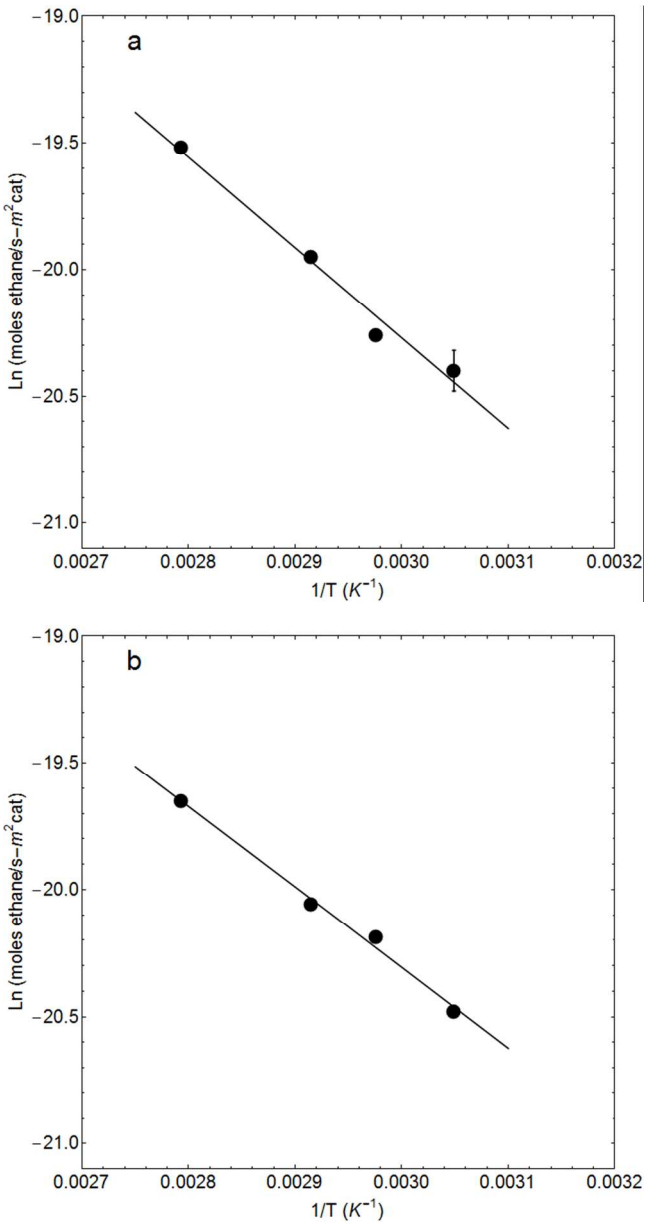

Figure S6. Arrhenius plots for ethylene hydrogenation on (a) Ni_8Zn_{44} and (b) $Ni_{11}Zn_{41}$. Reaction conditions were using 10 Torr ethylene, 200 Torr hydrogen with balance He and from 55-85°C.

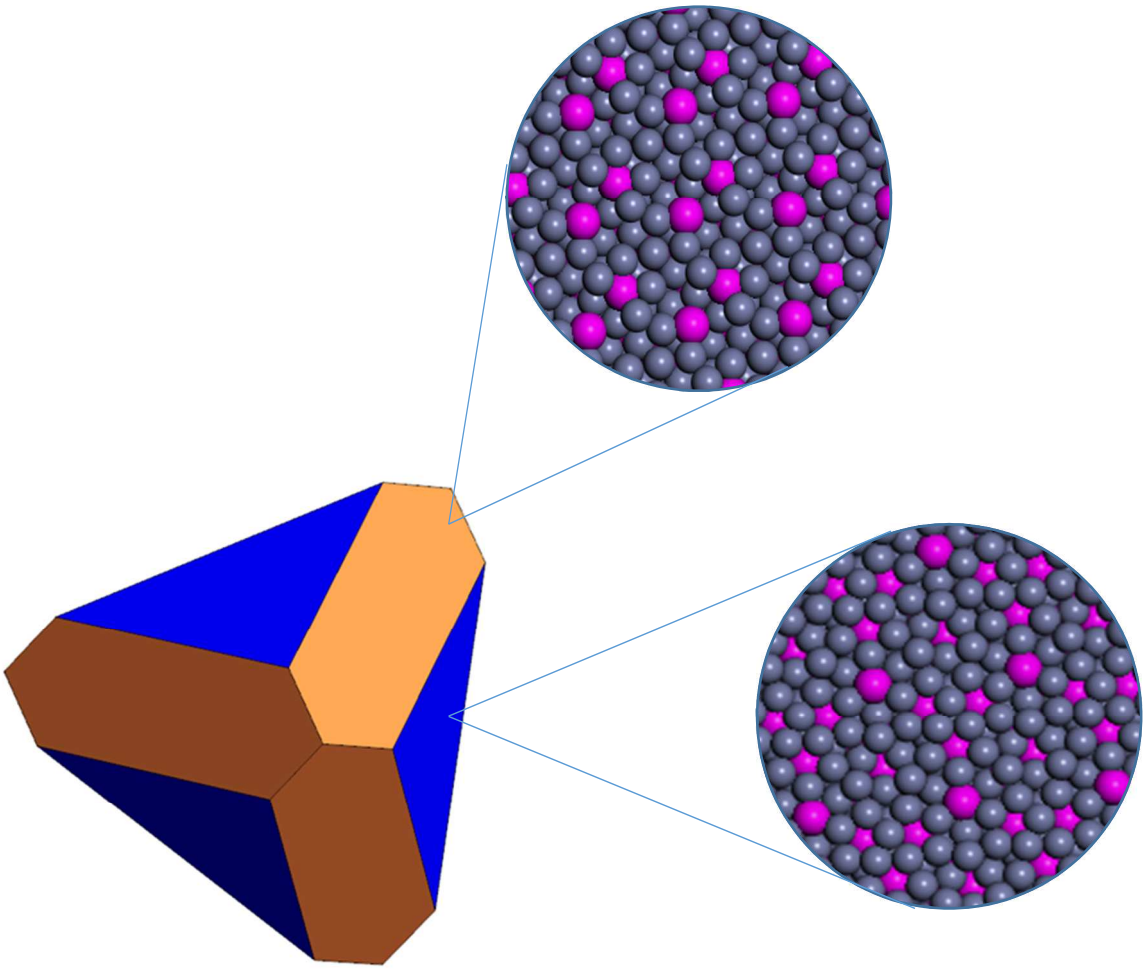

Figure S7. Wulff Construction of Ni_9Zn_{43} particle shape. Orange depicts {0 0 1} and blue {1 1 1} facets. Ni is marked in pink and Zn in grey in the magnified insets. No Ni-Ni-Ni trimers are seen on the exposed surface.