

Supplementary Information

Potential-Dependent Removal of Cu, Sn, Ni, and Cr from Molten Fe in Contact with FeS-Containing Slag

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Supplemental Note 1: Current–time curves

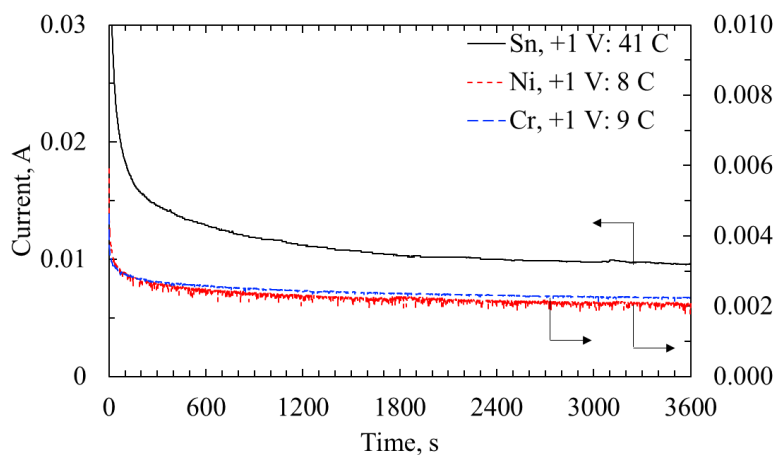


Fig. S1 | Time variations of current during constant-potential electrolysis. Current–time curves for experiments #2, #4, and #6 are shown as representative results of constant-potential electrolysis.

Supplemental Note 2: Formal Standard Formation Potentials for Oxidation and Sulfidation (1873 K)

This supplemental table summarizes formal standard electrode potentials (E°) at $T = 1873$ K for oxide and sulfide formation reactions of Fe, Cu, Sn, Ni, and Cr. The standard Gibbs energy change is expressed as:

$$\Delta G^\circ(T) = A + BT \log T + CT \text{ [J/mol]} \quad (\text{S1})$$

$$E^\circ(T) = \frac{\Delta G^\circ}{nF} \text{ [V]}, F = 96485 \text{ [C/mol]} \quad (\text{S2})$$

Here, $\Delta G^\circ(T)$ denotes the standard Gibbs energy change normalized to 1 mol of the compound produced (e.g., divide by 2 for reactions producing 2 mol of oxide/sulfide), n is the number of electrons associated with forming 1 mol of the compound (e.g., $n = 2$ for MO with M^{2+} ; $n = 2$ for Cu_2O and Cu_2S ; $n = 6$ for Cr_2O_3 ; $n = 4$ for Ni_3S_2).

Table S1 | Estimated standard electrode potentials for oxidation and sulfidation (1873 K).

A. Oxide systems (O_2 basis)

Formation reaction	ΔG° at 1873 K [kJ]	ΔG° per mol compound [kJ/mol]	n	E° [V]
$4\text{Cu(l)} + \text{O}_2(\text{g}) = 2\text{Cu}_2\text{O(l)}$	−79.802	−39.901	2	−0.2068
$2\text{Sn(l)} + \text{O}_2(\text{g}) = 2\text{SnO(g)}$	−174.917	−87.458	2	−0.4532
$2\text{Ni(l)} + \text{O}_2(\text{g}) = 2\text{NiO(s)}$	−149.004	−74.502	2	−0.3861
$2\text{Fe(l)} + \text{O}_2(\text{g}) = 2\text{FeO(l)}$	−295.767	−147.883	2	−0.7664
$4/3\text{Cr(s)} + \text{O}_2(\text{g}) = 2/3\text{Cr}_2\text{O}_3(\text{s})$	−436.490	−654.735	6	−1.1310

B. Sulfide systems (S_2 basis)

Formation reaction	ΔG° at 1873 K [kJ]	ΔG° per mol compound [kJ/mol]	n	E° [V]
$4\text{Cu(l)} + \text{S}_2(\text{g}) = 2\text{Cu}_2\text{S(l)}$	−142.424	−71.212	2	−0.3690
$2\text{Sn(l)} + \text{S}_2(\text{g}) = 2\text{SnS(g)}$	−122.675	−61.338	2	−0.3179
$3\text{Ni(l)} + \text{S}_2(\text{g}) = \text{Ni}_3\text{S}_2(\text{l})$	−116.081	−116.081	4	−0.3008
$2\text{Fe(l)} + \text{S}_2(\text{g}) = 2\text{FeS(l)}$	−110.248	−55.124	2	−0.2857
$\text{Cr(s)} + 1/2 \text{S}_2(\text{g}) = \text{CrS(s)}$	−96.723	−96.723	2	−0.5012

References

Knacke O, Kubaschewski O, Hesselmann K. Thermochemical Properties of Inorganic Substances. 2nd ed. Berlin: Springer-Verlag; 1991.

Oikawa K, Mitsui H, Ohtani H, Ishida K. Thermodynamic calculations of phase equilibria in the Fe–Cr–S system. ISIJ Int. 2000;40:182–190.

Supplemental Note 3: Metal-side activity-coefficient estimates using Wagner interaction parameters

Activities of dilute solutes in molten iron were discussed using Wagner's first-order interaction parameter formalism:

$$\ln \gamma_i^H = \ln \frac{\gamma_i}{\gamma_i^0} = \sum_j \varepsilon_{ij} x_j \quad (\text{S3})$$

where γ_i^H is the Henry-standard activity coefficient of solute i , ε_{ij} is the first-order interaction coefficient of solute j on solute i on a mole-fraction basis, and x_j is the mole fraction of solute j . On the grounds that insufficient data was found, the Cu–Ni interaction was set to zero ($\varepsilon_{\text{Cu,Ni}} = 0$). **Table S2** lists the interaction parameters ε_{ij} used for the five-component subspace: Cu, Sn, Ni, Cr, S. Temperature-dependent terms were evaluated at 1873 K.

Table S2 | First-order interaction coefficients ε_{ij} on a mole-fraction basis used in the present calculation at 1873 K.

i / j	Cu	Sn	Ni	Cr	S
Cu	–5.4	–7.48	0	3.9	–2.4
Sn	–6.42	–0.295	–6.8	3.28	–3.27
Ni	0	–6.8	0.118	0	–0.1
Cr	4.1	3.27	0	0.005	–22
S	–2.3	–3.28	–0.1	–22	–5.7

Contribution analysis of γ_i

To examine whether metal-side non-ideality could qualitatively contribute to the observed concentration changes, composition-dependent activity coefficients were estimated using Wagner's first-order interaction formalism. This analysis considers only interactions among solutes in the molten metal and does not constitute a calculation of metal–slag equilibrium or partitioning. The post-experimental metal compositions of experiments #7, #9, and #10 were converted from mass percent to mole fraction, with Fe taken as the balance to 100 wt%. Equation S3 was then evaluated using the interaction coefficients listed in Table S2. Table S3 presents the resulting Henry-standard activity coefficients:

Table S3 | Estimated activity coefficient of solute i in molten Fe.

Experiment	γ_{Cu}^H	γ_{Sn}^H	γ_{Ni}^H	γ_{Cr}^H	γ_{S}^H
#7, no bias	0.968	0.949	0.998	0.912	0.942
#9, +1 V	0.971	0.949	0.999	0.912	0.935
#10, +10 V	0.967	0.946	0.999	0.913	0.950

To facilitate comparison of the residual Cu, Sn, Ni, and Cr concentrations, a common assumed sulfur concentration of 0.286 wt% was used for the three calculations. This value was measured in experiment #9 and was used only as a reference concentration. The calculated relative activity-coefficient factors remained close to unity and varied only slightly among the three experiments. The Cr factor was lower than those of the other tramp elements because of the large negative Cr–S interaction coefficient; however, it remained nearly unchanged when the common sulfur concentration was used. The calculated Sn and Ni factors also exhibited only minor differences among the experiments. Therefore, the large differences in the observed metal-phase concentration changes cannot be explained solely by first-order metal-side interactions.

References

- Hino, M. & Ito, K. (eds) Thermodynamic Data for Steelmaking (Tohoku University Press, 2010).
 Ueda, S. Measurements and theoretical predictions of thermodynamic properties of trace elements in molten iron. PhD thesis, The University of Tokyo. <https://doi.org/10.15083/0002002001> (2019).

Supplemental Note 4: Regional chemical compositions of the solidified metal samples

To evaluate compositional heterogeneity after solidification, the central section of each metal sample was divided into upper, middle, and lower regions and analyzed separately by ICP–AES. The individual concentrations obtained from the three regions are listed below. The values reported in Table 1 of the main manuscript correspond to the arithmetic means of these regional measurements.

Table S4 | Regional chemical compositions of the solidified metal samples after treatment. Individual concentrations measured by ICP–AES in the upper, middle, and lower regions of each solidified metal sample. The values reported in Table 1 of the main manuscript correspond to the arithmetic means of these three regional measurements.

#	Atmosphere	Applied potential	Electric charge, C	Cu concentration in metal, wt%		Sn concentration in metal, wt%		Ni concentration in metal, wt%		Cr concentration in metal, wt%		S concentration in metal, wt%
				before	after	before	after	before	after	before	after	after treatment
1	Ar	None	–	–	–	0.500	0.084 0.033 0.069 0.066	–	–	–	–	0.225 0.722 0.350 0.182
2	Ar	+1 V	41	–	–	0.502	0.064 0.121	–	–	–	–	0.197 0.222 0.177
3	Ar	None	–	–	–	–	–	0.501	0.452 0.469 0.466 0.457	–	–	0.145 0.151 0.227
4	Ar	+1 V	8	–	–	–	–	0.501	0.461 0.478	–	–	0.234 0.234
5	Ar	None	–	–	–	–	–	–	–	0.490	0.031 0.030 0.032 0.138	0.229 0.220 0.232 0.231
6	Ar	+1 V	9	–	–	–	–	–	–	0.499	0.131 0.134 0.089	0.170 0.175
7	Ar	None	–	0.498	0.458 0.459 0.473 0.494	0.202	0.059 0.057 0.046	0.201	0.202 0.187 0.196 0.192	0.202	0.084 0.086 0.009	not detected. 0.705
8	Ar	+1 V	393	0.500	0.484 0.491 0.455	–	–	0.199	0.194 0.195 0.212	0.201	0.009 0.011 0.122	0.759 0.787 0.321
9	Ar	+1 V	110	0.498	0.460 0.468 0.496	0.201	0.023 0.025 0.002 0.037	0.201	0.212 0.215 0.208	0.200	0.117 0.121 0.052	0.258 0.273 0.246
10	Ar	+10 V	844	0.501	0.497 0.491 0.450	0.199	0.020 0.014 0.020	0.199	0.210 0.203 0.179	0.200	0.052 0.052 0.130	0.249 0.254 0.328
11	Ar	–1 V	–19	0.501	0.447 0.453 0.452	0.199	0.004 0.005 0.032	0.199	0.175 0.178 0.194	0.200	0.130 0.129 0.122	0.309 0.321 0.127
12	Ar	–10 V	–12455	0.502	0.464 0.461 0.462	0.199	0.029 0.022 0.031	0.199	0.194 0.195 0.190	0.201	0.120 0.119 0.083	0.133 0.142 0.660
13	Ar–1%O ₂	None	–	0.498	0.452 0.456 0.469	0.201	0.042 0.024 0.052	0.199	0.187 0.189 0.193	0.201	0.077 0.075 0.069	0.630 0.737 0.348
14	Ar–1%O ₂	–1 V	–84	0.498	0.450 0.453 0.476	0.199	0.022 0.058 0.010	0.200	0.180 0.179 0.204	0.200	0.069 0.068 0.088	0.278 0.330 0.334
15	Ar–1%H ₂	None	–	0.501	0.487 0.478 0.454	0.200	0.015 0.047 0.009	0.200	0.227 0.205 0.187	0.200	0.086 0.087 0.080	0.353 0.347 0.150
16	Ar–1%H ₂	+1 V	86	0.501	0.466 0.462	0.202	0.080 0.073	0.200	0.183 0.183	0.198	0.079 0.076	0.155 0.161