

Elemental partitioning and corrosion resistance of Ni-Cr alloys revealed by accurate ab-initio thermodynamic and electrochemical calculations

Liang-Feng Huang,^{1,2} Yusi Xie,³ Karl Sieradzki,³ and James M. Rondinelli^{1,*}

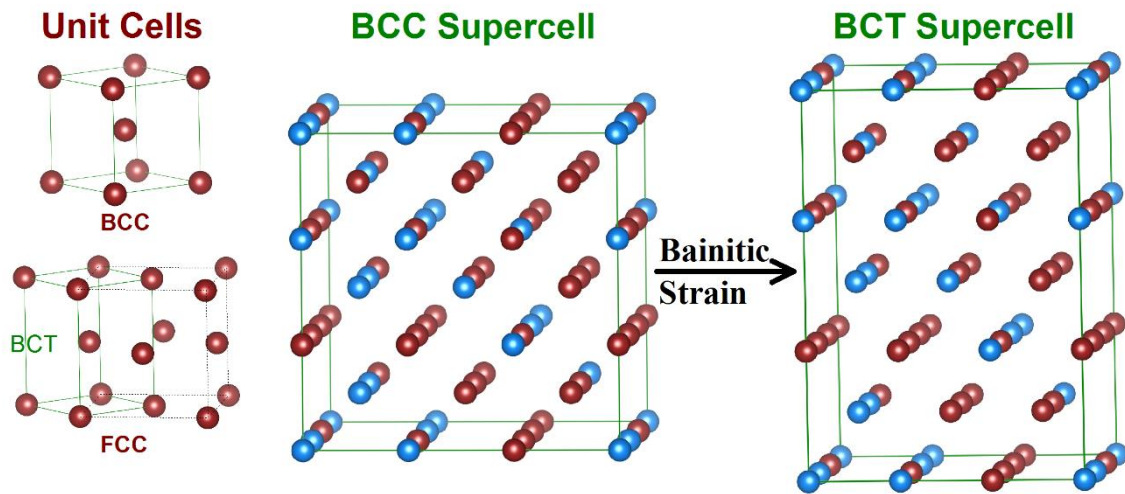
1. Department of Materials Science & Engineering, Northwestern University, Evanston, IL 60208, USA
2. Research Center for Advanced Interdisciplinary Sciences, Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences, Ningbo 315201, China
3. Ira A. Fulton School of Engineering, Arizona State University, Tempe, AZ 85287, USA

*Corresponding Email: jrondinelli@northwestern.edu

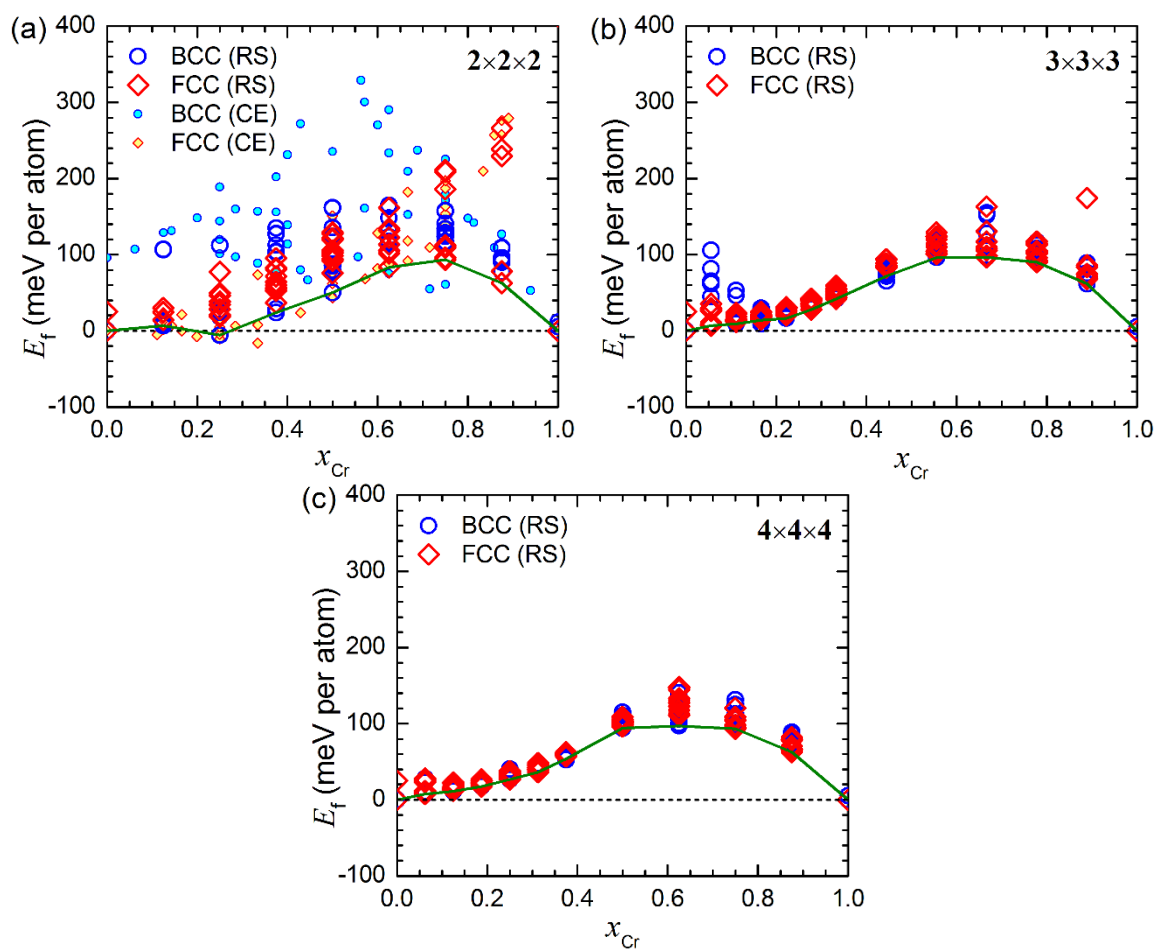
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(A) Supplementary Structural Models for Solid-Solution Ni-Cr Alloys



Supplementary Figure 1. The BCC and BCT (FCC) unit cells, as well as the BCC and BCT supercell models for Ni-Cr solid solutions.



Supplementary Figure 2. The electronic formation energies of Ni-Cr solid solutions in different sizes of supercells: (a) $2 \times 2 \times 2$, (b) $3 \times 3 \times 3$, and (c) $4 \times 4 \times 4$, where the results from cluster-expansion (CE) model [1] are compared with our random-solute (RS) model in panel (a).

(B) Supplementary Theoretical Details for Debye Model

The free energy of a solid-solution Ni-Cr alloy can be expressed by

$$G(T) = E_e + \tilde{F}_e(T) + F_{\text{vib}}(T) - TS_c, \quad (1)$$

where E_e is the total electronic energy obtained from DFT calculations; $\tilde{F}_e$ is the temperature-dependent electronic free energies derived from electronic density of states [2]; F_{vib} is the vibrational free energy [2,3]; S_c is the configurational entropy [3]. Using pure Ni and Cr as the reference systems, the free energy of formation ($\Delta_f G$) can be expressed by

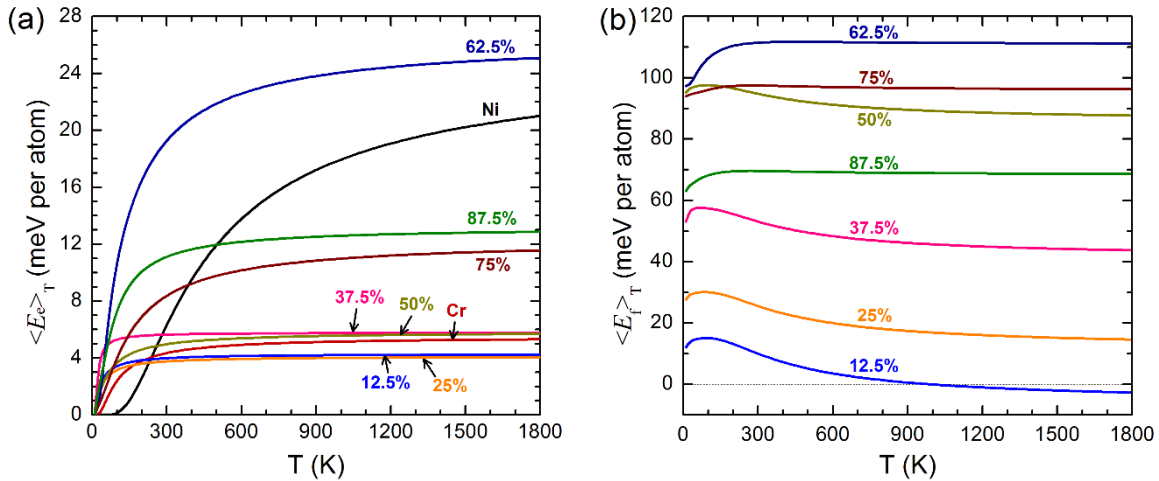
$$\Delta_f G(T) = E_f + \Delta \tilde{F}_e(T) + \Delta F_{\text{vib}}(T) - TS_c, \quad (2)$$

where $E_f (= \Delta E_e)$ is electronic formation energy.

There are many atomic structures and magnetic configurations at a specific Ni-Cr composition, and they should coexist in a macroscopic-scale random solid-solution sample. The possible number of coexisting structure-magnetism configurations should increase with increasing temperature, and the E_e in the **Supplementary Equation (1)** above should be replaced by its thermal average, i.e.,

$$\langle E_e \rangle_T = \sum_i E_e^i \cdot \exp\left(-\frac{E_e^i}{k_B T}\right) / \sum_i \exp\left(-\frac{E_e^i}{k_B T}\right), \quad (3)$$

where E_e^i is the electronic energy of the i -th structure-magnetism configuration. Correspondingly, the E_f in the **Supplementary Equation (2)** above should also be replaced by its thermal average $\langle E_f \rangle_T$. The calculated $\langle E_e \rangle_T(T)$ and $\langle E_f \rangle_T(T)$ curves for Ni, Cr, and Ni-Cr alloys are shown in the **Supplementary Figure 3**.



Supplementary Figure 3. The temperature-dependent thermal averages $\langle E_e \rangle_T$ s and $\langle E_f \rangle_T$ s for Ni, Cr, and Ni-Cr alloys.

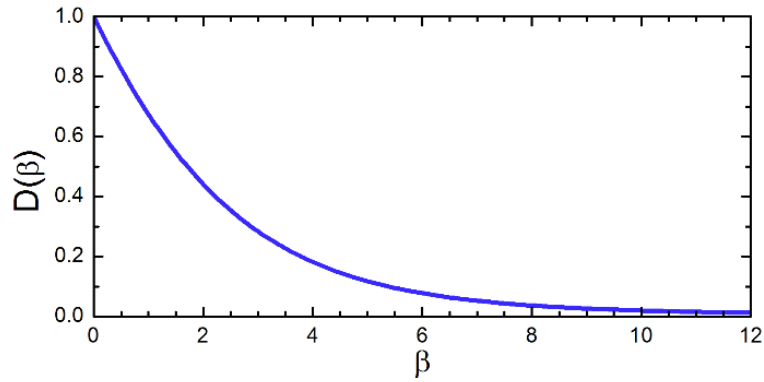
Debye model [4-6] is an efficient choice to accurately calculate the $F_{\text{vib}}(T)$ curves for alloy systems. Based on the approximated linear relationship between phonon frequency (ν) and wave vector ($\mathbf{q}$), as well as on the conservation of total number of phonon modes ($= 3N_{\text{atom}}$), i.e.,

$$\left\{ \begin{array}{l} v = c \cdot |\vec{q}| \\ \frac{V}{(2\pi)^3} \int_0^{q_{\max}} 4\pi q^2 \cdot dq = 3N_{\text{atom}} \end{array} \right. , \quad (4)$$

we can derive F_{vib} to be

$$\begin{aligned} F_{\text{vib}}(T) &= \frac{k_B T}{N_{\text{at}}} \cdot \int_0^{v_{\max}} \ln \left[2 \sinh \left(\frac{h\nu}{2k_B T} \right) \right] \cdot g(\nu) \cdot d\nu \\ &= k_B T \cdot \left\{ \frac{9}{8} \left(\frac{\Theta_D}{T} \right) + 3 \ln \left[1 - \exp \left(-\frac{\Theta_D}{T} \right) \right] - D \left(\frac{\Theta_D}{T} \right) \right\}, \end{aligned} \quad (5)$$

where $g(\nu)$ ($= \frac{V}{2\pi^2 c^3} \cdot \nu^2$, V is volume) is the phonon density of states; Θ_D is the Debye temperature ($= \frac{h\nu_{\max}}{k_B}$); $D(\beta)$ ($\beta = \frac{\Theta_D}{T}$) is the Debye integral [5,6]. The calculated $D(\beta)$ curve is shown in the **Supplementary Figure 4**.



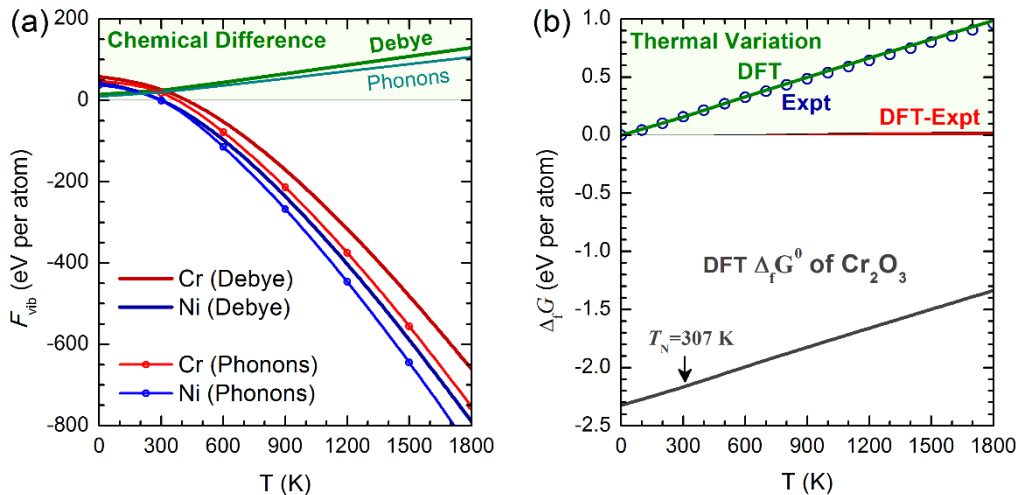
Supplementary Figure 4. The calculated $D(\beta)$ curve.

(C) Supplementary Accuracy Analysis for the $\Delta_f G$ Data of Metals and Oxides

The comparison between the Debye temperatures for Ni-Cr alloys from our theoretical calculations and experimental measurements in the main text (Figure 3c) has already clearly showed the accuracy of our Debye model. The comparison between the vibrational free energies (F_{vib}) calculated from different methods (e.g., Debye model and phonon spectra) can further prove the accuracy of our $\Delta_f G$ data. In the **Supplementary Figure 5(a)** below, it can be seen that these two kinds of methods can give out the same chemical order in F_{vib} between the elemental Ni and Cr, and their differential- F_{vib} values, i.e., $F_{\text{vib}}(\text{Cr}) - F_{\text{vib}}(\text{Ni})$, from these two theoretical methods have a very small deviation from each other (only by 8~19 meV) at temperatures of 600~1500 K, i.e., the usual thermal-treatment temperatures.

It is extremely expensive to calculate the phonon spectra of Ni-Cr alloy structures in the $4 \times 4 \times 4$ supercell, thus an accurate enough Debye model will become demanded for alloy systems. From the analysis above for elemental metals (Ni and Cr), it can be readily expected that the difference in $\Delta_f G$ (see Equation 2 in the main text) for any Ni-Cr alloy between the two theoretical methods will be in a similar small magnitude.

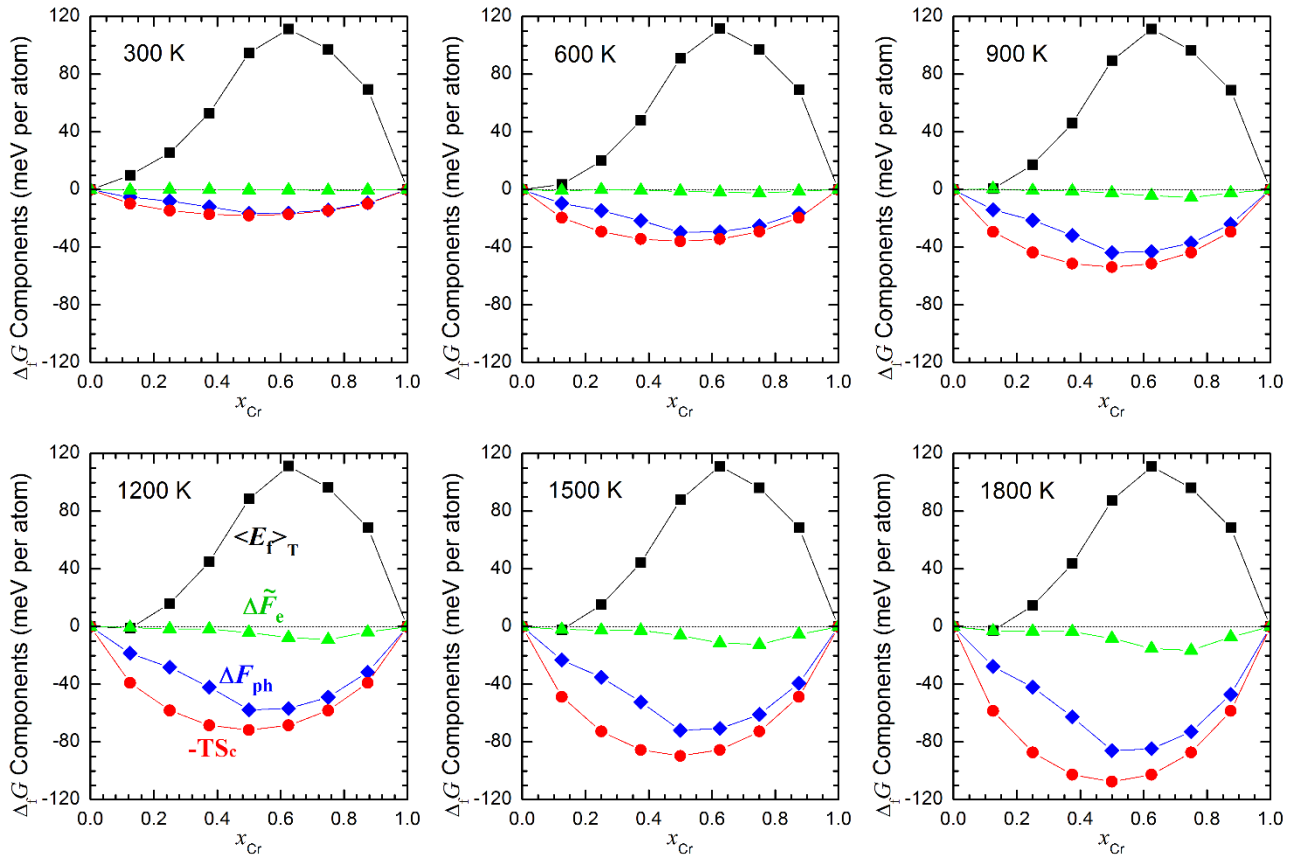
In the calculations of the $\Delta_f G$ values for both alloys and compounds (oxides, hydroxides, and oxyhydroxides) of Ni and Cr, the effects of thermal expansion and magnetic excitation are neglected for convenience in this work (see Equation 2 and 3 in the main text). Actually, the accuracy in $\Delta_f G$ is obviously guaranteed under such simplifying treatment here, according to the theory-experiment comparisons for alloys and oxides shown in the main text (Figure 3-5). As further analyzed in the **Supplementary Figure 5(b)**, the theory-experiment difference in the temperature-dependent part of $\Delta_f G$ is totally negligible (<25 meV, at $T < 1500$ K) for Cr_2O_3 . The major reason for the guaranteed accuracy here should be the cancellations of these effects between the solids involved in the calculations of $\Delta_f G$ values for alloys and metals. In addition, the magnetic excitation at finite temperatures frequently results in a prominent λ -shaped curve for heat capacity around the critical Curie/Neel temperature for a magnetic solid [7-10], but as usual, does not have an observable contribution to $\Delta_f G$, as shown in the **Supplementary Figure 5(b)**.



Supplementary Figure 5. (a) The vibrational free energies (F_{vib}) of elemental Ni and Cr derived from both the Debye model and phonon spectra, as well as the difference between Ni and Cr. (b) The calculated standard free energy of formation ($\Delta_f G$) of Cr_2O_3 , and the thermal-dependent parts in the calculated and experimental $\Delta_f G$ values.

(D) Supplementary Decomposition of $\Delta_f G$ Data for Ni-Cr Alloys

The composition dependencies of all the component terms of $\Delta_f G$ (i.e., $\langle E_f \rangle_T$, $\tilde{F}_e$, F_{vib} , $-TS_c$) at different temperatures (300-1800 K) are shown in the **Supplementary Figures 6**.



Supplementary Figure 6. The composition-dependent $\Delta_f G$ components of Ni-Cr alloys at different temperatures.

(E) Supplementary Experimental $\Delta_f G$ Data for Ni-Cr Alloys

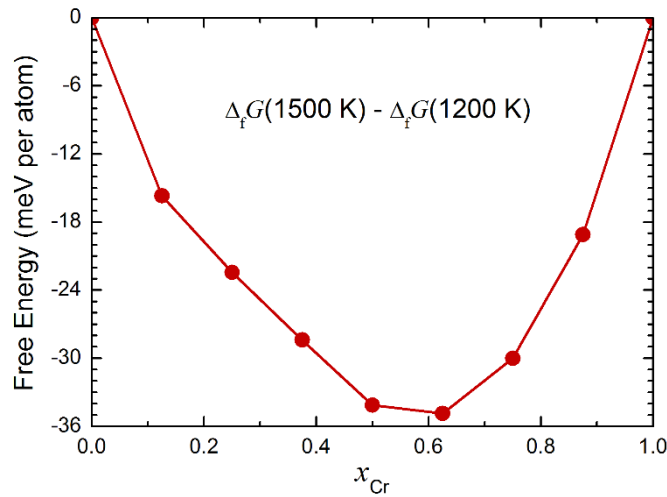
The experimental $\Delta_f G$ data for Ni-Cr alloys at 1550 and 1423 K are available [11,12]. In order to compare them with the calculated $\Delta_f G$ data at 1500 K, the experimental data should be adequately corrected due to the difference in temperature. From the calculated temperature dependence of $\Delta_f G$, we find the $\Delta_f G(T)$ curve has a high degree of linearity around 1500 K (i.e., from 1200 to 1800 K). Thus, the thermal correction in $\Delta_f G$ can be calculated using

$$\Delta_T = \left(\frac{\delta \Delta_f G}{\delta T} \right) \Big|_{\text{Theory}} \times (T - 1500) \Big|_{\text{Experiment}}, \quad (6)$$

and the derivative between the theoretical $\Delta_f G$ and T is calculated using

$$\left(\frac{\delta \Delta_f G}{\delta T} \right) \Big|_{\text{Theory}} = \frac{\Delta_f G(1500) - \Delta_f G(1200)}{1500 - 1200}, \quad (7)$$

where the term in the numerator is shown in the **Supplementary Figure 7**. The original experimental $\Delta_f G$ data are then corrected using the calculated Δ_T values, as listed in the **Supplementary Table 1**.



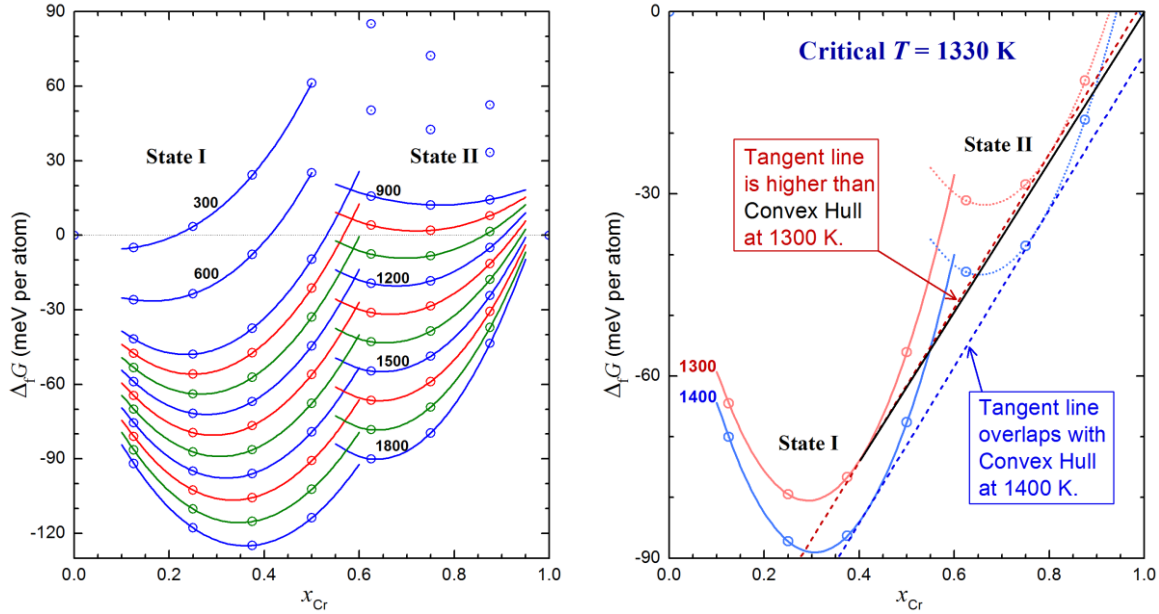
Supplementary Figure 7. The difference in $\Delta_f G$ between 1500 and 1200 K.

Supplementary Table 1. The original and corrected experimental $\Delta_f G$ values (in meV per atom).

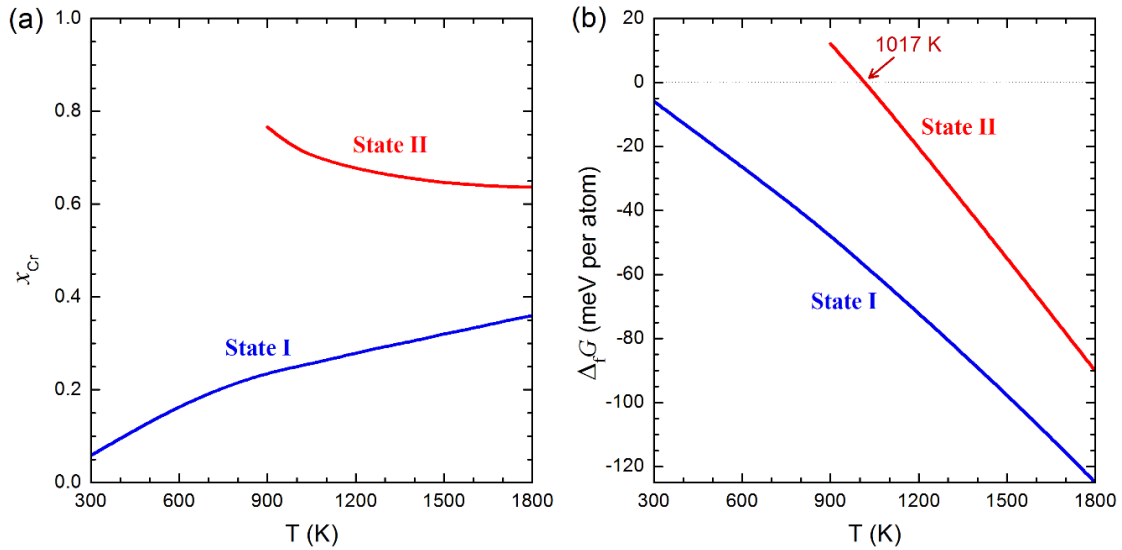
Tso [11]			Udovsky [12]		
x_{Cr}	Original $\Delta_f G$ at 1550 K	Corrected $\Delta_f G$ at 1500 K	x_{Cr}	Original $\Delta_f G$ at 1423 K	Corrected $\Delta_f G$ at 1500 K
0.65	-66.5	-60.8	0.42	-118.8	-126.6
0.50	-82.4	-76.7	0.21	-113.0	-118.2
0.40	-89.3	-84.6	0.80	-85.0	-91.6
0.30	-88.4	-84.3	0.60	-106.3	-115.3
0.20	-77.4	-73.6			
0.10	-52.6	-50.5			

(F) Supplementary Details for the Two Equilibrium States of Ni-Cr Alloys

The calculated composition-dependent $\Delta_f G$ values for Ni-Cr alloys at different temperatures (from 300 to 1800 K) are shown in the **Supplementary Figure 8**, where the parabolic fittings for the two equilibrium states (State I and II) are also carried out. State II becomes metastable at temperatures < 1330 K, and is unstable at temperatures < 900 K. Thus, the calculated data for State II at 300 and 600 K cannot be fitted by parabolic curves. From the fitted curves, the equilibrium x_{Cr} and $\Delta_f G$ values for State I and II at different temperatures can be readily located, and the analyzed results are shown in the **Supplementary Figure 9**.



Supplementary Figure 8. The calculated composition-dependent $\Delta_f G$ values for Ni-Cr alloys at different temperatures, as well as the parabolic fittings to reveal the thermodynamic properties of two equilibrium states.



Supplementary Figure 9. The temperature-dependent equilibrium x_{Cr} and $\Delta_f G$ values for State I and II.

(G) Supplementary Information on the Industrial Grades of Ni-Cr Alloys

There are various well-established industrial grades of Ni-Cr-based alloys with superior mechanical properties, thermal stability, and corrosion resistance under different kinds of aggressive environments. Composition and heat treatment are two essential factors that dictate the properties of these Ni-Cr alloys. The available compositions and heat-treatment temperatures (T_{HT}) for many industrial Ni-Cr alloys are collected in the **Supplementary Table 2** below.

The Cr contents in these Ni-Cr alloys distribute between 12.5 and 31 wt.% (14.3—33.5 at.%). If the contents of all the Cr-column elements (Cr, Mo, W) are summed up, they comprise 14-35 wt.% (15.5—34.8 at.%), except for the specially higher content of 37—45.4 wt.% (33.3—40.6 at.%) in Inconel 686.

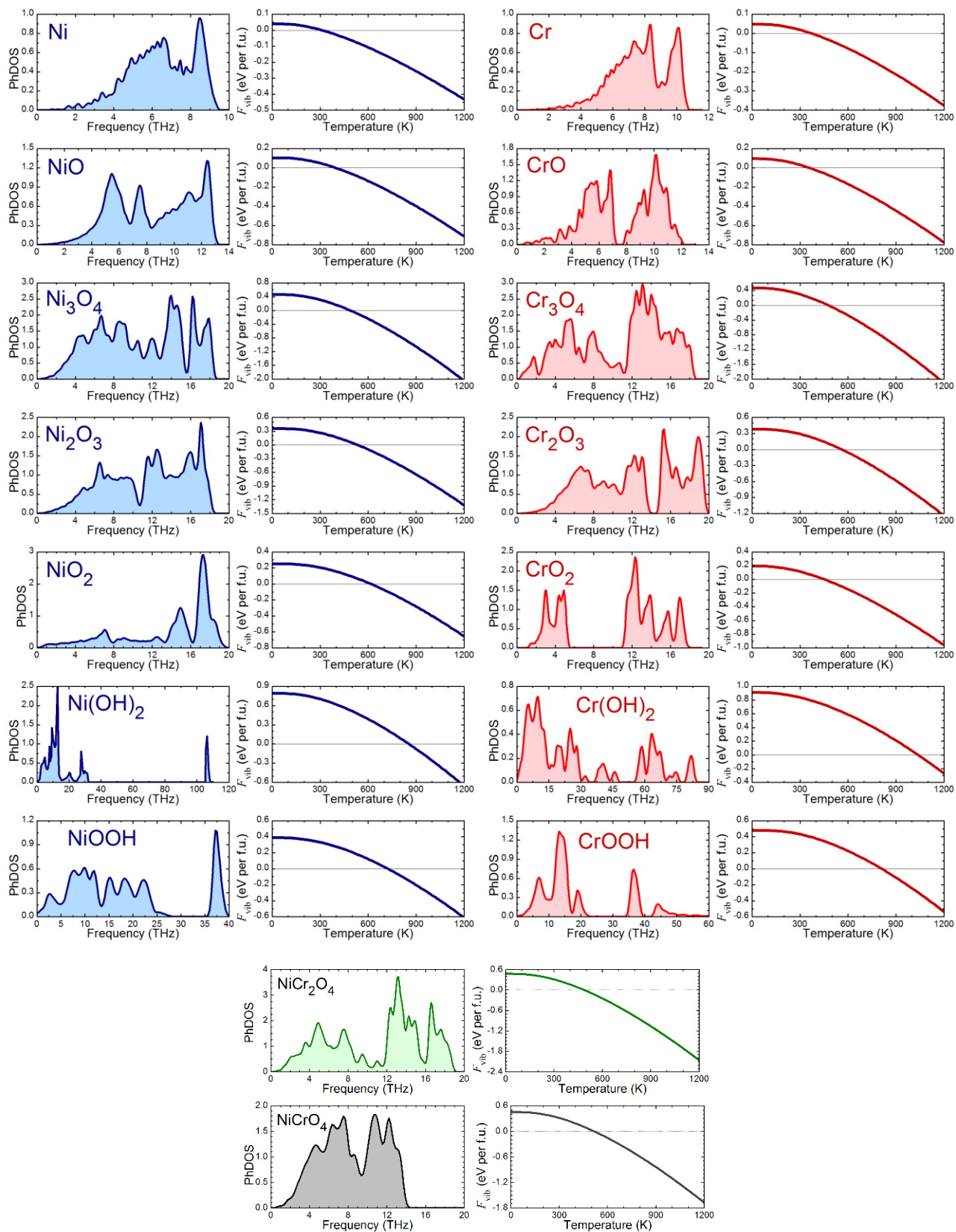
The T_{HT} values, which have been precisely determined by empirical design, are required for a variety of metallurgical reasons, e.g., solid-solution homogenization (usually at a higher T_{HT} level) and aging processes for precipitation hardening, grain growth, and internal-stress release (usually at a lower T_{HT} level). The solution-treatment temperatures of these Ni-Cr alloys mostly reside within the range of 1200-1500 K, and the other aging processing temperatures mostly reside within 900-1200 K (sometimes reach ≈ 1450 K).

Supplementary Table 2. The compositions and heat-treatment temperatures for various industrial Ni-Cr alloys.

Grade	Composition (wt.%)	T_{HT} (K)
Inconel 600	Ni ≥ 72 , Cr 14-17 , Fe 6-10, C ≤ 0.15 , Mn ≤ 1.0 , S ≤ 0.015 , Si ≤ 0.5 , Cu ≤ 0.5	1283-1422
Inconel 601	Ni 58-63, Cr 21-25 , Fe 7.7-21, Al 1.0-1.7, C ≤ 0.1 , Mn ≤ 1.0 , S ≤ 0.015 , Si ≤ 0.5 , Cu ≤ 1.0	1228-1422
Inconel 617	Ni ≥ 44.5 , Cr 20-24 , Co 10-15, Mo 8-10, Al 0.8-1.5, Ti ≤ 0.6 , Fe ≤ 3.0 , C 0.05-0.15, Mn ≤ 1.0 , Cu ≤ 0.5 , Si ≤ 1.0 , S ≤ 0.015 , B ≤ 0.006	1450
Inconel 625	Ni ≥ 58 , Cr 20-23 , Fe ≤ 5.0 , Mo 8-10, Nb+Ta 3.15-4.15 C ≤ 0.1 , Co ≤ 1.0 , Mn ≤ 0.5 , Si ≤ 0.5 , P ≤ 0.015 , S ≤ 0.015 , Al ≤ 0.4 , Ti ≤ 0.4	1366-1478
Inconel 686	Ni 53-60, Cr 19-23 , Mo 15-17, W 3.0-4.4, Fe ≤ 2.0 , Ti 0.02-0.25, C ≤ 0.01 , Mn ≤ 0.75 , S ≤ 0.02 , S ≤ 0.08 , P ≤ 0.04	1150-1478
Inconel 690	Ni ≥ 58 , Cr 27-31 , Fe 7-11 C ≤ 0.05 , Si ≤ 0.5 , Mn ≤ 0.5 , Cu ≤ 0.5 , S ≤ 0.015	1311
Inconel 718	Ni 50-55, Cr 17-21 , Nb+Ta 4.75-5.5, Mo 2.8-3.3, Ti 0.65-1.15, Al 0.2-0.8, C ≤ 0.08 , Co ≤ 1.0 , Mn ≤ 0.35 , Cu ≤ 0.3 , Si ≤ 0.35 , P ≤ 0.015 , S ≤ 0.015 , B ≤ 0.006	1200-1339, 991-1033, 894-922
Inconel 725	Ni 55-59, Cr 19-22.5 , Mo 7-9.5, Nb 2.75-4.0, Ti 1.0-1.7, Al ≤ 0.35 , Fe (bal.), C ≤ 0.03 , Mn ≤ 0.35 , Si ≤ 0.2 , P ≤ 0.015 , S ≤ 0.01	1310, 1005, 894
Inconel X-750	Ni (+Co) ≥ 70 , Cr 14-17 , Co ≤ 1.0 , Fe 5-9, Ti 2.25-2.75, Al 0.4-1.0, Nb+Ta 0.7-1.2, C ≤ 0.08 , Mn ≤ 1.0 , Cu ≤ 0.5 , Si ≤ 0.5 , S ≤ 0.01	1422, 1116, 978
Inconel 792	Ni (bal.), Cr 12.5 , Co 9.0, W 4.2, Ta 4.2, Ti 4.0, Al 3.4, Mo 1.9, C 0.08, Zr 0.018, B 0.015	1393, 1118
Incoloy 800	Ni 30-35, Cr 19-23 , Fe ≥ 39.5 , Ti 0.15-0.6, Al 0.15-0.6, C 0.05-0.10, Mn ≤ 1.5 , Cu ≤ 0.75 , S ≤ 0.015 , Si ≤ 1.0	1255-1339
Incoloy 825	Ni 38-46, Cr 19.5-23.5 , Fe ≥ 22 , Mo 2.5-3.5, Cu 1.5-3.0, Ti 0.6-1.2, Al ≤ 0.2 , C ≤ 0.05 , Mn ≤ 1.0 , Si ≤ 0.5 , S ≤ 0.03	1200-1255
Incoloy 890	Ni 42.5, Cr 25.0 , Fe (bal.), Nb 0.4, Mo 1.5, Ta 0.2, Al 0.1, Ti ≤ 1.0 , Si 1.8, C 0.1, Mn ≤ 1.0 , Cu ≤ 0.75 , P ≤ 0.03 , S ≤ 0.015	1394-1478
Incoloy 925	Ni 42-46, Cr 19.5-22.5 , Fe ≥ 22 , Mo 2.5-3.5, Cu 1.5-3.0, Ti 1.9-2.4, Al 0.1-0.5, C ≤ 0.03 , Mn ≤ 1.0 , Si ≤ 0.5 , Nb ≤ 0.5 , S ≤ 0.03	1311, 1014

Incoloy 945	Ni 45-55, Cr 19.5-23 , Fe (bal.), Mo 3-4, Nb 2.5-4.5, Cu 1.5-3.0, Ti 0.5-2.5, Al 0.01-0.7, C 0.005-0.04, Mn ≤1.0, Si ≤0.5, S ≤0.03, P ≤0.03	1283-1339, 978-1005, 880-908
Nimonic 75	Ni (bal.), Cr 18-21 , Fe ≤5.0, Mn ≤1.0, Ti ≤1.0, Cu ≤0.5, C 0.08-0.15, Si ≤1.0	1322
Nimonic 80A	Ni (bal.), Cr 18-21 , Fe ≤3.0, Ti 1.8-2.7, Al 1.0-1.8, Co ≤2.0, Mn ≤1.0, C ≤0.1, Cu ≤0.2, Zr ≤0.15, Pb ≤0.0025, Si ≤1.0, B ≤0.008, S ≤0.015	1353, 973
Nimonic 81	Ni (bal.), Cr 30 , Co 2.0, Ti 1.8, Al 0.9, Fe 1.0, Cu 0.2, Mn 0.5, Mo 0.3, C 0.05, Zr 0.06, Si 0.5, B 0.003, S 0.015	1373, 973
Nimonic 86	Ni (bal.), Cr 25 , Mo 10, C 0.05, Mg 0.015, Ce 0.03	1423,
Nimonic 90	Ni (bal.), Cr 18-21 , Co 15-21, Ti 2-3, Al 1-2, Fe ≤1.5, Mn ≤1.0, C ≤0.13, Cu ≤0.2, Pb ≤0.002, Zr ≤0.15, Si ≤1.0, B ≤0.02, S ≤0.015	1311-1422, 1200, 1022
Nimonic 105	Ni (bal.), Cr 14-15.7 , Co 18-22, Mo 4.5-5.5, Ti 0.9-1.5, Al 4.5-4.9, C ≤0.17, Fe ≤1.0, Mn ≤1.0, Cu ≤0.2, Pb ≤0.0015, Zr ≤0.15, Si ≤1.0, S ≤0.01, B ≤0.01	1423, 1323-1338
Nimonic 115	Ni (bal.), Cr 14-16 , Co 13-15.5, Ti 3.5-4.5, Al 4.5-5.5, Mo 3-5, Fe ≤1.0, Mn ≤1.0, C 0.12-0.2, Cu ≤0.2, Zr ≤0.15, Pb ≤0.0015, Si ≤1.0, B 0.01-0.025, S ≤0.015	1463, 1373
Nimonic 263	Ni (bal.), Cr 19-21 , Co 19-21, Mo 5.6-6.1, Ti 1.9-2.4, Ti+Al 2.4-2.8, Mn ≤0.6, Fe ≤0.7, C 0.04-0.08, Cu ≤0.2, Ag ≤0.0005, Pb ≤0.002, Bi ≤0.0001, Si ≤0.4, S ≤0.007, B ≤0.005	1423, 1073
Nimonic 901	Ni 42.5, Cr 12.5 , Fe (bal.), Mo 5.75, Ti 2.9, Co ≤1.0, Cu ≤0.5, Mn ≤0.5, Al ≤0.35, C ≤0.1, Si ≤0.4, S ≤0.03	1363, 1048, 978-993
Nimonic PK33	Ni (bal.), Cr 16-20 , Co 12-16, Mo 5-9, Ti 1.5-3.0, Al 1.7-2.5, Fe ≤1.0, Mn ≤0.5, Cu ≤0.2, C ≤0.07, Zr ≤0.06, Si ≤0.5, B ≤0.005, S ≤0.015	1373-1393, 1123
Udimet R41	Ni (bal.), Cr 18-20 , Co 10-12, Mo 9-10.5, Al 1.4-1.8, Ti 3.0-3.3, Fe ≤5.0, C ≤0.12, B 0.003-0.010	1450
Incotherm TD	Ni (bal.), Cr 22 , Mo 3, Si 1.4, C ≤0.01	/
Waspaloy	Ni (bal.), Cr 18-21 , Co 12-15, Al 1.2-1.6, Ti 2.75-3.25, Mo 3.5-5.0, Fe ≤2.0, Mn ≤1.0, C 0.02-0.10, Cu ≤0.5, Zr 0.02-0.12, Si ≤0.75, B 0.003-0.12, S ≤0.03, P ≤0.03	1353, 1118, 1033

(H) Supplementary Phonon Spectra and Vibrational Free Energies



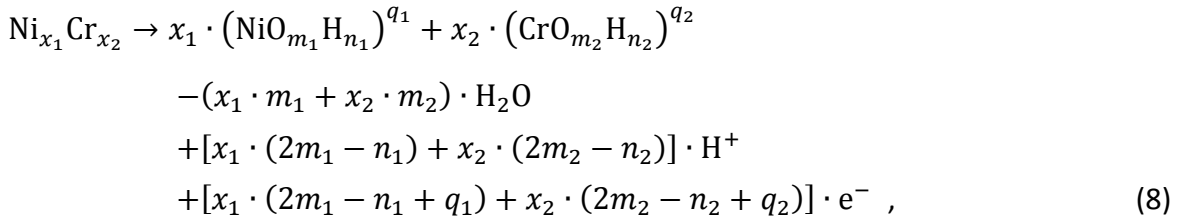
Supplementary Figure 10. The phonon densities of states (PhDOS) and vibrational free energies (F_{vib}) for Ni and Cr elements, oxides, hydroxides, and oxyhydroxides, as well as for NiCr₂O₄ and NiCrO₄.

(I) Supplementary Theory for the Construction of Pourbaix Diagrams

(1) Theoretical Formula for Pourbaix diagrams

To construct a Pourbaix diagram, the reaction equations between different species, e.g., metals, oxides, (oxy)hydroxides, H_2O , and aqueous ions, are constructed to derive their relative chemical potentials within a given electrochemical phase space in terms of solution pH and electrode potential (U , with respect to the standard hydrogen electrode, SHE) [13].

In an electrochemical reaction, we first consider the oxidation process of a Ni-Cr alloy into mono-metal species, generally described as $(MO_mH_n)^q$, where M is Ni or Cr; m and n are the atom numbers of O and H per metal cation; q is the aqueous-ion charge (i.e., zero for solids). For example, NiO, $Ni(OH)_2$, Ni^{2+} ion, and $CrOH^{2+}$ ion can be written as $(NiO_1H_0)^0$, $(NiO_2H_2)^0$, $(NiO_0H_0)^{2+}$, and $(CrO_1H_1)^{2+}$. Thus, the electrochemical reaction of a Ni-Cr alloy can be expressed by

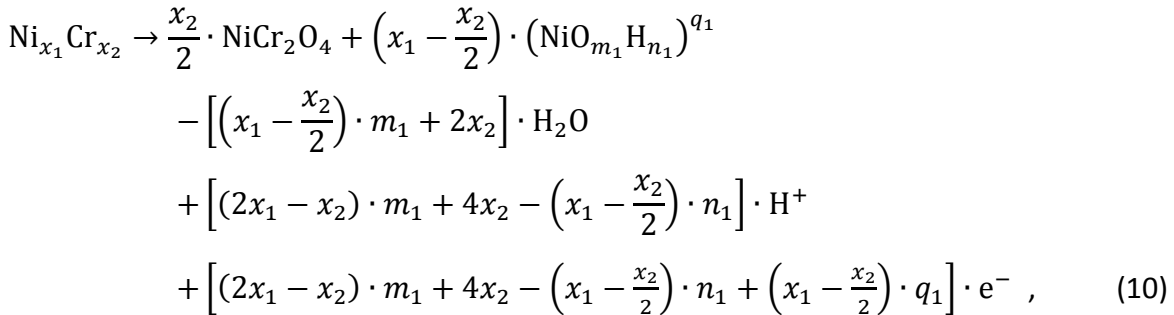


where the condition of $x_1 + x_2 = 1$ is preserved. The corresponding chemical potential of reaction ($\Delta\mu$) can be written by

$$\begin{aligned} \Delta\mu = & x_1 \cdot \mu_0[(NiO_{m_1}H_{n_1})^{q_1}] + x_2 \cdot \mu_0[(CrO_{m_2}H_{n_2})^{q_2}] - \mu_0[Ni_{x_1}Cr_{x_2}] \\ & - (x_1 \cdot m_1 + x_2 \cdot m_2) \cdot \mu_0[H_2O] \\ & + [x_1 \cdot (2m_1 - n_1) + x_2 \cdot (2m_2 - n_2)] \cdot (-1) \cdot k_B T \cdot \ln(10) \cdot pH \\ & + [x_1 \cdot (2m_1 - n_1 + q_1) + x_2 \cdot (2m_2 - n_2 + q_2)] \cdot (-1) \cdot |e| \cdot U , \end{aligned} \quad (9)$$

where μ_0 is the standard chemical potential, i.e., the free energy of formation at the standard condition (298.15 K, 1 bar, pH 0, 1 M) for solid compounds and aqueous ions.

When the binary-metal oxide $NiCr_2O_4$ (i.e., spinel phase) is involved in the reaction of a Ni-Cr alloy at $x_{Cr} < 66.7$ at. %, the Cr element will be fully consumed, and the remaining Ni will transform into mono-metal species. The corresponding reaction equation and $\Delta\mu$ are expressed by



$$\Delta\mu = \frac{x_2}{2} \cdot \mu_0[NiCr_2O_4] + \left(x_1 - \frac{x_2}{2}\right) \cdot \mu_0[(NiO_{m_1}H_{n_1})^{q_1}] - \mu_0[Ni_{x_1}Cr_{x_2}]$$

$$\begin{aligned}
& - \left[\left(x_1 - \frac{x_2}{2} \right) \cdot m_1 + 2x_2 \right] \cdot \mu_0[\text{H}_2\text{O}] \\
& + \left[(2x_1 - x_2) \cdot m_1 + 4x_2 - \left(x_1 - \frac{x_2}{2} \right) \cdot n_1 \right] \cdot (-1) \cdot k_B T \cdot \ln(10) \cdot \text{pH} \\
& + \left[(2x_1 - x_2) \cdot m_1 + 4x_2 - \left(x_1 - \frac{x_2}{2} \right) \cdot n_1 + \left(x_1 - \frac{x_2}{2} \right) \cdot q_1 \right] \cdot (-1) \cdot |e| \cdot U . \quad (11)
\end{aligned}$$

When $x_{\text{Cr}} > 66.7$ at. %, the Ni element will be fully consumed by the electrochemical oxidation reaction of Ni-Cr alloy to form NiCr_2O_4 , and the remaining Cr element will transform into mono-metal species, for which the corresponding $\Delta\mu$ can be readily derived in the same way as the **Supplementary Equation (10)** and **(11)**. According to the thermodynamic stability of Ni-Cr alloys calculated in this work (see the **Supplementary Figure 8** above and Figure 4 in main text), good Ni-Cr solid solutions free of compositional separation require $x_{\text{Cr}} < 30$ at.% at 900 K (45 at.% at 1800 K). Therefore, the construction of Pourbaix diagram here is carried out based on the **Supplementary Equation (9)** for the formation of mono-metal product species and the **Supplementary Equation (11)** for the formation of spinel NiCr_2O_4 . It should be noted that comparing to the electrochemical $\Delta\mu$ values for metal oxidations, the $\Delta_f G$ values of Ni-Cr alloys at 300 K (0.0 – 0.08 eV per atom, see Figure 4 in main text) actually are relatively low.

At a given phase-space coordinate (in terms of pH and U), all of the possible compounds and aqueous ions can be considered as the reaction products of a Ni-Cr alloy. Their standard chemical potentials (μ_0 , listed in the **Supplementary Table 3** below) are used into the **Supplementary Equation (9)** and **(11)** to compute all the $\Delta\mu$ values for these possible reaction paths, which yields the relative electrochemical stabilities of all the possible combinations of products, and then locates the product group with the lowest $\Delta\mu$ at this condition. When a given phase space is fully scanned, a Pourbaix diagram can be generated.

(2) Standard Chemical Potentials of the Involved Species

Supplementary Table 3. Standard chemical potentials (μ_0 , in eV per f.u.) of different species.

NiO	-2.697	CrO	-3.120	NiCr ₂ O ₄	-13.585
Ni ₃ O ₄	-6.953	Cr ₃ O ₄	-14.325	NiCrO ₄	-7.356
Ni ₂ O ₃	-4.057	Cr ₂ O ₃	-10.833		
NiO ₂	-1.343	CrO ₂	-5.060	H ₂ O	-2.458
Ni(OH) ₂	-5.040	Cr(OH) ₂	-5.592		
NiOOH	-3.470	CrOOH	-6.891		
Ni ²⁺	-0.479	Cr ²⁺	-1.811		
Ni ³⁺	+3.745	Cr ³⁺	-2.230		
[HNiO ₂] ⁻	-3.620	[CrO ₂] ⁻	-5.569		
[NiO ₂] ²⁻	-2.792	[CrO ₃] ³⁻	-6.254		
		[CrO ₄] ²⁻	-7.574		
		[Cr ₂ O ₇] ²⁻	-13.506		
		[CrOH] ²⁺	-4.466		

(3) Solution pH Values

In the electrochemical formula above for the construction of Pourbaix diagrams, solution pH is just a parameter. When comparing the theoretical results to experimental electrochemical measurements, the pH values for experimental solutions should be calculated accurately. For this purpose, the Debye-Hückel model [14] can be used, which accounts for the contribution of ion-ion interactions to the pH value, and may be important for the highly acid/basic solutions.

The pH value is derived from the activity of H^+ by using $pH = -\log\{a(H^+)\}$. In an ideal situation with the non-interacting aqueous ions (e.g., a dilute enough solution), $a(H^+)$ can be well approximated by the concentration of H^+ ($[H^+]$). Then, we can readily calculate the ideal pH using $pH = -\log\{[H^+]\}$. When the ion concentration is high enough, the interaction between ions tends to influence the activity. According to the Debye-Hückel model, the ion activity is proportional to ion concentration, i.e.,

$$a(H^+) = f(H^+) \cdot [H^+]. \quad (12)$$

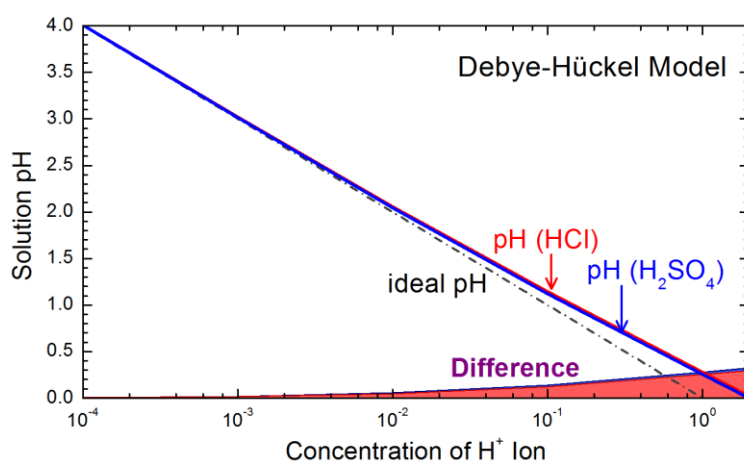
The activity coefficient $f(H^+)$ is calculated using

$$\log(f) = \frac{-0.509 \cdot q^2 \cdot \sqrt{I}}{1 + \sqrt{I}}, \quad (13)$$

where q is the ion charge ($= +1$ for H^+), and I is the ionic strength. I is calculated using

$$I = \frac{1}{2} \sum_i c_i \cdot q_i^2, \quad (14)$$

where c_i and q_i are the concentration and charge of the i th ion, and the summation should run over all the influential ions in the solution ($q = +1$ for H^+ , -1 for Cl^- , -2 for SO_4^{2-}). The calculated pH values for both HCl and H_2SO_4 solutions at different $[H^+]$ s are shown in the **Supplementary Figure 11**. It can be seen that the ion-ion interaction only brings a small variation in pH at $[H^+]$ of < 0.1 M ($pH > 1.0$). The solutions used in the experiments shown in Figure 1 (see main text) is 0.1 M H_2SO_4 ($[H^+] = 0.2$ M), and the pH value is calculated to be 0.88, slightly higher than the ideal pH of 0.70.

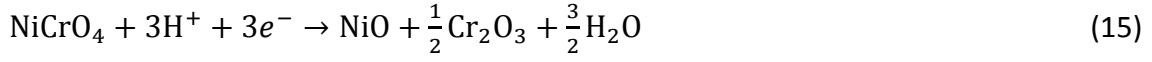


Supplementary Figure 11. The pH values for ideal, HCl, and H_2SO_4 solutions.

(4) Relative Electrochemical Stability of NiCrO₄

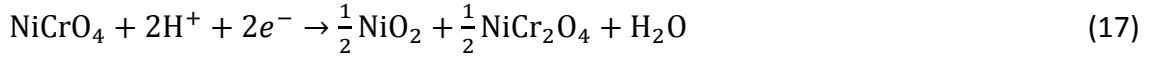
The relative stability of the metastable binary-metal oxide NiCrO₄ under electrochemical conditions can be well reflected by calculating the $\Delta\mu$ values for its possible reactions into different combinations of mono-metal species. Three reaction paths and the corresponding $\Delta\mu$ values are described below, for which the numerical results are shown in Figure 5 (see main text).

Path 1: Transition into NiO plus Cr₂O₃



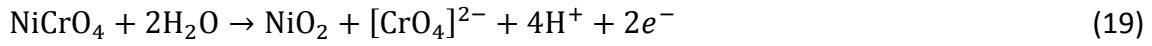
$$\begin{aligned} \Delta\mu = & \mu_0[\text{NiO}] + \frac{1}{2}\mu_0[\text{Cr}_2\text{O}_3] + \frac{3}{2}\mu_0[\text{H}_2\text{O}] - \mu_0[\text{NiCrO}_4] \\ & + 3k_B T \cdot \ln(10) \cdot \text{pH} + 3|e| \cdot U \end{aligned} \quad (16)$$

Path 2: Transition into NiO₂ plus NiCr₂O₄



$$\begin{aligned} \Delta\mu = & \frac{1}{2}\mu_0[\text{NiO}_2] + \frac{1}{2}\mu_0[\text{NiCr}_2\text{O}_4] + \mu_0[\text{H}_2\text{O}] - \mu_0[\text{NiCrO}_4] \\ & + 2k_B T \cdot \ln(10) \cdot \text{pH} + 2|e| \cdot U \end{aligned} \quad (18)$$

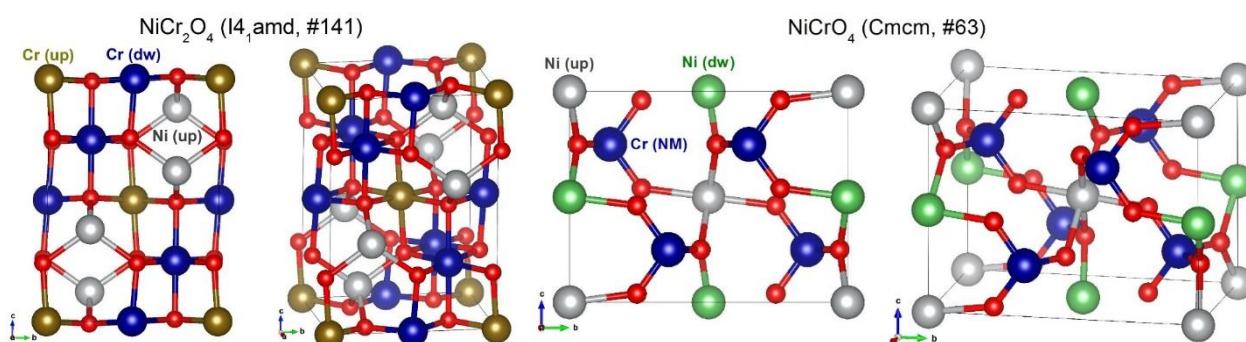
Path 3: Transition into NiO₂ plus [CrO₄]²⁻



$$\begin{aligned} \Delta\mu = & \mu_0[\text{NiO}_2] + \frac{1}{2}\mu_0[\text{CrO}_4^{2-}] - 2 \cdot \mu_0[\text{H}_2\text{O}] - \mu_0[\text{NiCrO}_4] \\ & - 4k_B T \cdot \ln(10) \cdot \text{pH} - 2|e| \cdot U \end{aligned} \quad (20)$$

(J) Supplementary Unit Cells of NiCr₂O₄ and NiCrO₄

The databases of ICSD [15], OQMD [16], and Materials Project [17] are referred to for the initial atomic structures of Ni and Cr oxides, hydroxides, and oxyhydroxides, which are then optimized by DFT calculations using PBE [18] and HSE06 [19] functionals, subsequently. The detailed information about the most stable structures and magnetic configurations of NiO, NiO₂, Ni(OH)₂, NiOOH, Cr₂O₃, CrO₂, and CrOOH have been listed in our previous publications [13,20], and the most stable atomic structures and magnetic configurations for the binary-metal oxides (NiCr₂O₄ and NiCrO₄) are described in detail below.



Supplementary Figure 12. Front and perspective views of the unit cells of NiCr₂O₄ and NiCrO₄.

NiCr₂O₄: $a = 6.011$, $b = 5.830$, $c = 8.226$ Å

Atom	Fractional Coordinates			M (μ_B)
Ni	0.000000	0.249474	0.378662	+1.7
Ni	0.000000	0.751248	0.620540	+1.7
Ni	0.500000	0.748701	0.879792	+1.7
Ni	0.500000	0.250287	0.122672	+1.7
Cr	0.000000	-0.000287	-0.000358	+2.8
Cr	0.500011	0.000629	0.500666	-2.8
Cr	0.249161	0.750145	0.249784	-2.8
Cr	0.749179	0.249868	0.749613	-2.8
Cr	0.250822	0.249868	0.749609	-2.8
Cr	0.750848	0.750139	0.249783	-2.8
Cr	0.500000	0.500000	0.500857	+2.8
Cr	0.000000	0.499883	0.000092	-2.8
O	0.000000	0.524555	0.239934	0
O	0.000000	0.477513	0.758391	0
O	0.500000	0.476613	0.741996	0
O	0.500000	0.524723	0.259416	0
O	0.724210	0.750918	0.491880	0
O	0.278738	0.249690	0.509918	0
O	0.776030	0.250048	0.989934	0

O	0.222192	0.749153	0.008733	0
O	0.777806	0.749150	0.008734	0
O	0.223968	0.250046	0.989936	0
O	0.721272	0.249694	0.509912	0
O	0.275808	0.750916	0.491866	0
O	0.500000	0.023319	0.740867	0
O	0.500000	0.976358	0.259384	0
O	0.000000	0.974970	0.240221	0
O	0.000000	0.022370	0.757160	0

NiCrO₄: $a = 5.457$, $b = 8.245$, $c = 6.207$ Å

Atom	Fractional Coordinates			M (μ_B)
Ni	0.000000	0.000000	0.000000	+1.7
Ni	0.000000	0.000000	0.500000	-1.7
Ni	0.500000	0.500000	0.000000	-1.7
Ni	0.500000	0.500000	0.500000	+1.7
Cr	0.000000	0.355292	0.250000	0
Cr	0.000000	0.644707	0.750000	0
Cr	0.500000	0.855291	0.250000	0
Cr	0.500000	0.144707	0.750000	0
O	0.000000	0.241636	0.040890	0
O	0.000000	0.758365	0.959110	0
O	0.000000	0.758365	0.540892	0
O	0.000000	0.241635	0.459108	0
O	0.500000	0.741634	0.040889	0
O	0.500000	0.258367	0.959112	0
O	0.500000	0.258367	0.540891	0
O	0.500000	0.741633	0.459109	0
O	0.246480	0.971298	0.250003	0
O	0.753520	0.028702	0.749997	0
O	0.753520	0.971298	0.250003	0
O	0.246480	0.028702	0.749997	0
O	0.746481	0.471301	0.250000	0
O	0.253519	0.528699	0.750000	0
O	0.253519	0.471301	0.250000	0
O	0.746481	0.528699	0.750000	0

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