Supporting Information

Calculation of the activity coefficient (γ) and references of interaction parameters.

The activity coefficient γ for element M in an Al–M binary alloy was obtained using Equation (S1) and the thermodynamically assessed Redlich-Kister parameter $\Omega_{\mathrm{Al-M}}$ for the Al–M binary system. Table S1 shows references [S1–S37] for the calculation of γ, Table S2 shows standard Gibbs energy of oxidation and chlorination reaction, and Table S3 shows vapor pressures of metals:

$$RT \ln \gamma_{\mathrm{M}} = {}^{0}\Omega_{\mathrm{Al-M}} x_{\mathrm{Al}}^{2} + {}^{1}\Omega_{\mathrm{Al-M}} x_{\mathrm{Al}}^{2}(4x_{\mathrm{Al}} - 3) + {}^{2}\Omega_{\mathrm{Al-M}} x_{\mathrm{Al}}^{2}(2x_{\mathrm{Al}} - 1)(6x_{\mathrm{Al}} - 5) + {}^{3}\Omega_{\mathrm{Al-M}} x_{\mathrm{Al}}^{2}(2x_{\mathrm{Al}} - 1)^{2}(8x_{\mathrm{Al}} - 7) \tag{S1}$$

The standard Gibbs energy of oxide formation and the vapor pressure of pure elements were obtained from thermodynamic Tables [S38].

Table S1. References table for estimation of the activity coefficient.

Element	Reference	Element	Reference
Ag	[S1]	Mn	[S3,S20]
As, Ga	[S2,S3]	Na	[S21]
Au	[S4]	Nb	[S22]
B	[S5]	Ni	[S23]
Be	[S6]	Pb	[S3,S24]
Bi	[S7]	Pd	[S25]
Ca	[S3,S8]	Pt	[S26]
Ce	[S9]	Sb	[S27]
Co	[S10]	Sn	[S3,S28]
Cr	[S11]	Sr	[S29]
Cu, Si	[S3,S12]	Ta, V	[S30]
Dy, Gd, Ho	[S13]	Ti	[S31]
Fe, Zr	[S3,S14]	U	[S32]
Ge, Mg	[S3,S15]	Yb	[S33]
In	[S3,S16]	Zn, Y	[S3,S34]
Ir	[S17]	Cd	[S35]
La	[S18]	Hg	[S36]
Li	[S19]	W	[S37]

Table S2. The standard Gibbs energies of chloride formation of pure elements [S38].

Reaction	ΔG^0/J·mol^{-1}	Reaction	ΔG^0/J·mol^{-1}
Ag(l) + 1/2 Cl_2(g) = AgCl(l)	−115990 + 33.1T	Li(l) + 1/2 Cl_2(g) = LiCl(l)	−383552 + 54.0T
Al(l) + 3/2 Cl_2(g) = $AlCl_3$(l)	−668546 + 163.4T	Mg(l) + Cl_2(g) = $MgCl_2$(l)	−594415 + 111.9T
As(s) + 3/2 Cl_2(g) = $AsCl_3$(l)	−302369 + 145.2T	Mn(l) + Cl_2(g) = $MnCl_2$(l)	−445930 + 87.6T
Au(l) + 1/2 Cl_2(g) = AuCl(s)	−48247 + 80.3T	Na(l) + 1/2 Cl_2(g) = NaCl(l)	−426633 + 105.5T
B(s) + Cl_2(g) = BCl_2(g)	−80169 + 42.2T	Nb(l) + Cl_2(g) = $NbCl_2$(s)	−429506 + 141.2T
Be(l) + Cl_2(g) = $BeCl_2$(l)	−479508 + 122.2T	Ni(l) + Cl_2(g) = $NiCl_2$(s)	−318596 + 154.5T
Bi(l) + 3/2 Cl_2(g) = $BiCl_3$(l)	−350039 + 155.3T	Pb(l) + Cl_2(g) = $PbCl_2$(l)	−324163 + 102.9T
Ca(l) + Cl_2(g) = $CaCl_2$(l)	−759317 + 118.9T	Pd(l) + Cl_2(g) = $PdCl_2$(l)	−181232 + 122.2T
Cd(l) + Cl_2(g) = $CdCl_2$(l)	−392786 + 154.6T	Pt(l) + Cl_2(g) = $PtCl_2$(s)	−123623 + 46.5T
Ce(l) + 3/2 Cl_2(g) = $CeCl_3$(l)	−980929 + 173.2T	Sb(l) + 3/2 Cl_2(g) = $SbCl_3$(l)	−420609 + 210.8T
Co(l) + Cl_2(g) = $CoCl_2$(l)	−268739 + 84.2T	Sn(l) + Cl_2(g) = $SnCl_2$(l)	−310534 + 105.4T
Cr(l) + Cl_2(g) = $CrCl_2$(l)	−365290 + 87.8T	Si(l) + Cl_2(g) = $SiCl_2$(g)	−220359 − 5.9T
Cu(l) + 1/2 Cl_2(g) = CuCl(l)	−146215 + 30.8T	Sr(l) + Cl_2(g) = $SrCl_2$(l)	−799640 + 129.7T
Dy(l) + 3/2 Cl_2(g) = $DyCl_3$(l)	−959721 + 195.1T	Ta(l) + Cl_2(g) = $TaCl_3$(s)	−572391 + 216.7T
Fe(l) + Cl_2(g) = $FeCl_2$(l)	−302026 + 76.2T	Ti(l) + Cl_2(g) = $TiCl_2$(s)	−52510 + 162.7T
Ga(l) + 3/2 Cl_2(g) = $GaCl_3$(l)	−513269 + 210.2T	U(l) + 3/2 Cl_2(g) = UCl_2(l)	−812875 + 169.4T
Gd(l) + 3/2 Cl_2(g) = $GdCl_3$(l)	−960475 + 188.2T	V(l) + Cl_2(g) = VCl_2(s)	−467862 + 152.2T
Ge(l) + Cl_2(g) = $GeCl_2$(l)	−210245 − 7.3T	W(l) + Cl_2(g) = WCl_2(s)	−288374 + 122.4T
Hg(l) + Cl_2(g) = $HgCl_2$(l)	−206519 + 109.5T	Y(l) + 3/2 Cl_2(g) = YCl_3(l)	−960194 + 188.0T
Ho(l) + 3/2 Cl_2(g) = $HoCl_3$(l)	−965130 + 200.3T	Yb(l) + Cl_2(g) = $YbCl_2$(s)	−801829 + 144.5T
In(l) + 3/2 Cl_2(g) = $InCl_3$(s)	−531996 + 240.7T	Zn(l) + Cl_2(g) = $ZnCl_2$(l)	−411693 + 142.4T
Ir(s) + 3/2 Cl_2(g) = $IrCl_3$(s)	−268113 + 255.4T	Zr(l) + Cl_2(g) = $ZrCl_2$(l)	−412629 + 114.8T
La(l) + 3/2 Cl_2(g) = $LaCl_3$(l)	−994064 + 170.9T	–	

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