Recycling alloy scraps and CO_2 by paired molten salt electrolysis

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Supplementary table and figure captions:

Table S1. Standard reduction potential E^{θ} for involved redox reactions in molten $CaCl_2$-NaCl, calculated from thermodynamic data ($E_{Ca^{2+}/Ca} = 0$) at 700°C obtained from HSC Chemistry 6.0

Reactions	E^{θ}(V)
$Ca + FeCl_2 = Fe + CaCl_2$	2.216
$Ca + NiCl_2 = Ni + CaCl_2$	2.535
$Ca + CrCl_2 = Cr + CaCl_2$	1.933
$Ca+CoCl_2 = Co+CaCl_2$	2.422
$Ca + MnCl_2 = Mn + CaCl_2$	1.516
$Ca + MoCl_2 = Mo + CaCl_2$	2.617
$Ca + 2CuCl = 2Cu + CaCl_2$	2.392
$Ca + Cl_2(g) = CaCl_2$	3.363

Table S2. Standard reduction potential E^{θ} for involved redox reactions in molten $CaCl_2$-NaCl-$CaCO_3$, calculated from thermodynamic data ($E_{Ca^{2+}/Ca} = 0$) at 700°C obtained from HSC Chemistry 6.0

Reactions	E^{θ}(V)
$CaCO_3 + Fe = Ca + FeO + CO_2(g)$	1.862
$CaCO_3+Ni=Ca+NiO+CO_2(g)$	2.121
$CaCO_3 + Co = Ca + CoO + CO_2(g)$	2.045
$3CaCO_3+2Cr=3Ca+Cr_2O_3+3CO_2(g)$	1.386
$CaCO_3 + Mn = Ca + MnO + CO_2(g)$	1.278
$2CaCO_3 + Mo = 2Ca + MoO_2 + 2CO_2(g)$	1.838
$CaCO_3 + 2Cu = Ca + Cu_2O + CO_2(g)$	2.397
$2CaCO_3 = 2Ca + 2CO_2(g) + O_2(g)$	2.903

Table S3. The composition of the Hard-alloy.

Elements	Fe	Cr	Ni	Co	Cu	Mn	others
Composition (wt%)	57.03	12.38	8.15	1.96	0.63	6.18	13.67

Table S4 The element composition and content (wt%) table of oxide powder (A) after oxidation process, (B) water-leaching and (C) sulfation roasting products.

Elements Products	Fe	Cr	Ni	Co	Mn	Cu
A	15.81	5.82	2.83	0.73	1.90	0.18
B	45.43	14.86	6.45	1.16	3.93	0.32
C	20.51	4.65	2.03	0.65	1.92	0.21

Elements Products	O	S	Ca	Na	Cl	C
A	23.24	0	13.42	1.34	24.13	8.75
B	20.25	0	0.69	0	0	5.58
C	41.21	21.32	0.57	0	0	0

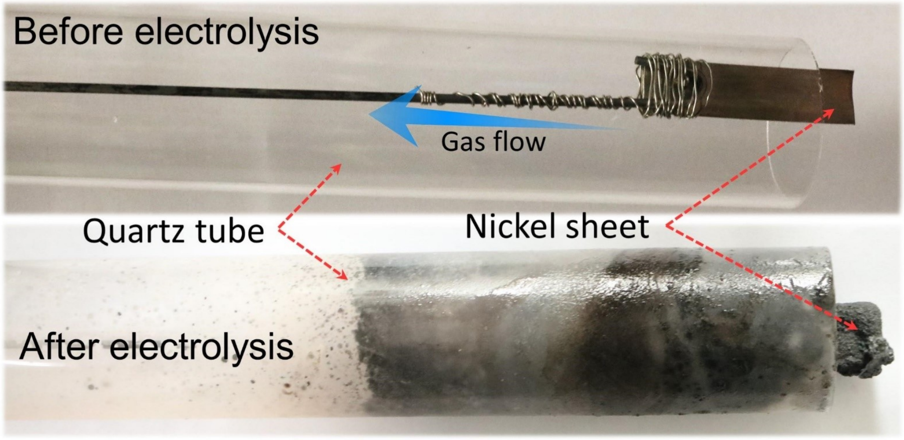
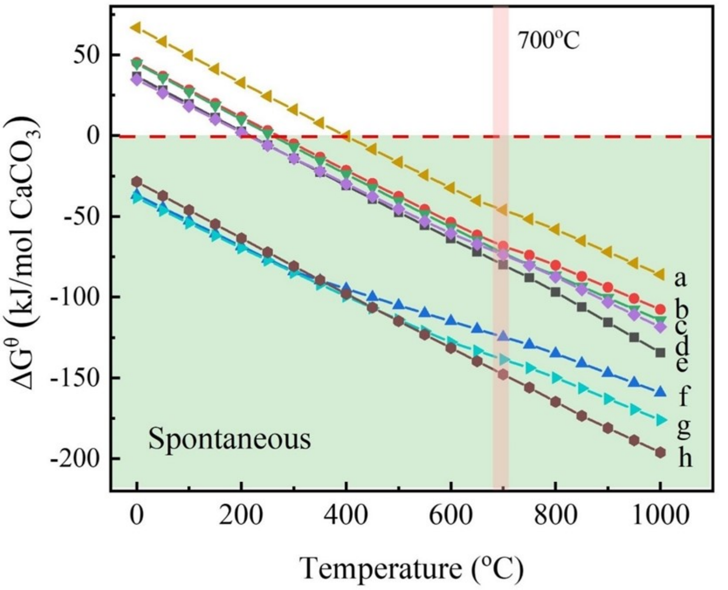


Fig. S1 Digital images of home-made quartz tube for collecting cathode gas products before and after electrolysis



a: $MnCl_2 + CaCO_3 = CaCl_2 + MnO + CO_2(g)$;

b: $FeCl_2 + CaCO_3 = CaCl_2 + FeO + CO_2(g)$;

c: $CoCl_2 + CaCO_3 = CaCl_2 + CoO + CO_2(g)$;

d: $CuCl_2 + CaCO_3 = CaCl_2 + CuO + CO_2(g)$;

e: $NiCl_2 + CaCO_3 = CaCl_2 + NiO + CO_2(g)$;

f: $2/3FeCl_3 + CaCO_3 = CaCl_2 + 1/3Fe_2O_3 + CO_2(g)$;

g: $2/3MnCl_3 + CaCO_3 = 1/3Mn_2O_3 + CaCl_2 + CO_2(g)$;

h: $2/3CrCl_3 + CaCO_3 = 1/3Cr_2O_3 + CaCl_2 + CO_2(g)$

Fig. S2 Gibbs energy change as a function of the temperature of the reactions between metal chloride and calcium carbonate.

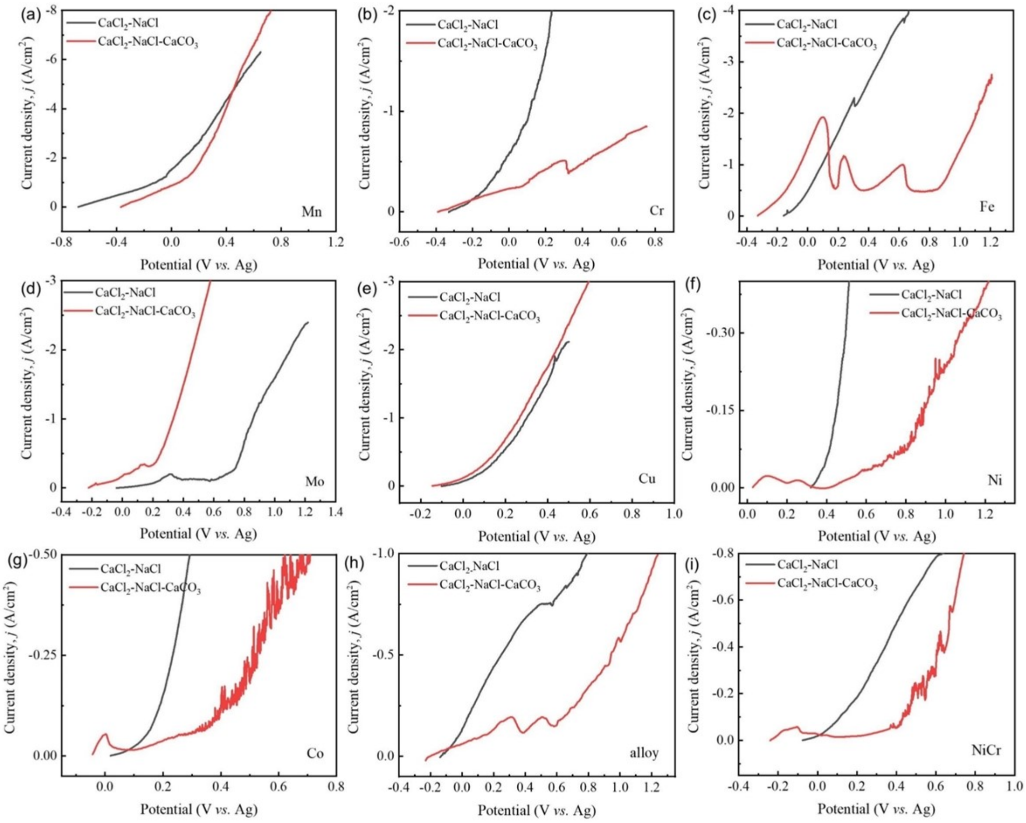


Fig. S3 Polarization curves of various metals in molten CaCl$_2$-NaCl and molten NaCl-CaCl$_2$-CaCO$_3$ (a = Mn, b = Cr, c = Fe, d = Mo, e = Cu, f = Ni, g = Co, h = hard-alloy and i = NiCr).

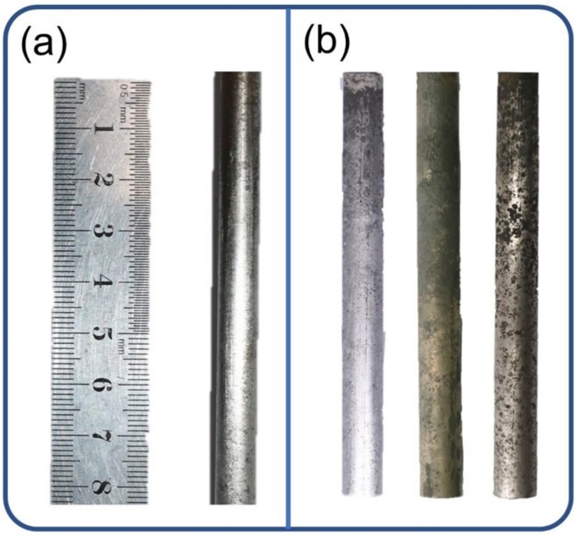


Fig. S4 Digital photos of (a) hard-alloy and (b) before and after oxidation in air at 700 ^oC for 6 h.

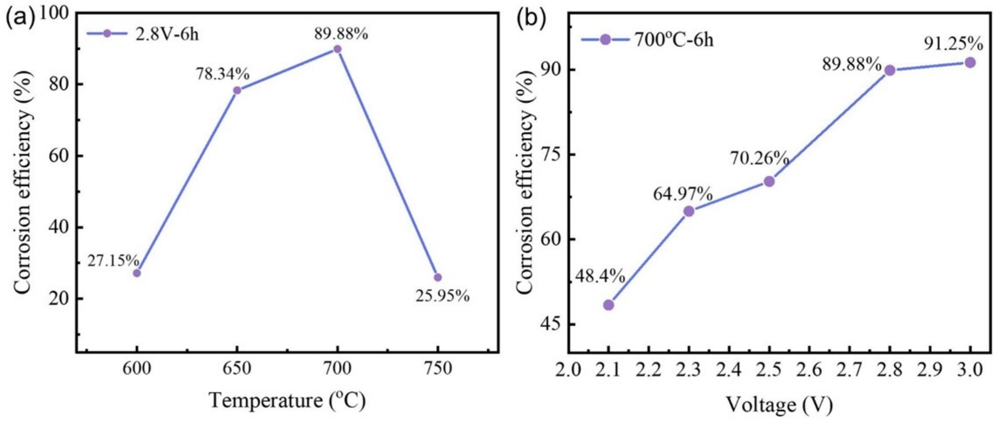


Fig. S5 Profiles of the corrosion efficiency (a) at different electrolysis temperatures and (b) the different cell voltages.

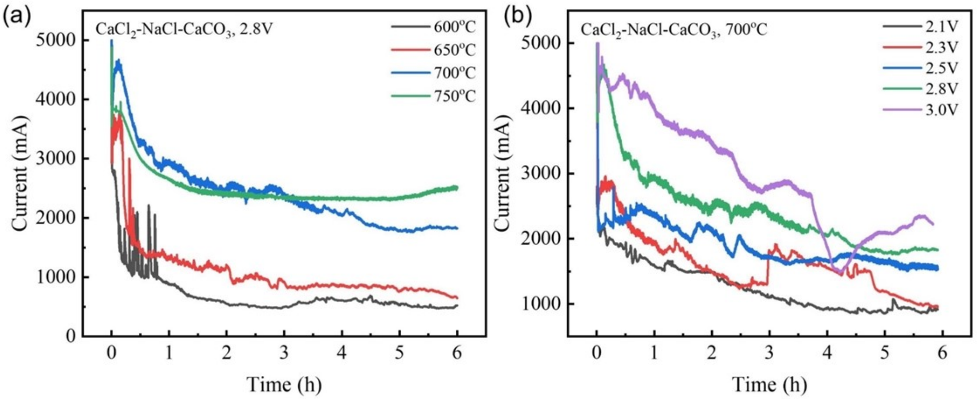


Fig. S6 I-t curves during the electrolysis of hard-alloy in molten $CaCl_2$-NaCl-$CaCO_3$ (a) at different temperatures (cell voltage was maintained at 2.8 V) and (b) at different cell voltages (electrolysis temperature was 700 °C) for 6h.

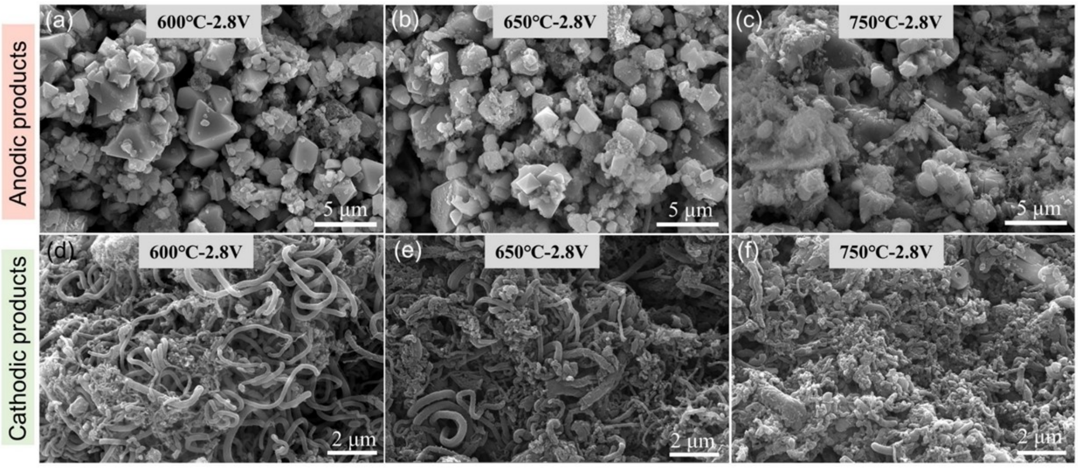


Fig. S7 SEM images of (a) anode products and (b) cathode products at different temperatures at 2.8 V for 6 h with hard-alloy as the anode and nickel sheet as the cathode.

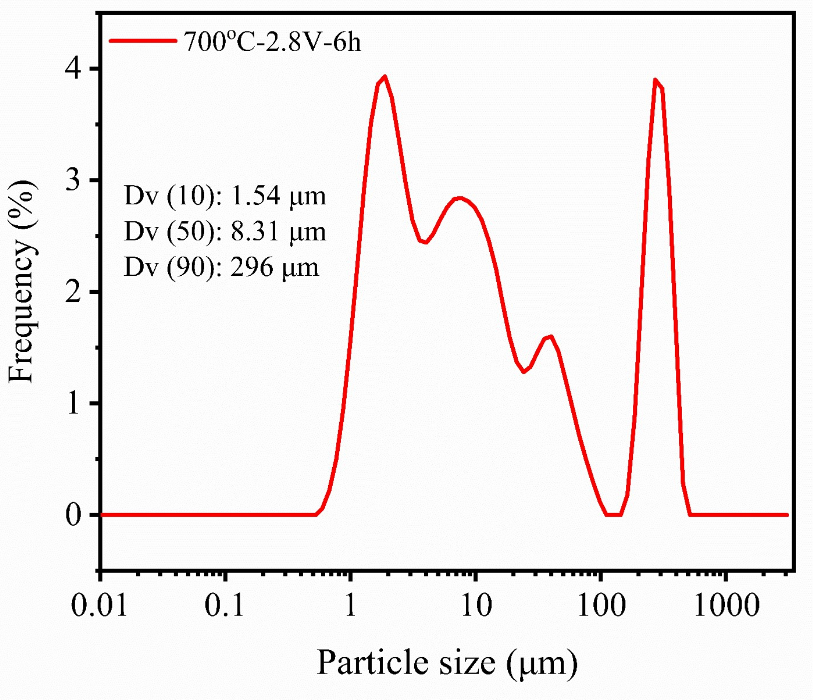


Fig. S8 Particle size distribution of the products after electrochemical oxidation of alloy scraps.

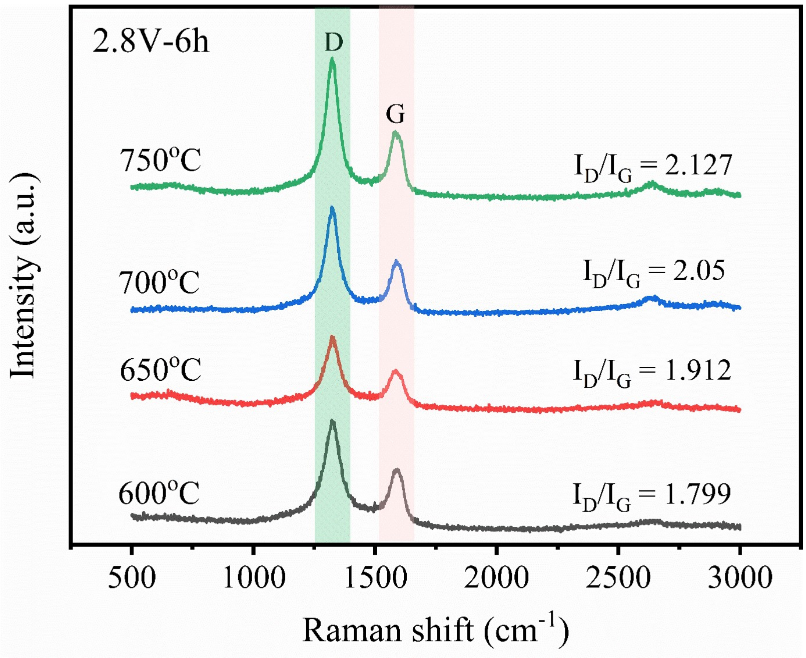


Fig. S9 Raman spectra of the cathode products at 2.8V for 6h.

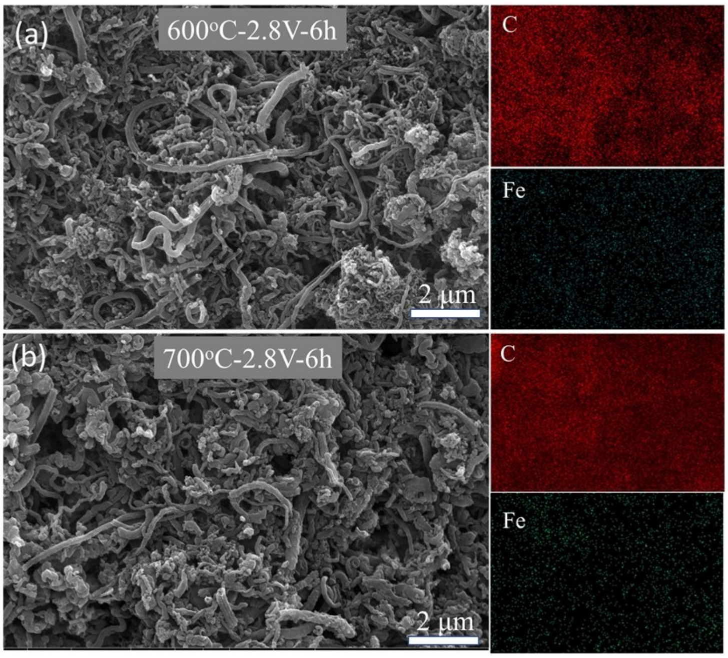


Fig. S10 SEM images and EDS element mapping of the cathode products at (a) 700 °C and (b) 600 °C, 2.8V for 6h.

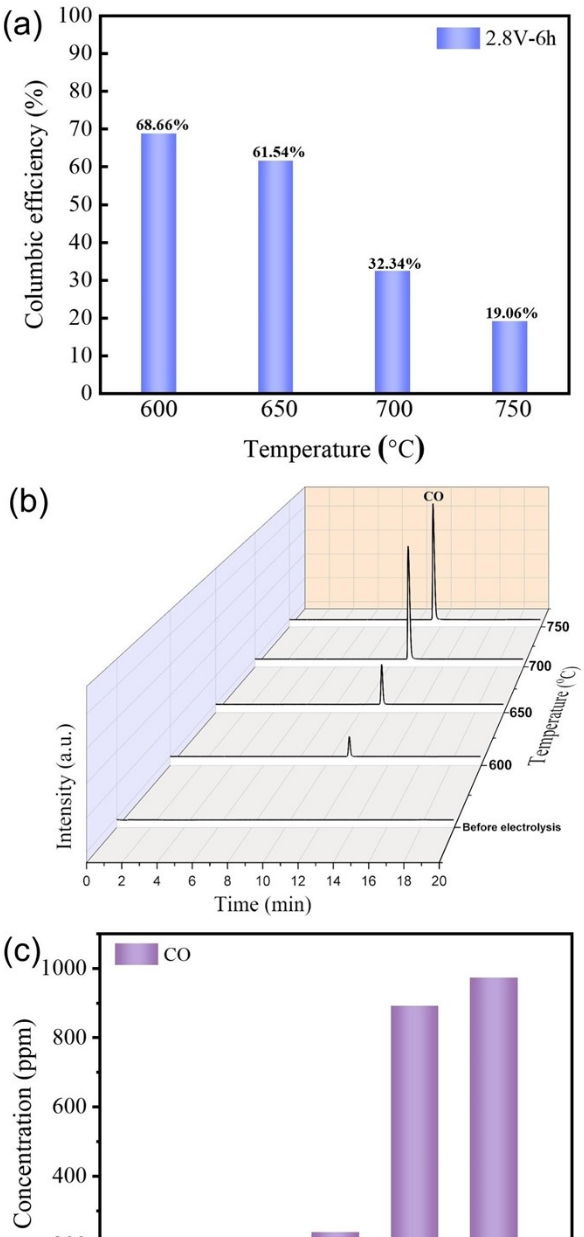


Fig. S11 (a) Bar graph of Columbic efficiency of cathode products carbon, (b) gas chromatograms of the outlet gas before and during electrolysis at different temperatures, and (c) bar graph of the CO content obtained under different temperatures at 2.8V for electrolysis time of 3h.

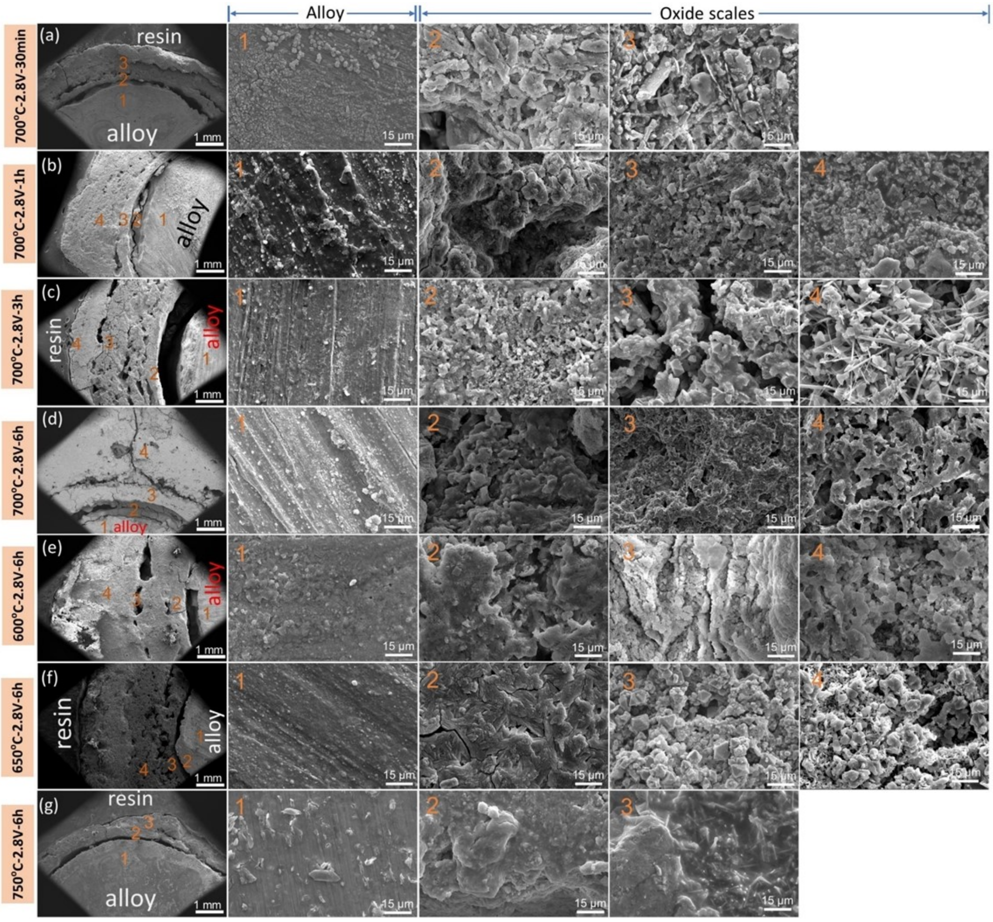


Fig. S12 SEM images of the cross section and the morphology at different areas (from left to right corresponding to the alloy substrate towards the oxides scale) of the alloy oxidation products in molten NaCl-$CaCl_2$ with 10wt% $CaCO_3$ at 700 ^{o}C, 2.8 V for (a) 30 min, (b) 1 h, (c) 3 h, (d) 6 h and at (e) 600 ^{o}C, (f) 650 ^{o}C, (g) 750 ^{o}C and 2.8 V for 6 h.

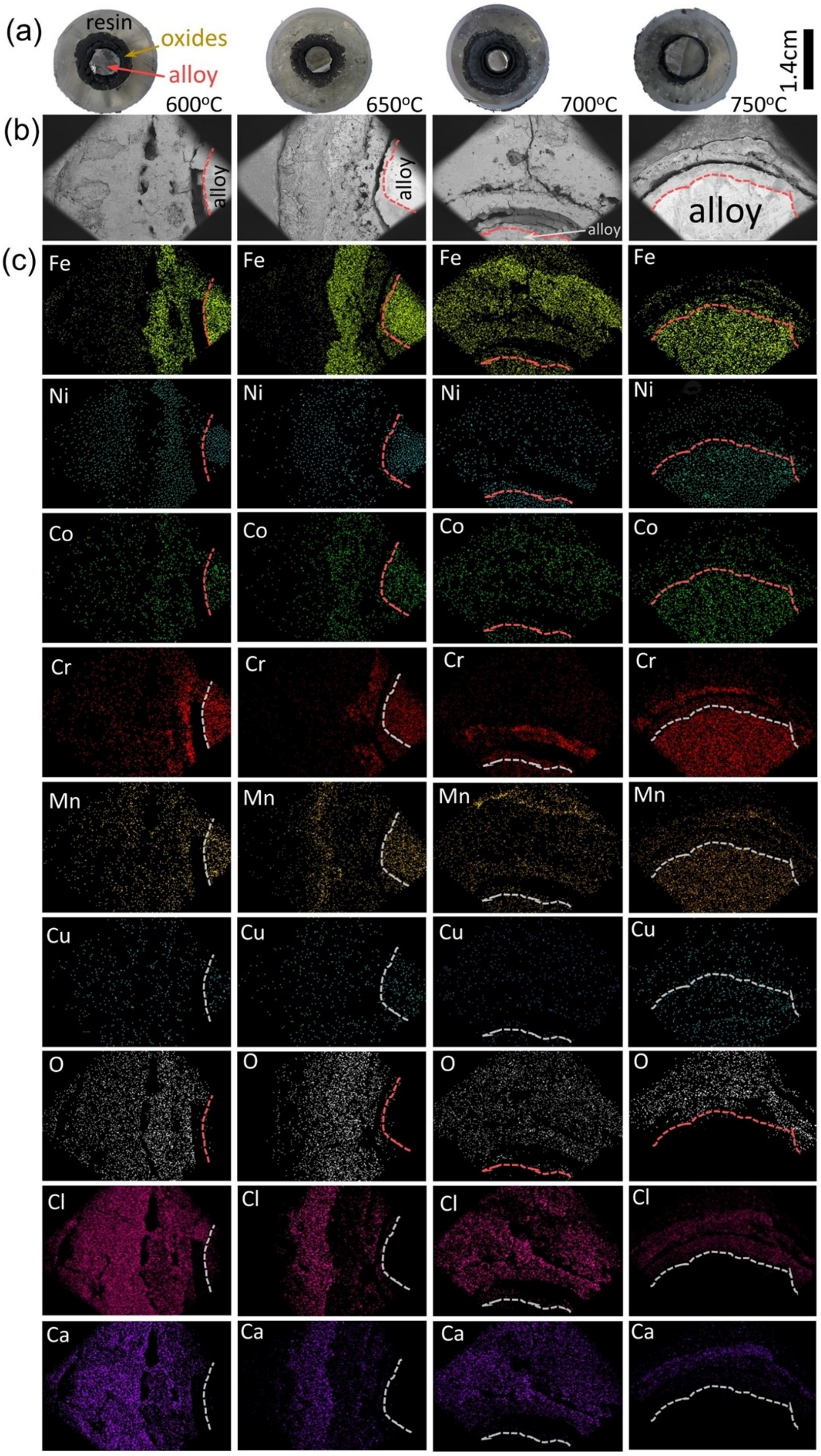


Fig. S13 (a) Digital photos, (b) SEM images, and (c) EDS mappings of the cross sections of the hard-alloy oxidation products after electrolysis at 600, 650, 700, and 750 °C for 6 h at 2.8 V in molten $CaCl_2$-NaCl with 10wt% $CaCO_3$.

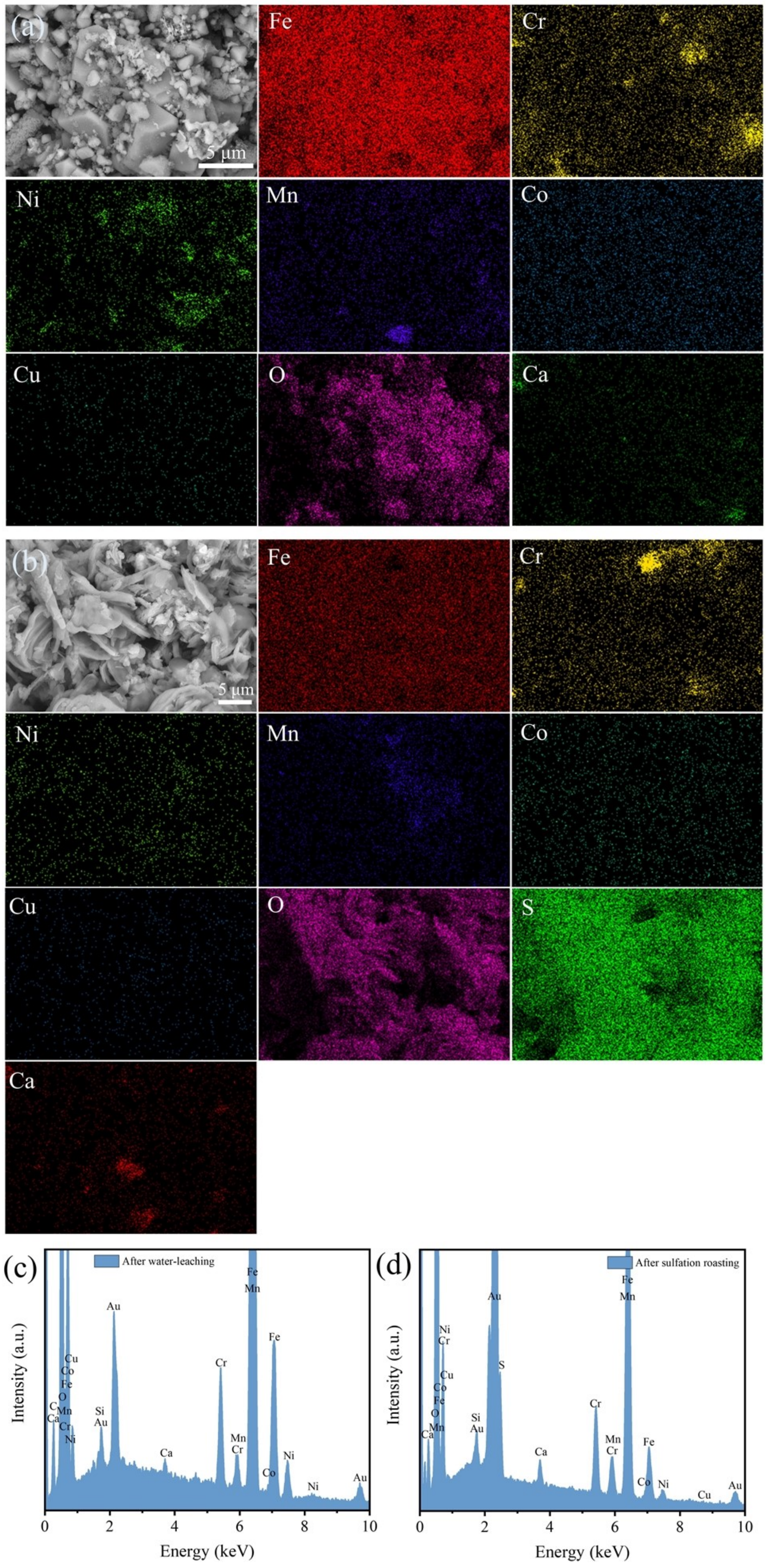


Fig. S14 SEM images and EDS mapping of the anode products after (a, c) water-leaching and (b,

d) sulfation roasting.

Details of economic assessment

The operational cost of this technology included reagents (e.g. electrolyte and sulfuric acid), material (e.g. electrode materials), and electricity (energy consumption for heating and holding process during molten salt electrolysis and sulfating roasting). The single experiment was calculated with 550 g molten salt electrolyte, in which 550 g molten salt was mixed with 500 g of $CaCl_2$-NaCl and 50 g of $CaCO_3$. The heating rate was calculated at 5 °C/min. The technological conditions for economic assessment were 700 °C, constant voltage electrolysis for 8 h at 2.8 V. The cost of sulfating roasting was calculated according to the experiment conditions: liquid-solid ratio of 0.8, roasting temperature of 150 °C and the roasting time of 4 hours. Note that the molten salt with mass of 550 g is capable of treatment for 185.3 g of alloy scraps. The assumption of the costs of electricity charge: the industrial electricity charge is \$0.158/kWh, and the energy consumption (E_p) is calculated as Equation S1.

$$E_p = P \times t \tag{S1}$$

Where the E_p is the energy consumption; P is the power of the vertical furnace; t is the time of heating or isothermal.

The reagent cost is calculated as Equation S2:

$$C_{reagent} = M \times U.P. \tag{S2}$$

Where the $C_{reagent}$ is cost of reagent; M is the mass of reagent; $U.P.$ is the unit price.

The specific costs are as follows:

$CaCl_2$: 337 g × \$4.72/kg=\$1.59;

NaCl: 163 g × \$2.03/kg=\$0.33;

$CaCO_3$: 50 g × \$10.54/kg=\$0.53;

Cathode material (Ni sheet): \$0.37;

Energy consumption for heating and holding process in molten salt electrolysis: 420 W × 2.5 h × \$0.158/kWh=0.17\$; 120 W × 80 h × \$0.158/kWh=\$1.52;

Total amount of sulfuric acid: 18.53 g × 0.8 ml/g × 10=148.24 ml;

Sulfuric acid cost: 148.24 ml × \$0.006/ml =\$0.89;

Energy consumption for heating and holding process during sulfating roasting:

420 W × 0.5 h × $0.158/kWh=$0.03; 120 W × 4 h × $0.158/kWh=$0.08;

The above costs add up to $5.51.

The price of product $NiSO_4·6H_2O$: 38.55 g × $82.28/500g=$6.34;

The price of product $CoSO_4·H_2O$: 8.78 g × $21.83/100g=$1.92;

The profit for entire processes (calculation for recovering 185.3g of alloy scraps): $6.34+$1.92-$5.51=$2.75;

The profit for recycling 1 kg of alloy scraps: $14.84.