

SUPPLEMENTARY MATERIAL FOR:

Low-pressure forming and reactive sintering for the synthesis of equimolar CoCrFeNi bulk alloys

Magdalena Lassinantti Gualtieri^{a*}, Elena Colombini^a, Enrico Paradisi^a, Cecilia Mortalò^b, Paolo Veronesi^a

^a *Department of Engineering “Enzo Ferrari”, University of Modena and Reggio Emilia, Via P. Vivarelli 10/1 - 41125 Modena, Italy*

^b *National Research Council of Italy - CNR, Institute of Condensed Matter Chemistry and Technologies for Energy – ICMATE, Corso Stati Uniti, 4, 35127 Padova, Italy*

* Corresponding author

FIGURES

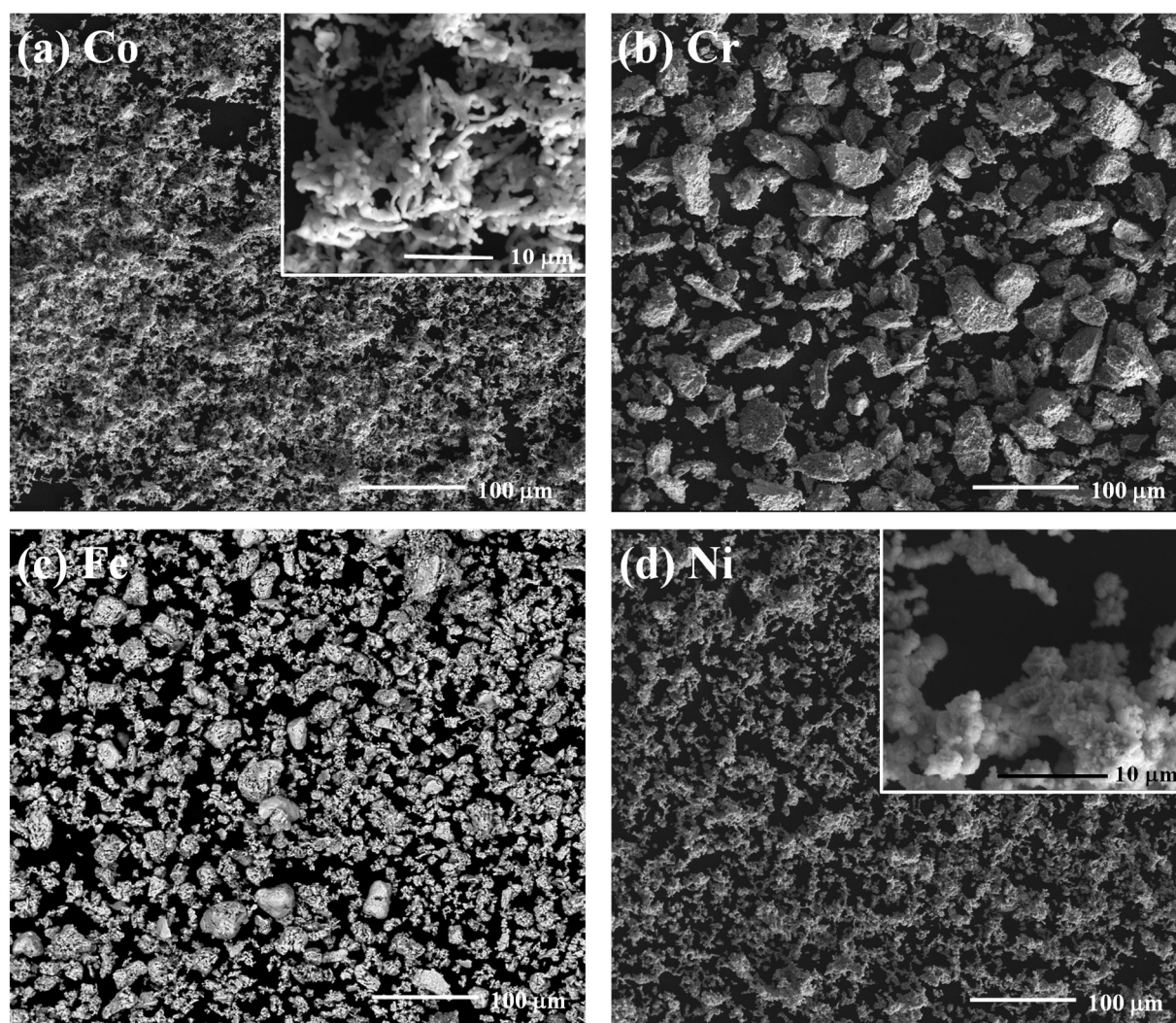


Figure S1. Backscattered electron SEM images of the as-purchased powder reagents. Images at higher magnifications are shown for Co and Ni in the inserts of (a) and (d), respectively.

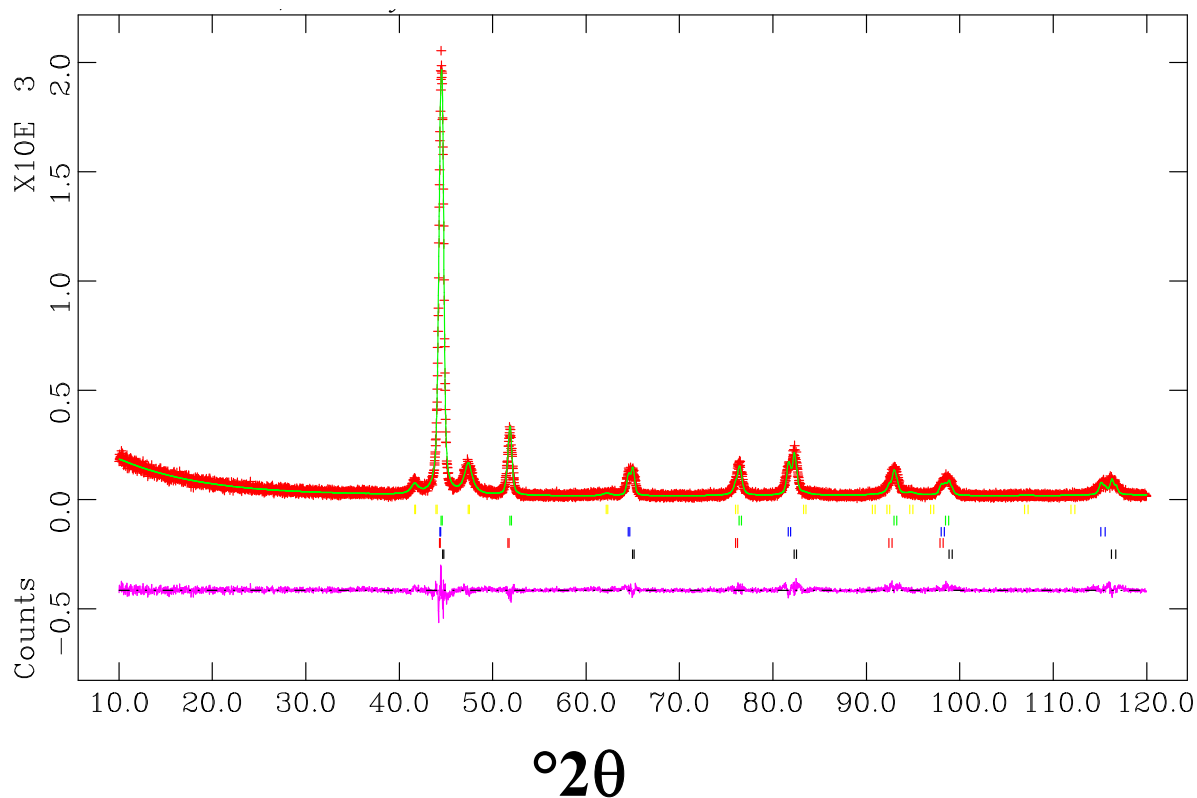


Figure S2. Graphical output, produced by GSAS, for the Rietveld refinement of equimolar CoCrFeNi base powder (elemental powders mixed by fast ball-milling). The graph shows the observed (red crosses), calculated (continuous line) and difference curves. The tick marks indicate positions of the Bragg reflections (from the bottom): Fe; Co (cubic); Cr, Ni, Co (hexagonal).

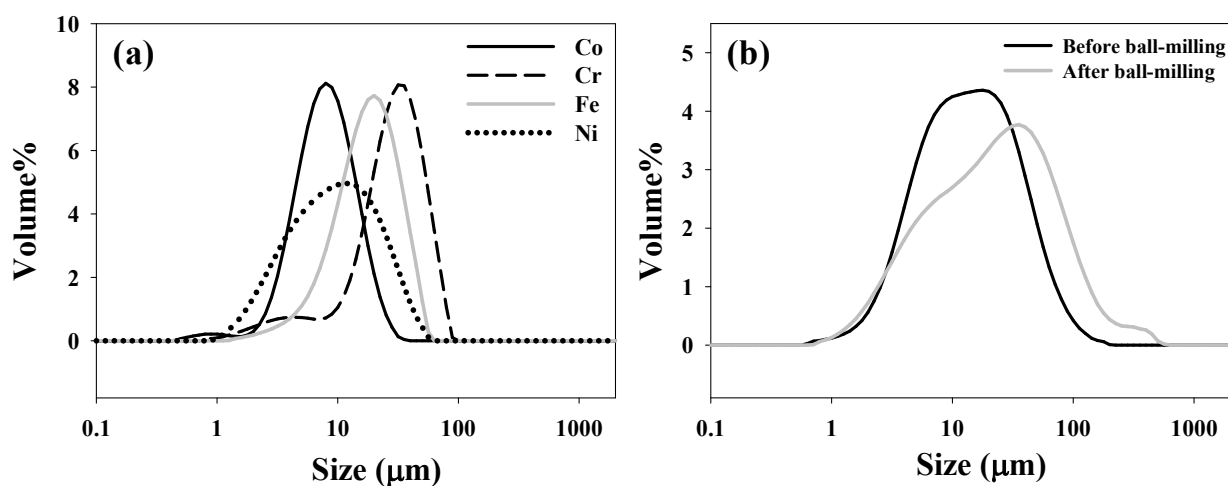


Figure S3. Particle size distribution of the as-purchased powders (a) and the powder mixtures (equimolar CoCrFeNi) before and after ball-milling for 1 h (b).

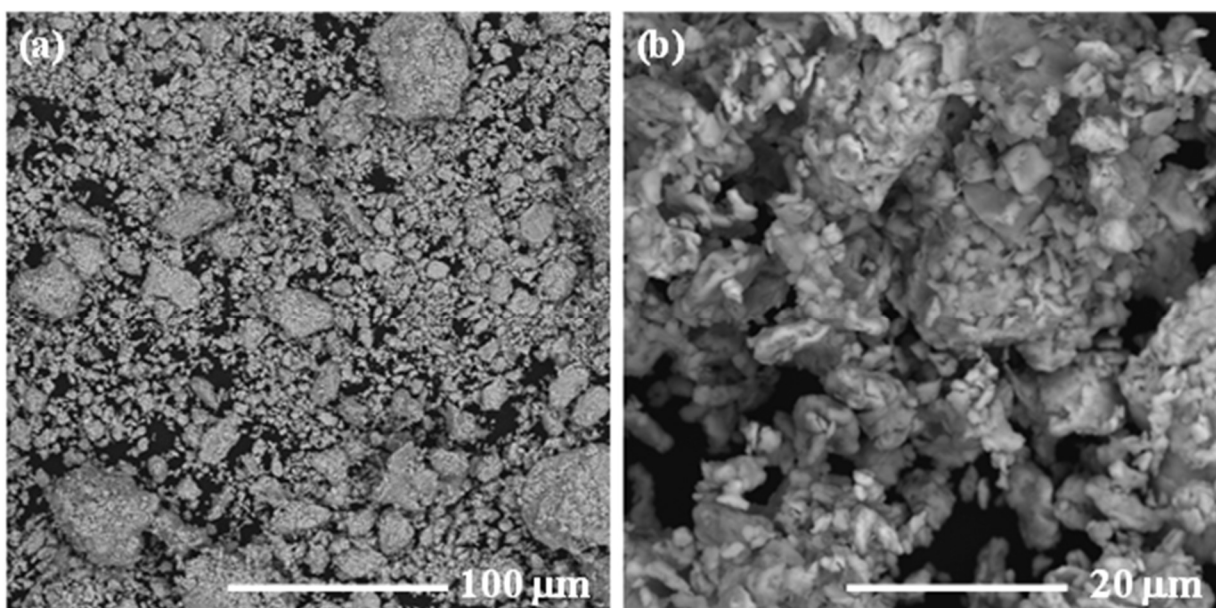


Figure S4. SEM images of the CoCrFeNi powder mixture (base powder) prepared by fast ball-milling of elemental powders before lubrication with stearic acid.

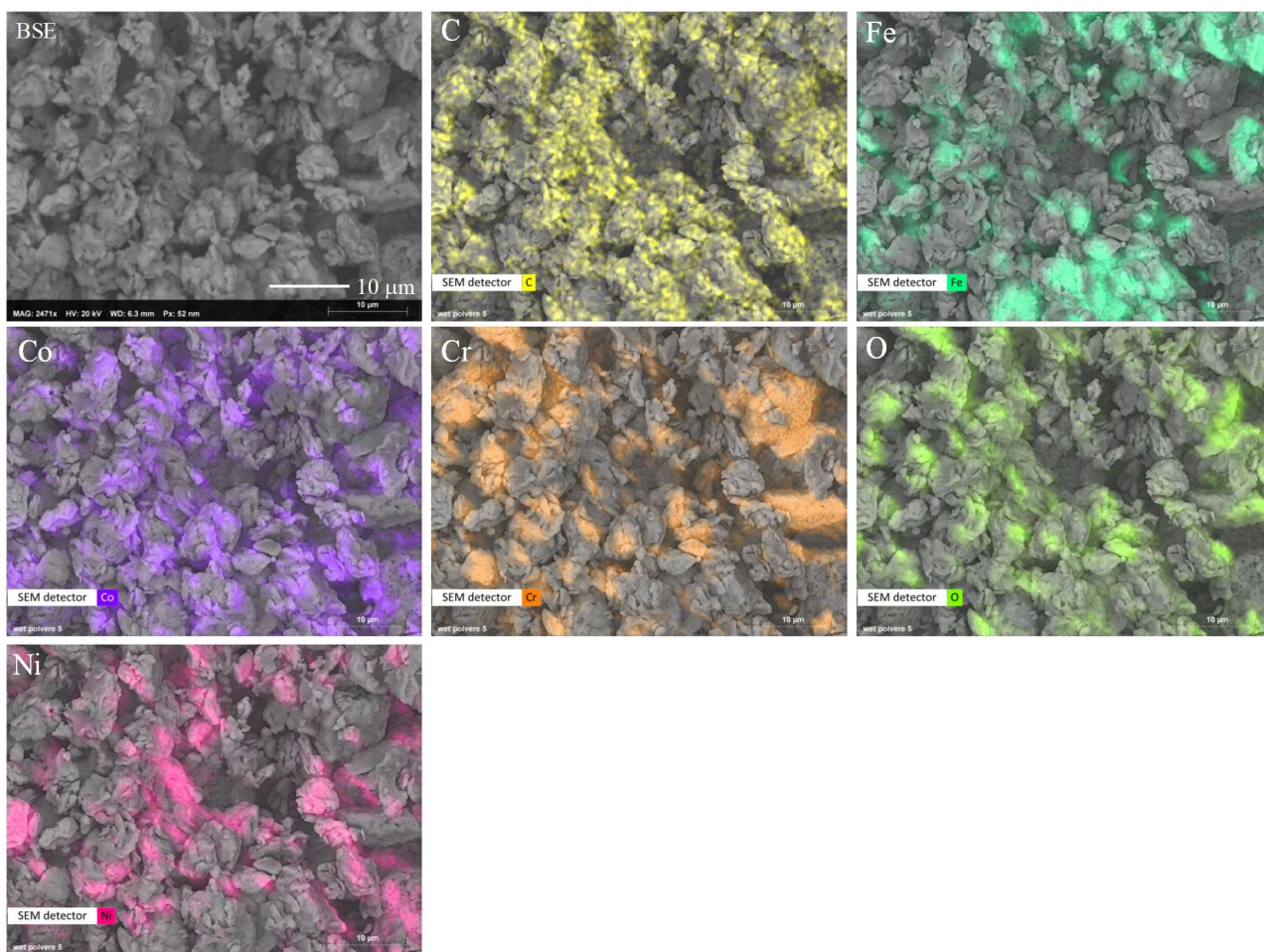


Figure S5. EDS elemental maps collected from the powder mixed with lubricant/binder (stearic acid) by the solvent-aided route. Observe an even distribution of the carbon and oxygen originating from the lubricant/binder. Oxygen is also found in association with chromium indicating some surface oxidation of this element.

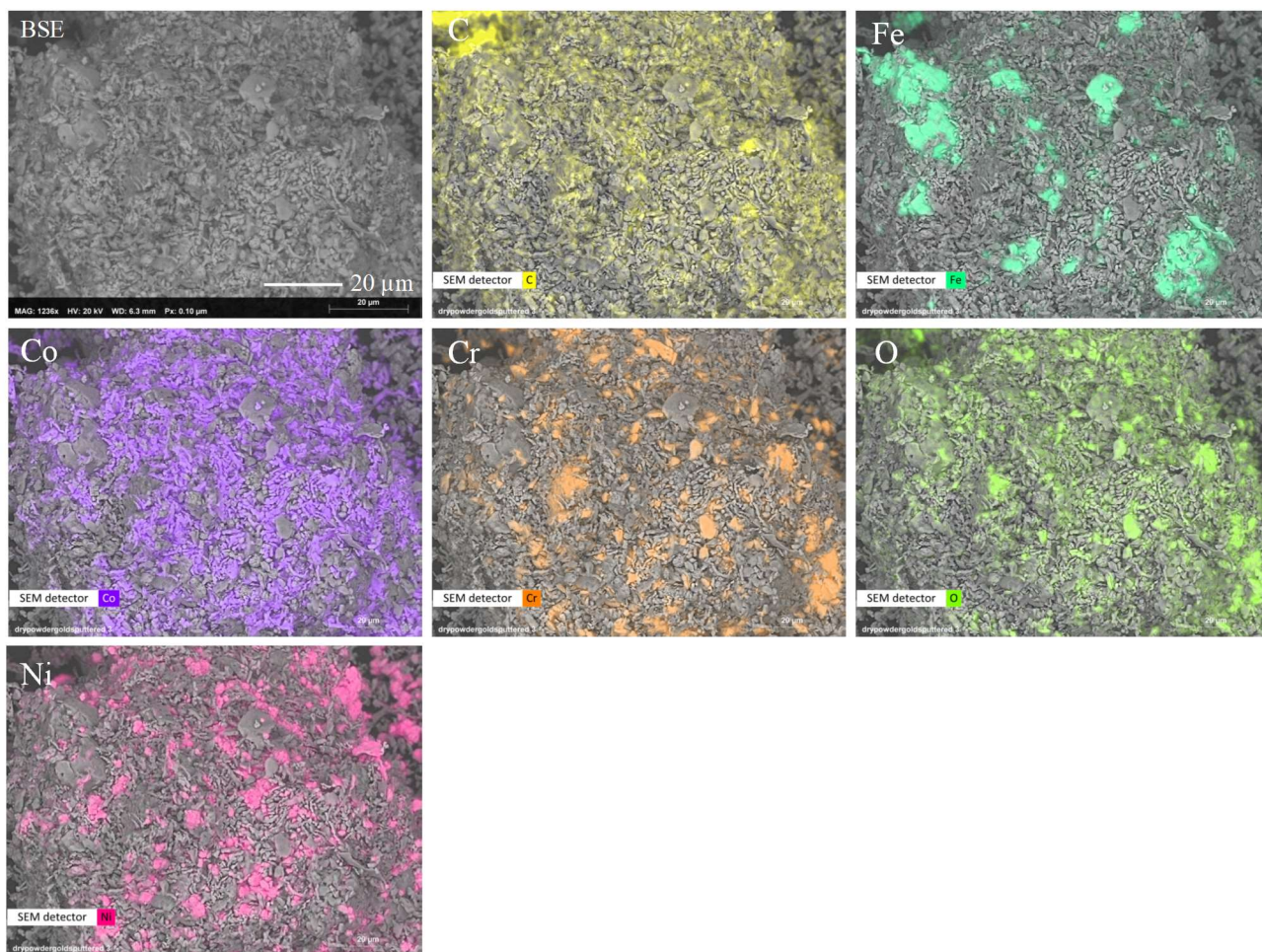


Figure S6. EDS elemental maps collected from a large agglomerate present in the powder prepared by mechanical mixing with the lubricant/binder (stearic acid).

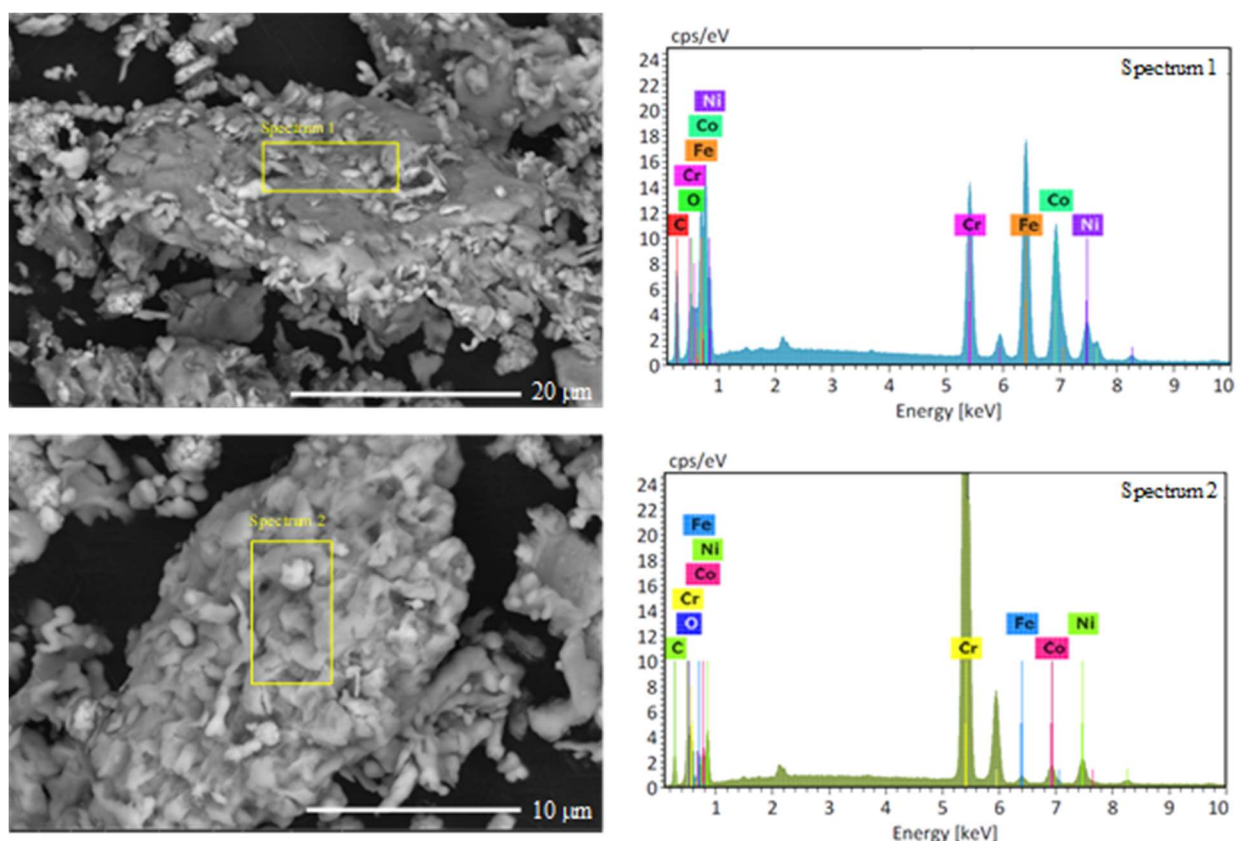


Figure S7. EDS area analyses of agglomerates identified in the powder mechanically mixed with lubricant/binder (stearic acid). The agglomerates are composed of intimately mixed metal particles and stearic acid.

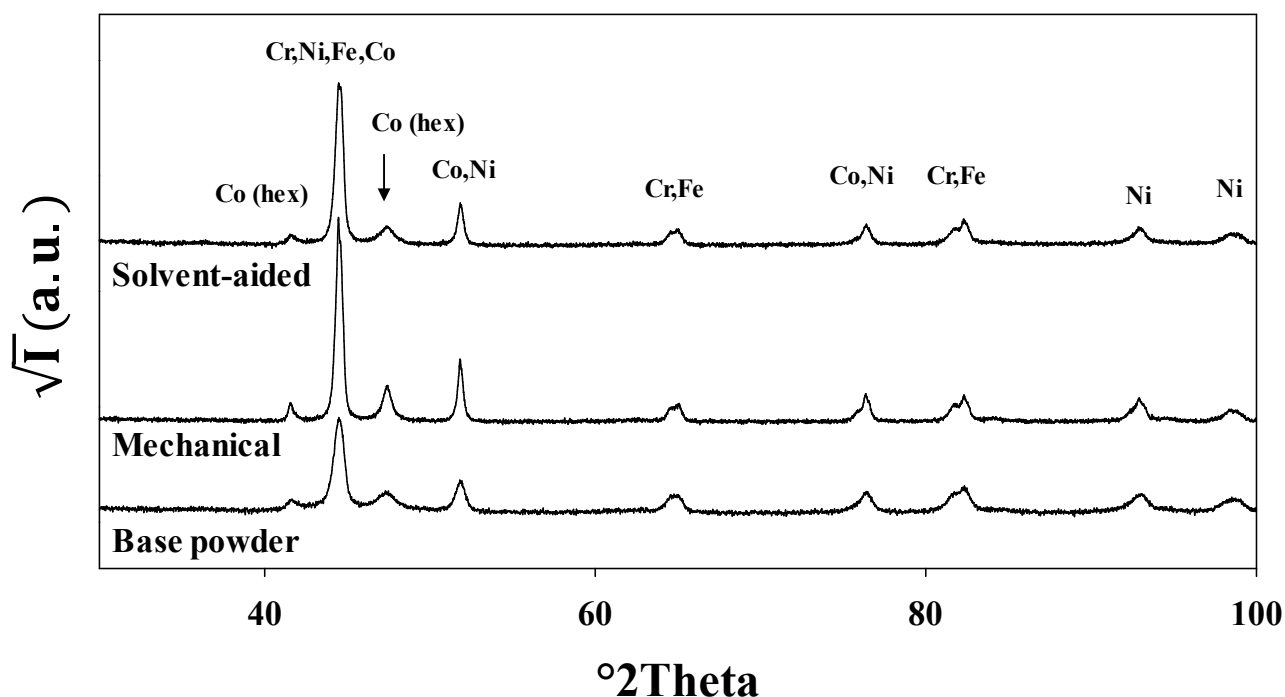


Figure S8. XRPD patterns collected from the CoCrFeNi as-mixed base powder and from powders after lubricant/binder (stearic acid) addition via either mechanical mixing or a solvent-assisted route. The diffractogram of the as-mixed base powder is shown for comparison. It was hypothesized that partial oxidation might occur during the admixing process. Mechanical mixing, although performed under Ar atmosphere, may expose fresh metallic surfaces that could become susceptible to oxidation during subsequent handling and pressing in air. In contrast, the solvent-assisted route involves treatment in a protonic solvent at moderate temperature, which could also potentially promote surface oxidation. As observed in the figure, no additional diffraction peaks attributable to newly formed oxide phases were detected in either case.

TABLES

Table S1. Results from the Rietveld refinement of equimolar CoCrFeNi mixed by ball-milling (wt%, unit cell and density (ρ) of each metal phase). The molar compositions, calculated from the refined wt%, are also reported. The agreement factors of the refinement were $R_{wp} = 15.81$; $R_p = 11.14$; $\chi^2 = 1.471$.

Phase	Wt%	At. %	Unit cell ($\text{\AA}$)	ρ (g/cm^3)
Co (cubic)	8.0 ± 0.4	7.6	$a = 3.5384 \pm 0.0006$	8.836
Cr	23.5 ± 0.3	25.5	$a = 2.8863 \pm 0.0001$	7.182
Fe	24.4 ± 0.3	24.6	$a = 2.8681 \pm 0.0001$	7.861
Ni	27.0 ± 0.3	25.9	$a = 3.5226 \pm 0.0002$	8.920
Co (hexagonal)	17.1 ± 0.1	16.4	$a = 2.5015 \pm 0.0006$; $c = 4.117 \pm 0.003$	8.772

Table S2. Numerical data extracted from particle size distribution curves collected by laser diffraction.

Sample	D-values (μm)		
	D10	D50	D90
Base powder	4.2	23.8	95.1
Solvent-aided	4.0	18.3	95.1
Solvent-aided-washed	3.7	17.5	72.6
Mechanical mixing	5.9	284.3	691
Mechanical mixing-washed	2.6	8.5	26.6