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Microwave-Assisted Preparation of Multi Principal Element Alloys by Powder Metallurgy Approach

Elena Colombini¹, Iuri Borromei², Lorenzo Trombi¹, Angelo Casagrande², Paolo Veronesi¹

¹ Department of Engineering “Enzo Ferrari”, University of Modena and Reggio Emilia, Via Vivarelli 10, 41125 Modena

² Department of Industrial Engineering, University of Bologna, Viale Risorgimento 4, 40137 Bologna

Abstract

According to literature, the synthetic route to produce High entropy alloys (HEAs) should guarantee short alloying time, efficient cooling and capability to operate in controlled atmosphere. Such conditions can be achieved using high frequency electromagnetic fields, like microwave heating. In this work FeCoNiCrAl and FeCoNiCuAl, both equiatomic and reinforced by the 10% wt. of SiC were prepared by microwave assisted techniques. Results show that direct microwave heating of the powder precursors occurs, until the ignition conditions are reached. The temperature and duration of the microwave-assisted process result much lower than other conventional powder metallurgy routes, but at the cost of a higher residual porosity. Sample characterization confirmed that the powder metallurgy approach is suitable to retain the shape of the load imparted during forming by uniaxial pressing. The homogeneity of the samples resulted in being good in all cases, without the dendritic segregation typically occurring by liquid phase processing.

Introduction

High-entropy alloys [1] overcome the traditional concept of alloys based on one main metal element [2], being instead composed by at least five principal elements, with the concentration of each one ranging between 35 and 5 at.%. [3]. They attract much attention across the world, due to their unique properties [4], such as high hardness [5], wear resistance [6] excellent high and low-temperature strength [7] and in general good oxidation and corrosion resistance [8]

According to the literature research [9][10][11][12][13], the processing routes for multi components alloy systems complies with one of the four following techniques:

- from the liquid state: e.g arc melting [14] and induction melting [15]; more recently splat quenching [16], selective electron beam melting [17], laser [18] and direct laser (DLF) [9] technologies have been introduced.
- from the solid state powder metallurgy, i.e. mechanical alloying [18], spark plasma sintering [20]: recently, the powder metallurgy process was successfully applied to overcome the many structural defects such as voids, porosity, low as-cast hardness, due to the traditional casting technique [21] [22].
- from the gas state, such as sputtering techniques, i.e magnetron sputtering [16]
- from electrochemical process [23] (mainly for coatings).

The above mentioned synthetic routes have in common short alloying time (high energy density on the load [21], rapid melting and reduced contamination by the surrounding environment), efficient cooling and capability to operate in controlled atmosphere [24]. Such conditions can be achieved also using high frequency electromagnetic fields, like in microwave heating, [25] provided the load is capable to couple with the incident electric and magnetic field. Since the authors have already explored the possibility to realize HEA by microwave assisted near-net-shape technology [26], in this study the role of possible microwave auxiliary absorbers, like SiC powders, in two different multi-principal element alloys matrixes obtained by combustion synthesis, is investigated, since Si should progressively go into the HEAs matrix and to improve the mechanical properties, as demonstrated by the author in previous work [34]. The advantage of applying microwaves to combustion synthesis reactions lies in high purity of the products, rapid ignition of the reaction [27], possibility to control the products microstructure [28] and cooling rate after synthesis, especially in presence of ferromagnetic reactants [29].

Among the HEA systems, FeCoCrNiAl and FeCoNiCuAl structure have been the most studied [22][12] and thus have been selected in this study as matrixes. The metal powder precursors of such alloys include at least one ferromagnetic element (Fe, Co, Ni) and one highly reactive element couple, like Al-Ni, Al-Fe, Al-Co, Cu-Si in order to improve heat generation in electromagnetic field, due to both

magnetic field contribution (microwave heating) and exothermal reaction contribution. Moreover, in one case the use of Al is expected to have the synthesis initiated below 700°C [30][26], roughly corresponding to the melting point of aluminum, and in the other case the use of Cu is expected to favour the formation of further liquid phase, below the 800°C, thanks to the formation of liquid phase (Cu-Si eutectic, with Si deriving from reactions with the SiC reinforcement) [31].

Materials and Methods

The following elemental powders, supplied by Sigma Aldrich, (Table 1) were used as reactants to prepare equiatomic FeCoCrNiAl and FeCoNiCuAl precursor mixtures.

Table 1: Composition of the metal powders used (BCC = body centered cubic; FCC = face centered cubic; HCP = Hexagonal close-packed arrangement).

Element	Purity (%)	Particle Size (μm)	Cell
Fe	97.00	<44	BCC
Co	99.80	<2	HCP
Ni	99.70	<5	FCC
Cr	99.00	<44	BCC
Al	99.00	<75	FCC
SiC	97.50	<40	HCP

Powders were mixed for 1 hour in planetary milling with steel balls using a Planetary Ball Mill PM 100 by Retsch GmbH, at 250 rpm in an argon atmosphere, BPR 10:1 and cycles of 20 min with 5 min as break time. Subsequently SiC was added at 10 %wt, as it is a well known microwave absorber and it is expected to lead to a better heat generation inside the precursors and to a larger penetration depth of the microwaves.

Uniaxial pressing was used at 400 MPa to form the reactive disc-shaped specimens of 20 mm as diameter and 10 g mass. A microwave single mode applicator (described in detail [32]) was used and Ar flux (20 NmL/min) was blown into the cavity. Temperature was monitored and recorded at 1-s intervals, during heating tests, using an optical pyrometer (IKS-T14-09, Sitel control Srl, Milan, Italy). As synthesized samples were annealed at 1200°C for 50 h in a tubular furnace, into a reactor containing titanium-shavings as getters, to reduce oxidative effects. The average bulk structure of all samples can be detected by X-ray diffractometer (X'Pert PRO - PANALytical) with Cu-K α radiation with λ of 15418 nm at a scan rate of 0.006°s⁻¹; the metallographic microstructure was observed by scanning electron microscopy (SEM/FEG Nova NanoSEM 450 - FEI), after metallurgical preparation and etching by FeCl₃+HCl solution.

Results

Microwave heating of the powders precursors occurred rapidly in both predominant magnetic or electric field position of the applicator, resulting in synthesis times lower than 200 seconds, as shown Fig. 1, in regarding the predominant eclectic field configuration, the only one which allows proper temperature measurement.

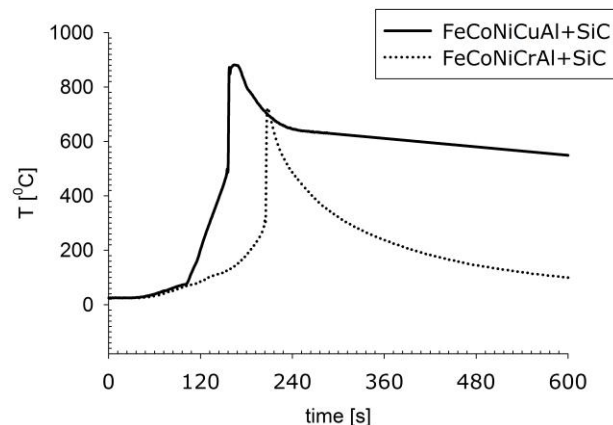


Fig. 1: Temperature vs time plot of two systems

Cu-containing HEAs lead also to an higher measured combustion temperature, likely to improve sample homogeneity. Compared to literature results referring to microwave assisted synthesis of SiC-free HEAs [34] the heat generation occurs more rapidly, for a given sample mass, confirming the positive effect of SiC.

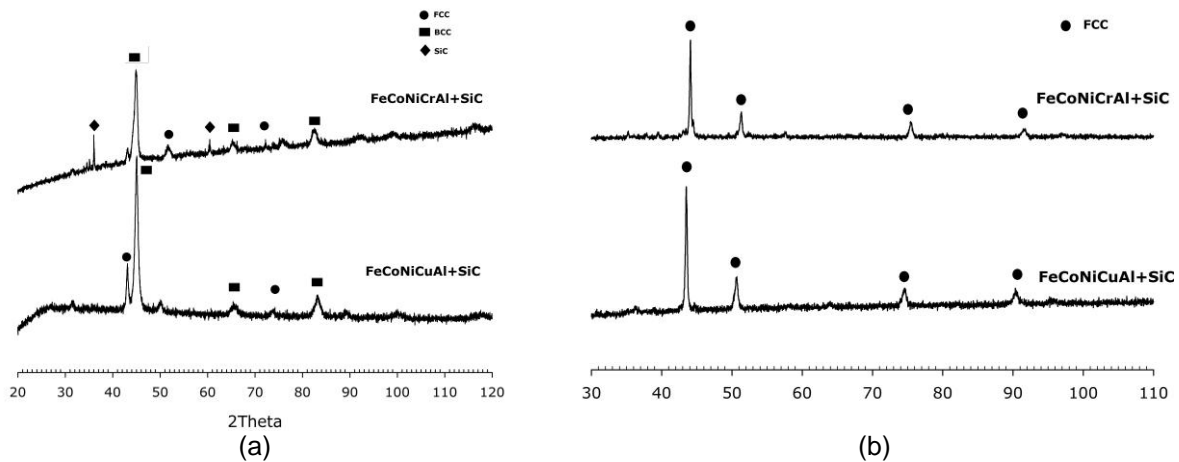


Fig. 2: XRD pattern before (a) and after (b) heat treatment

X-ray diffraction shows that, despite the expected tendency of SiC to react with the precursor elements, SiC is retained after synthesis. The X-ray diffraction patterns of samples after synthesis are shown in Fig. 2 (a) and they are in agreement with literature [33]. The diffraction patterns, after synthesis, show the presence of two crystalline structures, one BCC and one FCC, where the former is a minority phase and the latter is the main phase, as already demonstrated by the authors in a previous work [34]. These features reflect the metastable microstructure deriving from the rapid synthesis by microwave processing. This metastability is reflected by a gradient in chemical composition within the microstructure, as discussed later and supported by EDS-analysis.

The post-annealed (HT) phases (Fig. 2 (b)) can be identified as a simple FCC with diffraction peaks at about 20, 44, 50, 75, 90°, exactly positioned as α -Cu or steel austenite for both FeCoNiCrAl and FeCoNiCuAl disordered solid solution. Nevertheless, the variation of the peak intensities as well as their widths indicates that the HEAs alloys have a poor grain statistics and contains a large amount of large phases. It is also possible that the structure of alloys may not entirely be characterized as being of a simple FCC solid solution alloy. These considerations indicate the possible existence of either a minority phase of similar structure or a FCC phase of a different preferential ordering and composition, as in the case of the segregation of the Cu-Si-rich phase in FeCoNiCuAl. Fe, Cr, Ni and Co alloying elements are expected to solubilize in supersaturated HEAs solid solution, while Al is dissolved in FCC solid solution and does not influence significantly structure of lattice, but only causes an increase of elastic distortion. [11][24][33]

Co, Cu, and Ni elements promote FCC phase formation while Al and Cr promote BCC phase formation in the alloy system. BCC phases of the alloy system tend to form a spinodal structure during cooling [35]. Ternary Cu-Si-rich eutectic phase tends to segregate at the boundary of HEAs solid solution region, as shown in the optical micrograph of Fig. 3

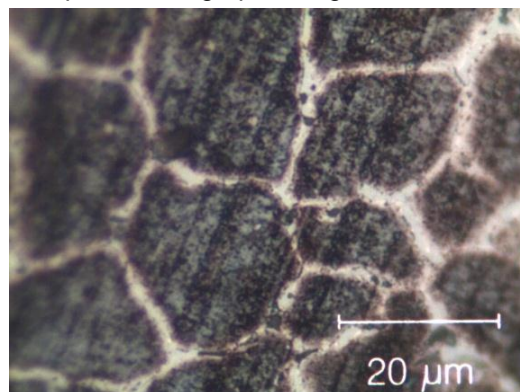


Fig. 3: MO of FeCoNiCuAl

The cross-section microstructures of FeCoNiCrAl+10% SiC and FeCoNiCuAl+10%SiC, after microwave synthesis and after annealing are shown in Fig. 4

The microstructure of both as synthesised HEAs, FeCoNiCrAl and FeCoNiCuAl, Fig. 4 (a) and (c) show that elements seems properly dispersed, despite the initial different particle size of the metal powders precursors. After annealing, SiC particles are partially reacted, bringing Si to the matrix, as evidenced by EDS analysis (Table 2). In annealed FeCoNiCrAl+SiC samples, the dark grey zone is Cr- and Fe-rich phase and Al and Si are present at less than 10 at%; the light grey zone is Al richer. The backscattered electrons image shows the partial decomposition of SiC, which is infiltrated by the matrix. In annealed FeCoNiCuAl+SiC samples, the Cu resulted strongly segregated, probably due to its participation to a liquid phase, thus the Cu-rich zones are evident (light grey zone-up to 40%at), as already demonstrated in literature [2], while the matrix is equally composed by Fe-Co-Ni-Al-Si element uniformly and near equiatomic composition (between 12-20%at). In both alloys nevertheless some SiC particle are yet unreacted (Fig. 4 (b-d)) During the microwave synthesis, due to the short reaction times (synthesis occurred in less than 30 seconds at 300 kW power) and permanence at high temperature, in case of FeCoNiCrAl HEA, the SiC reinforcement does not react with the newly formed solid solutions of the HEA, in the other HEA (FeCoNiCuAl) thanks to the greater liquid phase Si begins to reach with the matrix. After the homogenization heat treatment, instead, SiC is partially reacted and in the oxygen free atmosphere Si becomes available to diffuse into HEA matrix, as demonstrate by EDS analyses (Fig. 4). Similarly, it is expected an interstitial diffusion of C to occur, not evidenced by EDS analysis. Comparing the microstructures, the FeCoNiCuAl based samples present a lower porosity compared to the Cr-substituted ones, thanks to the earlier starting of the microwave reactive synthesis, as reported in Fig. 4

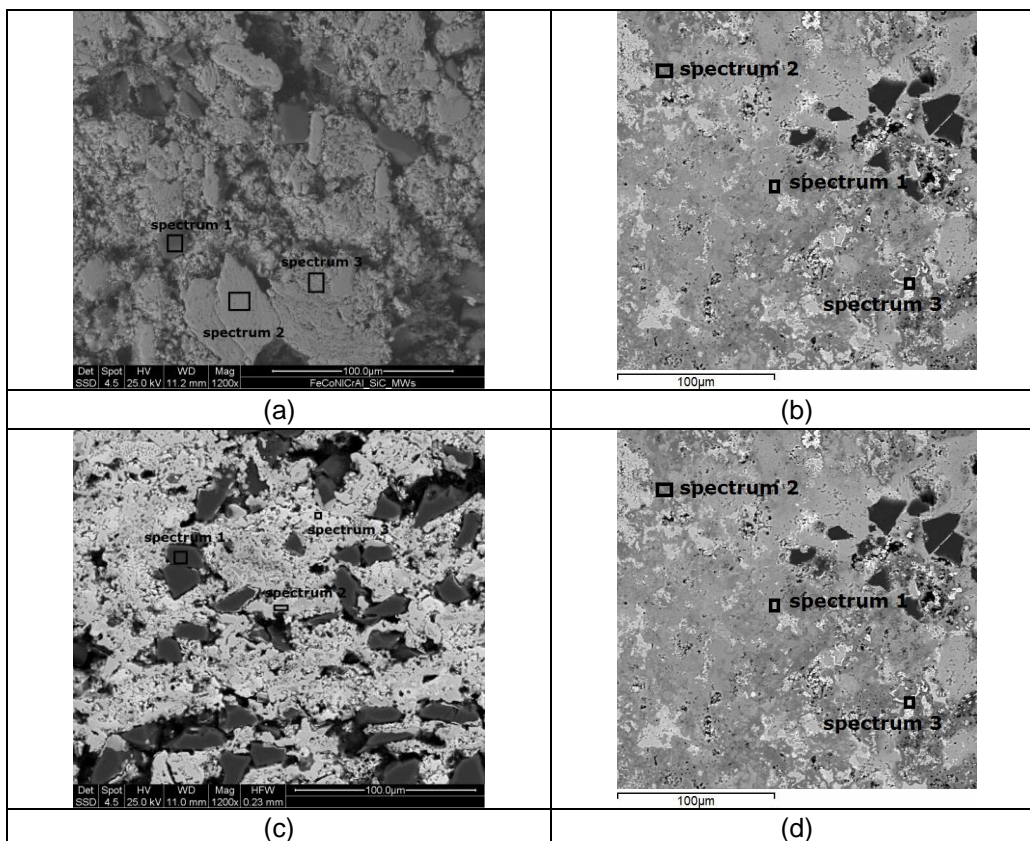


Fig. 4: HEAs before (left column) and after (right column) heat treatment (a) and (b) FeCoNiCrAl, (c) and (d) FeCoNiCuAl

Table 2: Semiquantitative analysis

FeCoNiCrAl-SiC												
	MWs - Fig 4. (a)						HT- Fig 4. (b)					
	1		2		3		1		2		3	
El.	Wt%	At%	Wt%	At%	Wt%	At%	Wt%	At%	Wt%	At%	Wt%	At%
Si	28.6	14.6					92.5	96.3	1.7	3.4	3.1	4.7
Al			3.4	6.6	15.1	27.8	1.2	0.6	4.5	9.1	31.0	48.2
Cr			52.8	53.3	18.7	17.4	2.5	1.2	47.7	46.0	19.0	14.2
Fe			19.1	18.0	16.2	14.1	2.4	1.3	18.7	17.1	23.3	16.5
Co			17.0	15.1	23.8	19.6	0.9	0.4	16.5	15.2	14.9	10.5
Ni			7.5	6.7	26.1	21.5			10.6	9.0	8.5	5.6
FeCoNiCuAl-SiC												
	MWs - Fig 4. (c)						HT - Fig 4. (d)					
	1		2		3		1		2		3	
Si	Wt%	At%	Wt%	At%	Wt%	At%	Wt%	At%	Wt%	At%	Wt%	At%
Si	45.7	27.1	0.3	2.4	0.86	1.66	7.85	13.2	6.29	9.59	0.56	1.19
Al			10.7	12.0	10.3	20.8	12.5	22.0	26.0	41.3	0.76	1.68
Fe			18.9	17.9	1.92	1.87	27.0	22.9	12.7	9.78	6.23	6.66
Co			20.2	18.2	8.79	8.11	19.5	15.7	22.2	16.1	20.5	20.8
Ni			21.3	19.2	9.75	9.03	22.8	18.4	21.1	15.4	27.5	27.9
Cu			22.6	22.1	68.3	58.4	10.1	7.59	11.5	7.77	44.3	41.7

Conclusions

In this work two high entropy alloys, FeCoNiCrAl and FeCoNiCuAl, both equiatomic and reinforced by the 10% wt. of SiC were successfully synthesized by microwave assisted techniques and annealed in a tubular furnace. The use of SiC, as microwave co-absorber, and the following heat treatment was performed in order to enhance the formation of a single solid solution FCC, improve samples homogeneity eventually to control the SiC decomposition. The temperature and duration of the microwave-assisted process result much lower than other conventional powder metallurgy routes, but at the cost of a higher residual porosity. Sample characterization confirmed that the powder metallurgy approach is suitable to retain the shape of the load imparted during forming by uniaxial pressing. In annealed FeCoNiCuAl+SiC and FeCoNiCrAl +SiC samples, both alloys show disordered solid solutions with FCC crystallographic structure. Comparing the microstructures, the FeCoNiCuAl based samples present a lower porosity compared to the Cr-substituted ones, thanks to the formation of a eutectic liquid phase since the starting of the microwave reactive synthesis.

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