A New Multi Principal Element Alloy Synthesized by Microwave Powder Metallurgy Technique

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Abstract

Multi principal element alloys (MPEAs), consisting of five or more alloying elements at near equiatomic concentrations, and forming bcc and/or fcc solid solution phase, were recently developed. According to the research literature, the synthetic route to produce MPEAs should guarantee short alloying time, efficient cooling and capability to operate in controlled atmosphere. Such conditions can be achieved using high-frequency electromagnetic fields, such as microwave heating. Microwave assisted combustion synthesis of pure metal powder mixtures as reactants has already been used during the last decade by the authors to prepare intermetallics, functionally-graded materials, and recently to produce multi-principle alloys. Moreover, the addition of SiC in these alloys, increases the mechanical properties and oxidation resistance at high temperature, as demonstrated in a recent paper by the authors.

A new MPEA ($Al_{15}Mn_{20}Fe_{25}Co_{15}Ni_{25}$) was prepared in this work with and without the addition of SiC, using powder metallurgy route and exploiting microwave as way of generating heat inside the precursors and hence to start the reactive sintering. Results show that direct microwave heating at 2,450 MHz of the powder precursors leads to the ignition conditions, with an evident exothermal event ascribable to the mixing enthalpy, and then self-sustaining of the synthesis occurs. The temperature and duration of the microwave-assisted process resulted 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.

1. Introduction

Multi principal element alloys (MPEA) are a class of multi-component alloys composed of five or more principal constituent elements, none of which is predominant, and each with a concentration between 5 and 35 atomic %. These alloys[1] have a tendency to form simple structures, like face centred cubic (FCC) and body centred cubic (BCC), instead of intermetallic compounds[2]. The MPEA family of alloys shows several interesting features; in particular they tend to form simple solid solution phases with the possible presence of nanostructures or even amorphous structures[3,4], presenting outstanding properties[5]. Among several production techniques the one most used is the arc melting technique[6], however, for elements with a low melting point, which are easy to evaporate, e.g., Mg, Zn and Mn, this route may not be the best choice because of the lack of control of the exact composition. Nevertheless, the arc melting is still one of the most promising technologies, as it guarantees a short alloying time, efficient cooling and the capability to operate in a controlled atmosphere. The same conditions can be achieved using higher frequency electromagnetic fields, as in microwave heating, provided the load is capable of coupling with the incident electric and magnetic field.

Microwave heating of powdered metals has been known since the pioneering work of Roy et al.[7], demonstrating how metallic powder compacts can be heated by microwaves; despite this finding, the scientific literature regarding the use of microwaves to prepare MPEA is limited to only few contributions by some of the authors[20-24], and a slightly different approach using non-metallic precursors has been proposed to achieve MPEA production using microwave combustion synthesis, but with subsequent generation of oxides[8].

In this work, a new HEA has been designed by the Calphad method[25]. Based on previous work[20-24] on the FeCoNiAlCu and FeCoNiCrAl HEA family, the authors chose to investigate a Mn-modified composition, namely: $Al_{15}Mn_{20}Fe_{25}Co_{15}Ni_{25}$. The new composition is

designed in order to increase the exothermicity, thanks to its low melting temperature which should increase the liquid phase formation bringing to a single solid solution structure. The known advantages of applying microwaves to combustion synthesis reactions (high purity of the products, rapid ignition of the reaction, and the possibility to control the products microstructure) and the cooling rate after synthesis, especially in the presence of ferromagnetic reactants[9-12], are expected to rapidly lead to the desired MPEA, with possible shape retention due to the formation of limited amounts of liquid phase during synthesis.

2. Materials and methods

In this work, the $Al_{15}Mn_{20}Fe_{25}Co_{15}Ni_{25}$ alloy has been prepared, starting from metallic powders mixtures, which include ferromagnetic elements (Fe, Co, Ni), likely to provide a further heating contribution when exposed to the electromagnetic field. The elemental powders used as reactants are listed in Table 1.

Table 1: Elemental powders used in this study

Element	Purity (%)	Particle size (μm)	Manufacture
Fe	97.0	< 44	Sigma-Aldrich
Co	99.8	< 2	Alfa Aesar
Ni	99.7	< 5	Sigma-Aldrich
Al	99.0	< 75	Sigma-Aldrich
Mn	99.9	< 44	Sigma-Aldrich

The possibility to use the aforementioned alloy as a matrix for insertion of partially reactive SiC particles has also been investigated. SiC has been selected as reinforcement due to its good coupling with microwaves at 2,450 MHz, and because of its instability in the presence of transition metals[30], which is expected to lead to moderate reaction of SiC with the matrix, and subsequent formation of silicides and/or carbides. Hence, a further powder has been added to a second subset of samples, namely SiC of 97.5% purity with particle size of 37-74 μm (Sigma-Aldrich).

To prepare the $Al_{15}Mn_{20}Fe_{25}Co_{15}Ni_{25}$ mixture with and without the addition of 5% wt. of SiC, the proper amount of powders was weighed and mixed in planetary ball milling, BPR 1:10, for 1 hour of active mixing. Uniaxial pressing was used at 300 MPa to form reactive disc-shaped specimens of 20 mm as diameter and 8 g as weight. Synthesis in rectangular TE10n single mode applicator[11] has been performed at 2.45 GHz and 3kW maximum power. The choice of the single mode applicator lies in its possibility to expose the load to regions of predominant electric or magnetic field[12], even if both contributions have to be considered to heating, due to the perturbation of the electromagnetic field in the cavity triggered by the presence of the load itself. In order to avoid excessive oxidation, a constant Ar flux (20 NmL/min) was blown into the single mode cavity during experiments. All samples were subsequently annealed at 1,200°C for 8 hours in a tubular furnace, into a reactor containing titanium-shavings as getters, to reduce oxidative effects.

The crystal structure of mixed powders and as- synthesized alloys was characterized by X-ray diffractometer (X'Pert PRO - PANAlytical) with Cu-Ka radiation. The microstructure of the powders was observed using scanning electron microscopy (SEM, ESEM - Quanta200 – FEI, and FEG-SEM Nova NanoSEM 450 - FEI), after cutting and polishing. Instrumented nano indentation (CSM Instruments) was used to perform depth-sensing nano-indentation tests on samples. A 100-mN force with linear loading/unloading rate of 150 mN/min was applied for 15 seconds. The indentations were performed using a Berkovich tip, and the elastic modulus and equivalent Vickers hardness were calculated according to the Oliver and Pharr method[25].

3. Results

In order to try to improve the heat generation in the metallic precursors powder compact when exposed to microwaves, 5 wt% of SiC was added. However, its known reactivity in the presence of transition metals is responsible for the possible decomposition of this reinforcement, unless extremely rapid heat treatments are performed. For this reason, microwave heating allowed to preserve part of the SiC unreacted, while the subsequent 50 hours heat treatment led to its almost complete decomposition, as shown in the XRD patterns of

the HEA before and after the heat treatment (Fig. 1 and Fig. 2).

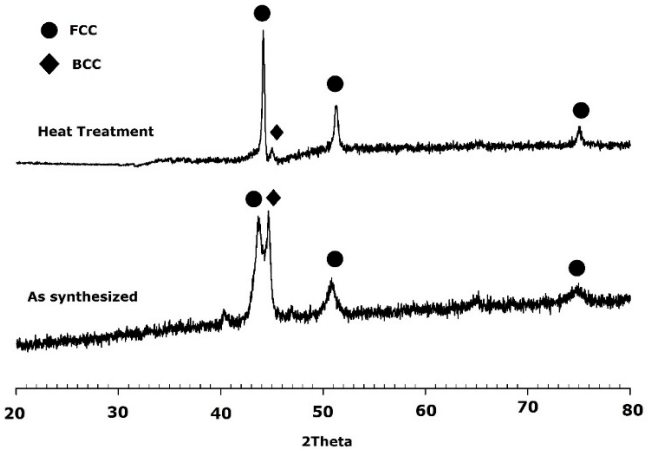


Figure 1: X-ray pattern of alloy without SiC before and after heat treatment

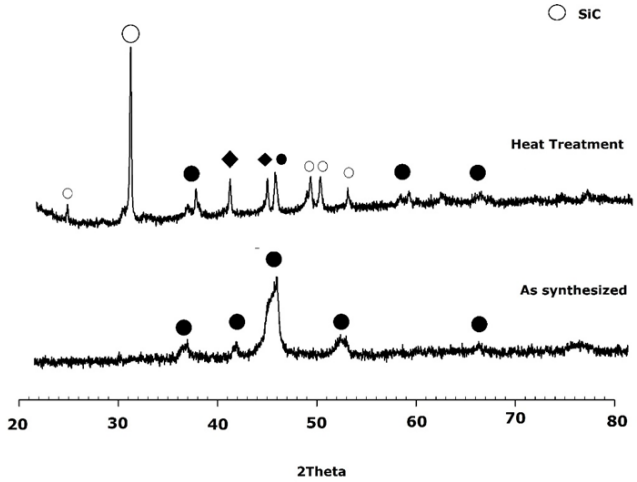
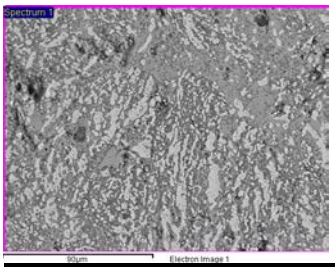


Figure 2: X- ray pattern of alloy with SiC before and after heat treatment

Before the heat treatment, both SiC-containing and SiC-free samples show the presence of mixed BCC/FCC phases. When SiC is added, the two characteristic peaks of hexagonal crystallographic structures of SiC is evident, as labelled in Fig. 2. In the SiC-free sample a completely FCC structure is developed after the heat treatment (Fig. 1).

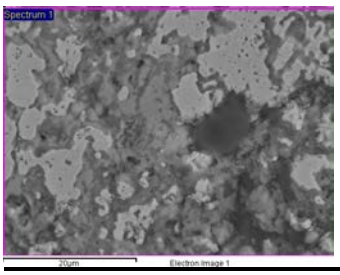
As already investigated by the authors in a previous study[31], Si driving from the SiC decomposition can enter the FeCoNiCrAl[29,30], but in the investigated $Al_{15}Mn_{20}Fe_{25}Co_{15}Ni_{25}$, the SiC is not decomposed after heat treatment, as confirmed both by XRD pattern (Fig. 2), BSE images (Fig. 5) and element maps distribution. This behaviour is ascribable to the much shorter time of the heat treatment (8 hours) compared to the 50 hours employed in our previous investigation[31], which guarantee the dissociation of SiC and the complete transformation of the original BCC/FCC structure into a single FCC structure.

The microstructure and the average chemical composition after heat treatment are shown in Figs. 3 and 4 referred respectively to samples without and with SiC. Despite the presence of peaks for a single phase, by XRD, even at low magnification three areas at different chemical composition are present, as demonstrated by the BSE images of Fig. 5 before and after heat treatment.



Element	Weight (%)	Atomic (%)
Al	10.95	15.93
Mn	16.17	20.66
Fe	21.34	23.93
Co	13.28	13.52
Ni	21.06	24.53

Figure 3: BSE images after heat treatment, to detect the average chemical composition indicated.



Element	Weight (%)	Atomic (%)
Al	8.70	15.59
Si	8.07	13.89
Mn	19.31	16.99
Fe	22.74	19.68
Co	16.12	13.22
Ni	25.06	20.63

Figure 4: BSE image of sample with 5% of SiC after heat treatment, to detect the average chemical composition indicated.

The EDS analysis shown in Table 2 and referred to the heat treated samples allowed to identify the different areas: the black regions are not reacted SiC particles, the two dark grey phases are Al-Mn-richer and Al-Mn-Fe richer, the remaining one being Co-Ni richer. The element distribution maps confirm the EDS observations and the pronounced segregation of Mn.

Mechanical properties of the samples were investigated by a nanoindentation test (Fig. 6). Both samples before heat treatment present a significantly lower hardness, compared to the heat-

treated ones, in agreement with the microstructure investigations. The presence of SiC in not affecting the hardness, but it must be taken into account that the nanoindentation provides a local value of hardness, and that the indentation zone has been selected far from the embedded SiC particles. The young module increases after heat treatment, it is due to the SiC reactivity[31]. Indeed, it goes into the matrix leading to the formation of reinforcing silicides and carbides, but the complete SiC decomposition occurs to a longer treatment time.

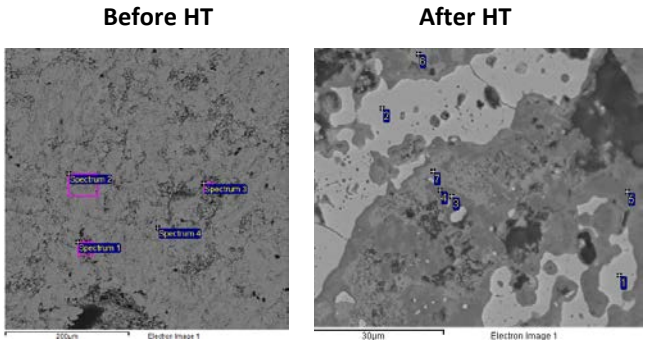


Figure 5: BSE images of samples before (left) and after (right) heat treatment.

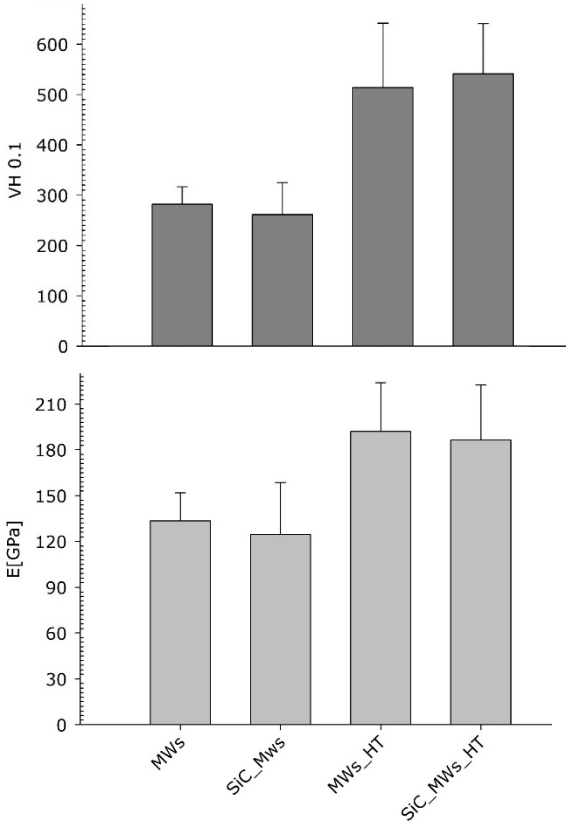


Figure 6: (a) Hardness value (VH 0.1) and (b) Young Module.

Table 2: Semiquantitive analysis

	Element [%]						
Spectra average	**C**	**Al**	**Si**	**Mn**	**Fe**	**Co**	**Ni**
without SiC							
1-2		0.00		1.35	27.08	18.82	30.58
4-5		34.73		27.40	4.23	0.46	0.36
6-7		11.10		45.14	17.51	1.49	0.94
with SiC							
2-3-4	37.91	1.48	0.00	27.82	21.31	9.35	2.14
5-6	28.46	0.00	0.00	1.37	6.01	19.23	44.93
7-9	25.13	20.37	0.00	22.24	23.54	6.70	2.02
1	56.80	0.00	42.46	0.26	0.29	0.11	0.09

Table 3: Semiquantitive analysis of local area in Fig. 7

Element	**Spectrum 3**				**Spectrum 1**		**Spectrum 2**	
	wt%	at%	Compound %		wt%	at%	wt%	at%
Al	26.07	25.28	Al2O3	49.25	40.41	58.66	4.84	9.87
Mn	14.58	6.94			17.83	12.71	3.36	3.37
Fe	15.95	7.47			22.8	15.99	15.19	14.98
Co	4.69	2.08			7.56	5.02	21.05	19.67
Ni	4.28	1.91			11.41	7.61	55.56	52.11
O	34.44	56.32						

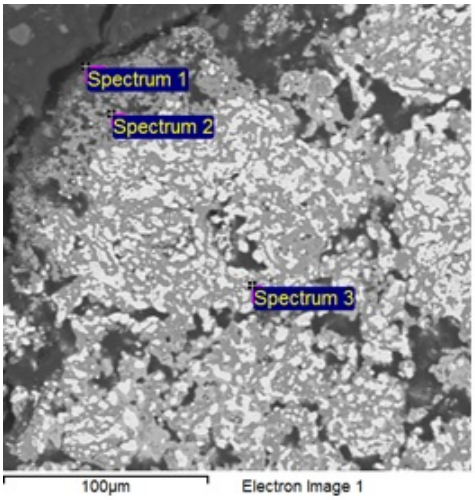


Figure 7: Cross section of heat treated sample

During the heat treatment, despite the presence of the oxygen getters, the formation of an Al_2O_3 layer was detected as shown in Table 3. A detail of the external side of heat treated sample cross section is shown in Fig. 8. In the inner part the EDS analyses (Table 3) revealed the presence of the two compositionally different phases, as shown where one phase is rich in Al and Mn, the other in Fe-Co-Ni ones. The possibly high temperature oxidation protection nature of this duplex layer will be subject of further investigations.

4. Conclusions

A new MPEA ($Al_{15}Mn_{20}Fe_{25}Co_{15}Ni_{25}$) was successfully prepared with and without the addition of SiC, using powder metallurgy route and exploiting microwave heating at 2,450 MHz. The SiC-containing as synthesized and post heat treated alloy retained the SiC particels added as a reinforcement, due to the extremely rapid synthesis time and short annealing time, which prevented SiC decomposition.

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Elena Colombini is a postdoctoral research fellow at the Department of Engineering "Enzo Ferrari", University of Modena and Reggio Emilia. Her research activity is focussed on the synthesis of new high entropy alloys through metal powder technology. Together with her supervisor (Prof. Paolo Veronesi) she also design new microwave applicators for several employments.

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Marco Gabriele Poletti hold a Post-Doctoral Position at the Laboratory of Metallurgy of the Department of Chemistry at the University of Turin. In 2015 he concluded his PhD thesis, mainly focused on the development of criteria to design new high entropy alloys. His present activity is focused on the development of new high entropy alloy compositions for application in different fields.

Livio Battezzati is a Full Professor in Science and Technology of Materials at the Chemistry Department of University of Turin. His main research topics are related to metastable materials, their processing (metallic glasses, quasi-crystals, novel compounds and micro-structures), thermodynamics and kinetics of phase transformations. He is responsible of contracts with industry, agencies and the EC.

Angelo Casagrande, Professor of Metallurgy at the Department of Industrial Engineering-DIN -Bologna University. His researcher is aimed to the production of innovative metal alloys, their behaviour in exercise, protective coatings and intermetallics, obtained by reactive synthesis and massive damping materials to reduce mechanical vibrations in structural components.

Paolo Veronesi, Professor of Material Science at the Department of Engineering "Enzo Ferrari", University of Modena and Reggio Emilia. His research activity is mainly focussed on the thermal applications of microwaves. He is also active in the ceramic field, in particular as far as composite materials and refractory materials are concerned. During last decade he has been using commercial electromagnetic modelling software (Concerto 3.5, Comsol Multyphisics) in order to design new microwave applicators for high and low temperature heat treatments and microwave plasmas. Recently, he dedicated intensively to the development of microwaves applications to metals, high entropy alloys and intermetallics. His research activity leads to many collaborations, either national or international, mainly regarding dielectric heating and materials processing.

Cristina Leonelli is a Full Professor (since 2005) in Chemical foundations of technologies. She has coordinated several national research projects and some international cooperation projects. Her field of interest has been solid state chemistry with particular interest in the reactivity of ceramic powders and transition from amorphous to crystalline state. She has a personal experience in designing new composition, preparation and characterization of different powder and bulk ceramic materials as well as for application developments. She has also been active in the field of several innovative preparation techniques and microwave heating applied to materials processing and synthesis. She has been interested in modelling of material nano- and micro-structure and their relationship with macroscopic properties, such as the determination of failure probability in composite or bulk materials. A recent research field from 2008 is the alkali activation of aluminosilicate materials to obtain cement-like formulation with sustainable starting powders as industrial wastes or mines residues and debris. She has been member of the Editorial Board of Korean Journal of Materials Research, Journal of Microwave Power and Electromagnetic Energy, Advances in Technology of Materials and Materials Processing Journal, and Inorganics. She is among the referees list in several international journals and is a reviewer for several research funding agencies in Italy (MIUR, CNR) all over the world (Royal Society, EPSRC, NTO, ISF, KU Leuven). She has been invited editor in a number of Special Issues in International Journal.