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Microwave assisted synthesis of Si-modified $Mn_{25}Fe_xNi_{25}Cu_{(50-x)}$ high entropy alloys

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ABSTRACT

Rapid microwave heating at 2450 MHz of metallic powders mixtures compacts was performed under Ar flux in a single mode applicator in order to produce Si-modified $Mn_{25}Fe_xNi_{25}Cu_{(50-x)}$, ($x$=25, 30, 35, 40) high entropy alloys. Microwave heating was conducted in presence of a SiC auxiliary absorber, so that the compacts are subjected to both direct heating by microwave absorption and indirect heating by the auxiliary absorber. Due to the extremely rapid processing times, including the cooling stage, depletion of the most oxygen-reactive elements was moderate, considering the not perfectly protective atmosphere used. FCC solid solutions have been obtained and the role of Si is discussed as a microstructure modifier and as increaser of the microhardness.

1. Introduction

High-entropy alloys (HEA) are a class of multi-component alloys composed of 5 or more principal constituent elements, none of which is predominant, and each with a concentration between 5 and 35 atomic % [1]. These alloys have a tendency to form simple structures, like FCC and BCC and show several interesting features, like good thermal stability and excellent resistance to anneal softening [2], age hardening capabilities, excellent corrosion, wear and oxidation resistance accompanied by high compressive strengths [3–5]. Due to this broad spectrum of properties, the HEA have many potential applications, especially in the medium-high temperature range or in corrosive environments [6].

Most of the production attempts followed one of the four following techniques: from the liquid state (arc melting, induction melting), from the solid state (mechanical alloying, powder metallurgy), from the gas state (sputtering techniques, mainly for coatings) and from electrochemical process (again mainly for coatings) [6]. In this study, microwave heating of metallic powders compacts is used for the first time as a rapid synthesis technique, exploiting both direct microwave absorption by the powder compact and indirect heating by an auxiliary SiC absorber. Microwave heating of powdered metals is known since the pioneering work of Roy et al. [7] and recently it has found many applications in the field of metallurgy [8], due to its peculiar selective and volumetric heating and sintering enhancement [9].

2. Materials and methods

Elemental powders, supplied by Sigma-Aldrich, have been used as reactants: Fe 97.0% purity, particle size less than 44 μm, Mn 99.0% purity particle size less than 44 μm, Ni 99.7% purity particle size less than 5 μm, Cu 99.0% purity particle size less than 10 μm. The required $Mn_{25}Fe_xNi_{25}Cu_{(50-x)}$ with x=25, 30, 35, 40 stoichiometry has been prepared by weighing the proper amount of powders, subsequently mixed under vacuum in an Al_2O_3 ceramic jar for approximately 30 min. A second set of samples was obtained substituting 2.5, 4, 5, 7 at% of silicon (Si 99.0% purity particle size less than 44 μm) to the Mn, as shown in Table 1.

Uniaxial pressing of 1 g of powder mixture was used at 300 MPa pressure to form disc-shaped specimens. Microwave heating occurred at the ISM frequencies of 2450 MHz in a rectangular TE10n single mode applicators, shown in Fig. 1 and whose geometry has been described in details elsewhere [10]. An insulating casket, enclosing a SiC auxiliary heating element has been used to host the sample during processing. Sample was contained in a small inner alumina crucible. The use of the auxiliary absorber allows to heat the sample directly, by microwave absorption within the penetration depth of the electromagnetic field, and by heat transfer from the microwave-heated auxiliary absorber.

An overall forward power of 1 kW was applied for 180 s, to reach temperatures in excess of 1400 °C, monitored using a

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Table 1
Theoretical atomic composition of the investigated HEA.

Sample composition	Id.	Mn (%)	Fe (%)	Ni (%)	Cu (%)	Si (%)
$Mn_{25}Fe_{25}Ni_{25}Cu_{25}$	Si0-x25	25	25	25	25	0
$Mn_{25}Fe_{30}Ni_{25}Cu_{20}$	Si0-x30	25	30	25	20	0
$Mn_{25}Fe_{35}Ni_{25}Cu_{15}$	Si0-x35	25	35	25	15	0
$Mn_{25}Fe_{40}Ni_{25}Cu_{10}$	Si0-x40	25	40	25	10	0
$Si_{2.5}Mn_{22.5}Fe_{25}Ni_{25}Cu_{25}$	Si2.5-x25	22.5	25	25	25	2.5
$Si_4Mn_{21}Fe_{30}Ni_{25}Cu_{20}$	Si4-x30	21	30	25	20	4
$Si_5Mn_{20}Fe_{35}Ni_{25}Cu_{15}$	Si5-x35	20	35	25	15	5
$Si_7Mn_{18}Fe_{40}Ni_{25}Cu_{10}$	Si7-x40	18	40	25	10	7

contacting sapphire fiber (shown in Fig. 1) connected to a signal conditioner (MIKRON M680). Specimens have been water quenched and sectioned to expose the whole cross section in order to investigate their microstructural and compositional features by means of Scanning Electron Microscopy (ESEM Quanta-200 Fei, Oxford Instruments) and Energy Dispersive X-ray Spectroscopy (EDS, Inca-350, Oxford Instruments). X-ray diffraction (XRD, X'Pert PRO, PANAlytical, Almelo, The Netherlands) using Ni-filtered Cu-Kα radiation ($\lambda = 1.5405$ Å) was used to verify the formation of the solid solutions typical of HEA, and microhardness testing (Volpert microhardenss tester, Vickers, 1000 g load for 15 s) was performed on selected regions of the samples, after polishing and etching with aqua regia for 10 s.

3. Results and discussion

Results confirmed that HEA can be produced using microwave heating, as shown in the X-Ray diffraction patterns of Fig. 2, where only a single FCC phase is present.

In case of Si-free alloys, the first FCC peak is divided in two different sub-peaks, indicating that probably two FCC solid solutions formed, and this is in agreement with the typical segregation tendency of such HEA, confirmed by metallographic observations. Some peaks, whose positions are not compatible with the general pattern of these systems, indicates the presence of $CaCO_3$, likely deriving from the thermosetting resin used for metallographic preparation. The presence of Si in the composition, which is characterized by an FCC crystalline structure, seems to enhance the FCC phase formation, evident by the reduced broadening of the peaks compared to the Si-free compositions.

Microstructural investigations, shown in Fig. 3 evidenced a dendritic structure, with iron-richer dendrites and copper-richer interdendritic regions. Samples containing silicon addition show

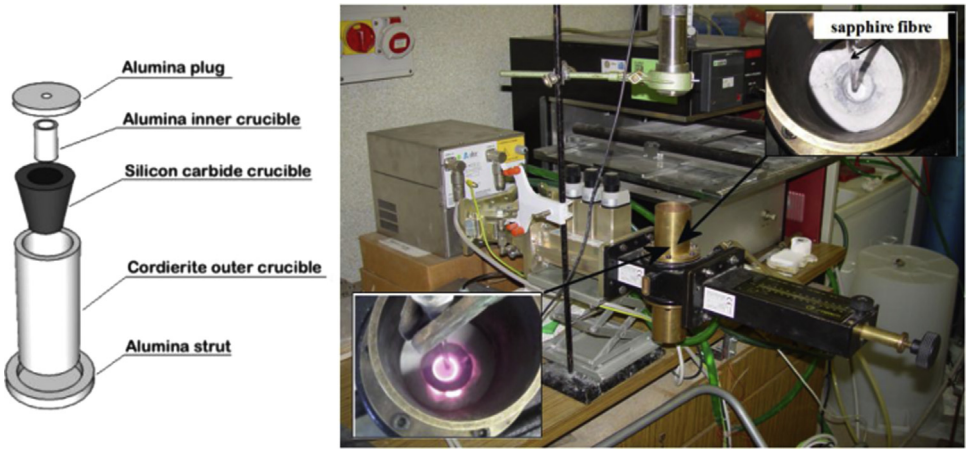

Fig. 1. Load arrangement (left) and microwave applicator used (right), showing the sapphire fiber used to monitor temperature.

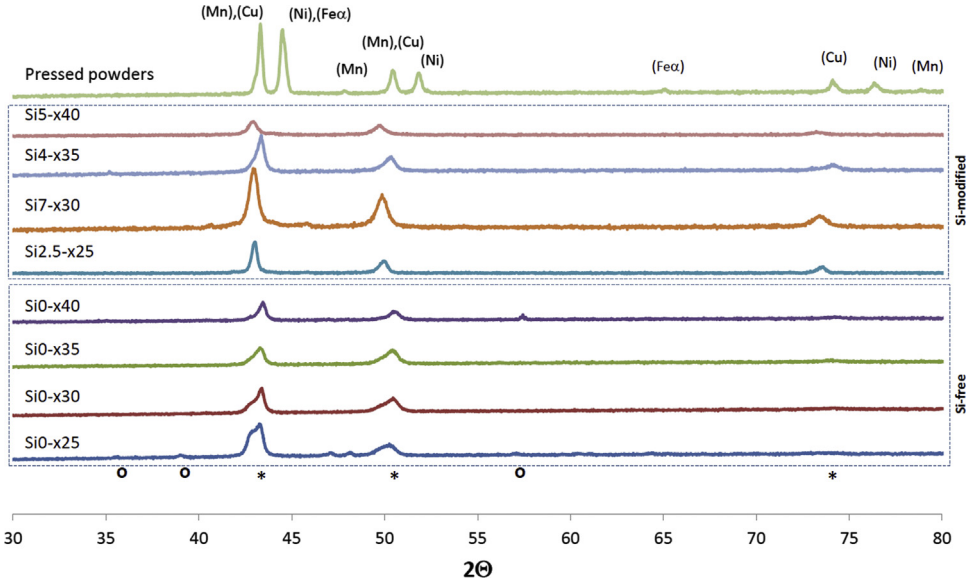

Fig. 2. X-Ray diffraction patterns of the pressed powders and the synthesized Si-modified $Mn_{25}Fe_xNi_{25}Cu_{(50-x)}$ HEA, showing (*) FCC phase and (°) $CaCO_3$ peaks.

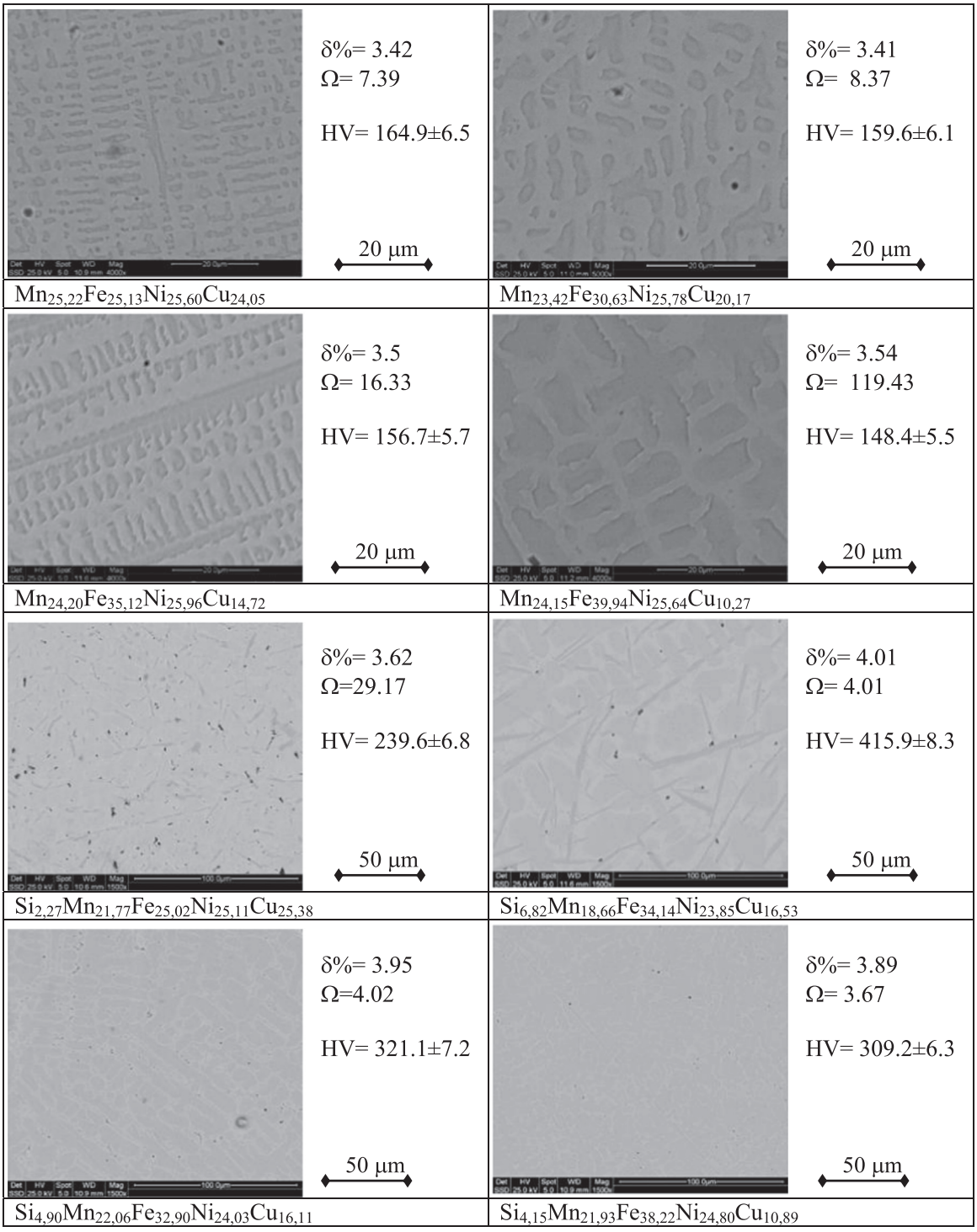

Fig. 3. Backscattered electron SEM micrographs of the HEA, whose average compositions are shown at the bottom of each figure and the calculated atomic size difference parameter (δ%), Ω parameter and measured HV1 hardness are indicated.

acicular structures, Si-richer, preferentially dispersed in the inter-dendritic phase (darker needle-like structures in the micro-structures of Si-modified samples of Fig. 3).

EDS analysis, whose averaged results are summarized in the labels of Fig. 3, was used to investigate the effective composition of the studied alloys, since elemental variations could occur as a result of the melting operations. It is evident that Mn and Si are the metals with the stronger-tough limited- variation from the theoretical values. This can be ascribed to the highly negative free energy of formation of the oxides of such metals, and to the non perfectly protective conditions offered by the Ar flux used during microwave processing.

Fig. 3 shows also the calculated atomic size difference parameter (δ%) and Ω parameter, the first adopted to describe the effect of atomic size difference in multi-component alloys, and the latter which combines the effects of entropy of mixing and enthalpy of mixing for predicting the solid solution phase formation [11]. Usually values of $\Omega > 1.1$ and $\delta\% < 6.6$ should be considered as a criteria for forming solid solution, as in the case of the present study.

Microhardness results shown in Fig. 3 clearly indicate a strong correlation between the measured microhardness and the Fe/Cu ratio, in case of Si-free composition, and a much more pronounced dependence on the Si content, according to the following interpolating polynomials, where the square brackets indicate the atomic percentage of the element:

$$HV = 0.4353([Fe]/[Cu])^2 - 7.6278([Fe]/[Cu]) + 171.62; \quad R^2 = 0.98 \tag{1}$$

$$HV = 2.361[Si]^2 + 16.683[Si] + 190.96; \quad R^2 = 0.99 \tag{2}$$

The strengthening effect of Si on hardness has already been previously reported in case of other HEA system [12]. The Fe/Cu dependence can be explained considering the presence of two regions in the Si-free samples: a dendritic (Fe-richer) one (darker regions in the Si-free micrographs of Fig. 3) and interdendritic (Cu-richer) one (lighter regions in in the Si-free micrographs of Fig. 3), whose equivalent minimum Vickers hardness, measured by Berkovich nanoindentation, resulted respectively of 245 and 301 HV.

4. Conclusions

Microwave assisted heating at 2450 MHz, in presence of an auxiliary absorber, proved to be an effective and rapid processing technique to prepare HEA from the liquid state. In the case of the Si-modified $Mn_{25}Fe_xNi_{25}Cu_{(50-x)}$ alloy, such synthetic route is able to retain the initial stoichiometry, despite the non perfectly protective conditions used, which led to a small depletion of the more oxygen-reactive elements. The effect of Si content is reflected in both the microstructure, with the formation of acicular structures in the interdendritic phase, and in the mechanical properties, with a positive trend of microhardness as the Si content increases.

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