Title: New (FeCoCrNi)-(B,Si) high-entropy metallic glasses, study of the crystallization processes by X-ray diffraction and Mössbauer spectroscopy

Abstract: The role of B and Si in the formation of (FeCoCrNi)BSi high-entropy metallic glasses is studied. A content of B between 10 and 20 at% and of Si between 5 and 15 at% is able to produce an amorphous structure. The microstructural evolution of two of these compositions have been studied by X-ray diffraction and Transmission Mössbauer Spectroscopy. In both, the first crystallization process corresponds to the formation of $\text{M}_3\text{B}$ and $\text{M}_2(\text{B, Si})$. In the Si containing sample a BCC phase also appears. At the second crystallization stage the metastable and the BCC phases disappear and $\text{M}_2\text{B}$ or $\text{M}_2(\text{B, Si})$ phases grow with an FCC structure that presents a distribution of possible environs. The fully crystallized structure consists of boride and silicide phases and a paramagnetic FCC phase. The presence of Si promotes the crystallization of a BCC phase and the refinement of the microstructure leading to smaller and more uniform grains.
Prime Novelty Statement

Dear Editor,

This is an original paper reporting our recent work on the characterization of new high-entropy metallic glasses obtained by adding B and Si to the high entropy FeCoCrNi alloy, which is known to form a disordered solid solution with FCC structure. There are similar approaches in recent literature; FeCoCrNi-B amorphous alloys have been already reported with different contents of B as well as FeCoNi-(B,Si). Both works are cited in the submitted manuscript. Never theless, as far as we know, we report for the first time FeCoCrNi-(B,Si) glass-forming compositions.

In our opinion, however, the main result presented in this work is a comprehensive characterization of the crystallization process of this family of high-entropy metallic glasses. We give detailed information of the crystallization route followed by two of these alloys, (FeCoCrNi)$_{80}$B$_{20}$ and (FeCoCrNi)$_{80}$B$_{10}$Si$_{10}$, taken as representatives of the glass-forming compositions containing only Boron and containing both Boron and Silicon. Although some issues remain to be solved, as for example the specific percentage of the different metallic elements in the phases which are identified as products of the crystallization reaction, we think that the devitrification route of these alloys is essentially settled.

The design of annealing protocols to induce a certain degree of nanocrystallinity in amorphous samples is a well-known strategy to improve some of their physical properties. We are of the opinion that the submitted work will be of significant importance to other researchers working in the field, helping them to produce and design new high entropy metallic glasses or metallic glass / crystalline composites with enhanced mechanical and magnetic properties.

Yours faithfully,

Pere Bruna
(On behalf of all the coauthors)
Journal of Non-Crystalline Solids

Confirmation of Authorship

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As corresponding author, I Pere Bruna, hereby confirm on behalf of all authors that:

1. This manuscript has not been published, was not, and is not being submitted to any other journal. If presented at a conference, the conference is identified. If published in conference proceedings, substantial justification for re-publication must be presented.

2. All necessary permissions for publication were secured prior to submission of the manuscript.

3. All authors listed have made a significant contribution to the research reported and have read and approved the submitted manuscript, and furthermore, all those who made substantive contributions to this work have been included in the author list.
Dear Editor,

Thank you very much for your communication accepting after minor revisions our submission to Journal of Non-Crystalline Solids (article reference code: NOC-D-20-00417).

Following your suggestions, details of the uncertainties have been included in all the tables and figures. In particular, in lines 188-189 a sentence has been added detailing the uncertainty in the measured temperatures from the DSC curves and this information has been also added in table I. In line 249 and 292 it is explained that the standard deviation of the Mössbauer parameters is obtained from the fitting software and included in figures 10 and 11 (although the error bar is smaller than the symbol point and it is not seen). Thus a sentence has been added in the corresponding captions. Finally, in lines 335-340, the standard deviation of the grain size distribution has been included together with the average value. In the Supplementary Materials document, all the values in the table already included the standard deviation.

All the changes made are marked in red in the revised version of the paper.

With my compliments,

Pere Bruna, on behalf of the authors.
Abstract

The role of B and Si in the formation of \((\text{FeCoCrNi})_{100-x-y}\text{B}_x\text{Si}_y\) high-entropy metallic glasses is studied. It is found that a content of B between 10 and 20 at% and of Si between 5 and 15 at% is able to produce a completely amorphous structure. The microstructural evolution of two of this high-entropy metallic glass compositions, \((\text{FeCoCrNi})_{80}\text{B}_{20}\) and \((\text{FeCoCrNi})_{80}\text{B}_{10}\text{Si}_{10}\), have been studied by X-ray diffraction and Transmission Mössbauer Spectroscopy. In both compositions, the first crystallization process corresponds to the formation of metastable, \(M_3\text{B}\), and stable, \(M_2(\text{B, Si})\), borides where M stands for metallic atoms. In the Si containing sample a BCC phase also appears. At the second crystallization stage the metastable and the BCC phases disappear and stable \(M_2\text{B}\) or \(M_2(\text{B, Si})\) phases begin to grow simultaneously with an FCC structure that presents a distribution of possible environs. The fully crystallized structure consists of boride and silicide phases and a paramagnetic FCC phase. The presence of Si promotes the crystallization of a BCC phase and the refinement of the microstructure leading to smaller and more uniform grains.
• (FeCoCrNi)-(BSi) new high entropy metallic glasses were produced.

• The compositional range showing glass-formation was assessed.

• The crystallization and microstructural development was fully characterized.
New (FeCoCrNi)-(B,Si) high-entropy metallic glasses, study of the crystallization processes by X-ray diffraction and Mössbauer spectroscopy.

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Abstract

The role of B and Si in the formation of (FeCoCrNi)₁₀₀₋ₓBₓSi₀⋅₅ high-entropy metallic glasses is studied. It is found that a content of B between 10 and 20 at% and of Si between 5 and 15 at% is able to produce a completely amorphous structure. The microstructural evolution of two of this high-entropy metallic glass compositions, (FeCoCrNi)₈₀B₂₀ and (FeCoCrNi)₈₀B₁₀Si₁₀, have been studied by X-ray diffraction and Transmission Mössbauer Spectroscopy. In both compositions, the first crystallization process corresponds to the formation of metastable, M₃B, and stable, M₂(B, Si), borides where M stands for metallic atoms. In the Si containing sample a BCC phase also appears. At the second crystallization stage the metastable and the BCC phases disappear and stable M₂B or M₂(B, Si) phases begin to grow simultaneously with an FCC structure that presents a distribution of possible environs. The fully crystallized structure consists of boride and silicide phases and a paramagnetic FCC phase. The presence of Si promotes the crystallization of a BCC phase and the refinement of the microstructure leading to smaller and more uniform grains.

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1. Introduction

High-entropy alloys (HEA) have attracted significant research efforts in materials science and engineering due to remarkable properties. In particular, their outstanding mechanical properties, such as excellent wear resistance, high strength and exceptional ductility, make them an excellent choice for industrial applications [1]. HEA are multicomponent solid-solutions of several elements, all of them in equal or near-equal atomic percent, this leading to a high entropy of mixing. In some cases, it is found a complex microstructure, including intermetallic compounds which make them brittle and difficult to process. However, for some HEAs only body-centered cubic (BCC) or face-centered cubic (FCC) solid solutions form, without the presence of intermetallic compounds [2]. This type of alloys has led to a new design strategy for the development of new metallic materials, in particular in the field of metallic glasses (MGs). The appearance of some high-entropy metallic glasses (HEMGs) has introduced a new way to obtain new metallic glass-forming compositions. Instead of tailoring the properties of MGs through microalloying, i.e. minor additions of elements with less than 1 or 2 at%, the adequate design of HEMGs can combine the excellent properties of high-entropy alloys with the unique characteristics of metallic glasses. The non-crystalline structure of MGs results in a large elastic region, ultrahigh strength as well as good soft magnetic properties [3]. Moreover, the high-entropy alloy design could lead to enhancements of the glass forming ability of metallic glasses. For example, glass-forming Zr-Ti-Cu-Ni-Be compositions (with or without Hf) have been studied showing an increased glass transition temperature and a slower crystallization process that leads to FCC and BCC solid solutions together with some intermetallic phases [4,5].

The HEA FeCoCrNi has been extensively studied and its strength has been improved through the addition of minor elements that induce the precipitation of second phase grains [6,7]. This composition was used by Ding et al. as a base composition for developing new HEMGs in which 18 to 22 at% of B was added [8], thus combining the characteristics of a well-known glass-forming alloy (Fe$_{80}$B$_{20}$) with the HEA design strategy in which the Fe atoms were substituted by equal amounts of Fe, Co, Cr and Ni. These HEMGs show a higher hardness, ductility and
improved corrosion resistance as compared with the Fe-B amorphous alloys. On the other hand, Qi et al. produced (FeCoNi)(B,Si) high-entropy bulk metallic glasses with good soft magnetic and mechanical properties [9]. Thus, HEMGs with this set of elements could offer a combination of properties very useful for industrial applications. However, a complete characterization of the microstructural development during annealing is needed in order to be able to tailor their properties by means of thermal treatments and to control the evolution of their properties during working conditions in actual applications.

In this work we report the production of new HEMGs within the (FeCoCrNi)_{100-x-y}B_xSi_y compositional system. The mechanical and magnetic properties of these alloys will be reported in a following paper. Here, we will focus on the characterization of the several stages of the relaxation of the amorphous structure and the crystallization process. The compositions with \( x=20, y=0 \) and \( x=10, y=10 \) were selected with this purpose, as representatives of non-Si and Si containing alloys, in order to perform a detailed study of the microstructural development from the as-quenched samples to the fully crystalline ones. The microstructural characterization was performed using X-ray diffraction and transmission Mössbauer spectroscopy. The use of Mössbauer spectroscopy yields the quantitative atomic percentage of Fe atoms in a particular phase or in a particular environment, thus giving quantitative information of the iron containing crystalline phases at each stage that is difficult to obtain with other techniques. Furthermore, being a local probe, information about the local structural or chemical order can be obtained and in further works correlated to the macroscopic properties. Due to the complexity of the system, with 4 different metal atoms in equal concentration, the characterization of the crystalline route was performed identifying the overall structure of the phases, without determining the exact distribution of metal atoms inside the boride and silicide structures, similarly to other works in this type of materials [9,10]. This strategy is supported by the use of Mössbauer spectroscopy that can identify or discard the presence of pure Fe-based phases through their hyperfine parameters.

2. Materials and methods

The (FeCoCrNi)(B,Si) master alloys with the different compositions were produced by arc-melting of pure elements: Iron sheet (99.9 wt%), Cobalt lumps (99.5wt%), Chromium lumps
(99.95 wt%), Nickel wire (99.98 wt%), Boron lumps (99wt%), and Silicon lumps (99.999 wt%). In all the compositions the master alloy is equiatomic in Fe, Co, Cr and Ni. For comparison purposes the B and Si free FeCoCrNi HEA (in this article labeled as composition A) was also produced. The arc-melting process was performed on water-cooled copper plate in a Ti-gettered argon atmosphere to avoid oxidation. The master alloys were re-melted three times to assure the compositional homogeneity. Afterwards, amorphous ribbons were prepared from the alloys by melt spinning at a linear speed of 40 m s⁻¹. The thickness and the width of the resulting ribbons were of 20-30 μm and 4 mm, respectively. The as-cast ribbons were annealed at different temperatures (673, 723, 773, 823, 873, 923, 973 K) with a heating rate of 6 K min⁻¹, under a flow of Nitrogen, keeping the samples at the maximum temperature for 60 minutes and then cooling it down to room temperature at a heating rate of 6 K min⁻¹.

The structural and compositional properties of both as-cast and annealed samples were investigated by X-Ray Diffraction (XRD) in an Advanced Brucker Diffractometer in 2θ geometry using CuKα radiation and at the MSPD beamline of ALBA Synchrotron using X-rays with wavelength of 0.425 Å. The diffraction was performed on the as-quenched and annealed ribbons; this may introduce some artefacts in the detected intensities of the Bragg reflections due to texture or structural differences between the bulk and the surface of the samples. However, the production of powder for the XRD analysis was discarded in order to avoid structural changes originated due to the milling process. Differential Scanning Calorimetry (DSC) was performed in a NETZSCH DSC 404 with a heating rate of 20 K min⁻¹ under N₂ atmosphere. Scanning Electron Microscopy (SEM) was realized in a Zeiss NEON 40 device. SEM characterization of the interior of the ribbons was performed by cutting a trench of approximately 15 μm depth, thus arriving to the center of the ribbons thickness. The trench was dug by Focused Ion Beam of Ga ions after depositing a Pt protective coating in order to avoid the damage of the superficial zone. The study of the size distribution of the grains was done from the SEM images using the ImageJ software [11]. The study of the homogeneity of the samples and their composition was done by Energy Dispersive X-ray spectroscopy (EDS) with the same SEM. Transmission Mössbauer Spectroscopy (TMS) spectra were obtained at room temperature and pressure using a conventional constant acceleration spectrometer with a 25 mCi source of ⁵⁷Co in Rh matrix. The spectra were recorded in a multichannel analyzer using a velocity range of ±12 mm s⁻¹. Experimental spectra were fitted with Brand’s NORMOS program [12], considering for the
amorphous phase a distribution of quadrupole splittings. The samples after the several heat
treatments were fitted with a distribution of quadrupole splittings or hyperfine magnetic fields
together with one or two doublets for the paramagnetic phases and in some cases with one sextet
for a ferromagnetic phase. The isomer shift values are given relative to the isomer shift of a
Mössbauer spectrum of BCC-Fe recorded at room temperature.

3. Results and discussion

3.1. Glass formation.

Figure 1 shows the different compositions of the \((\text{FeCoCrNi})_{100-x-y}B_x\text{Si}_y\) system that were produced, indicating the state of the as-quenched ribbons. Glass-forming ability is observed for composition \((\text{FeCoCrNi})_{80}B_{20}\), as shown previously [8], as well as for the series of compositions substituting B by Si up to \((\text{FeCoCrNi})_{80}B_{10}\text{Si}_{10}\). Within this range of compositions, the partial substitution of B by Si is not detrimental for the formation of an amorphous structure, thus obtaining, as far as we know, a new class of high-entropy metallic glasses with Si content. The further substitution of B by Si results in crystalline samples. The increase of Si content maintaining a constant 10 at% of B produces amorphous samples up to \((\text{FeCoCrNi})_{70}B_{10}\text{Si}_{20}\), the latter being already partially crystalline. The chemical homogeneity of the as-quenched amorphous structures was checked by EDS, showing a uniform distribution of the metallic elements. A representative result is shown in figure S1 of the supplementary materials.
Figure 1. Pseudo-ternary phase diagram of the produced compositions reflecting the state of the as-quenched ribbons.

Figure 2 (top) shows the XRD patterns of all as-quenched samples with glass-formability. They show the characteristic amorphous halo of metallic glasses. Only the (FeCoCrNi)$_{70}$B$_{10}$Si$_{20}$ sample shows small crystalline peaks, indicating this sample is mainly amorphous but contains a small volume fraction of crystallites, and (FeCoCrNi)$_{70}$B$_{15}$Si$_{15}$ shows broad peaks over the amorphous halo, indicating that this composition is also only partially amorphous. Figure 2 (bottom) shows the diffraction pattern of the FeCoCrNi alloy clearly containing a single FCC structure, in accordance with previous works [13]. The figure also shows the crystalline patterns of the remaining compositions that are composed by single FCC or BCC structures or by multiphase compositions. It is worth to mention that the XRD patterns of compositions (FeCoCrNi)$_{90}$B$_{10}$ and (FeCoCrNi)$_{70}$B$_{20}$Si$_{10}$ can be compatible with a mixture of crystalline phases with a certain content of amorphous phase.
HEAs can be produced in crystalline structures (simple FCC, BCC or HCP solid solution structures) or, in some cases, in amorphous arrangements (metallic glasses). It has been proposed that it is possible to predict the structure of the alloy with the help of two parameters [14]: the atomic size difference ($\delta$) and the mixing enthalpy ($\Delta H_{\text{mix}}$). The atomic size difference is defined as

$$\delta = \sqrt{\sum_{i=1}^{n} c_i \left(1 - \frac{r_i}{r_f}\right)^2} \quad (1)$$
where \( \hat{r} \) is the average atomic radius and \( c_i \) and \( r_i \) are the atomic percentage and atomic radius of the \( i \)-th component [15]. The mixing enthalpy is defined as

\[
\Delta H_{\text{mix}} = \sum_{i=1}^{n} 4\Omega_{ij} c_i c_j
\]  

Here \( \Omega_{ij} = \Delta H_{\text{mix}-ij} \) is a regular solution interaction parameter between the \( i \)-th and \( j \)-th elements, representing the enthalpy of mixing for binary equal atomic alloys composed of these two components. The values of these parameters determine if a solid solution or an amorphous phase is formed. In particular, a solid solution can be produced if \( \delta \) is small (\( \delta < \sim 0.066 \)) and \( \Delta H_{\text{mix}} \) is either slightly positive or significantly negative (\( \sim -11.6 < \Delta H_{\text{mix}} < 3.2 \text{ kJ mol}^{-1} \)) whereas an amorphous phase can be produced if \( \delta \) is large (\( \delta > 0.064 \)), and \( \Delta H_{\text{mix}} \) is negative (\( \Delta H_{\text{mix}} < -12.2 \text{ kJ mol}^{-1} \)) [16]. The regions in the \( \delta-\Delta H_{\text{mix}} \) map where solid solutions or amorphous phases are favored following this model are shown in Figure 3 as dashed regions.

**Figure 3.** \( \Delta H_{\text{mix}} \) versus \( \delta \) map for as-cast high entropy alloys showing the regions favorable for obtaining crystalline solid solutions (upper left dashed region) or amorphous alloys (lower right dashed region).

In order to validate this empirical model, we calculated the atomic size difference and the mixing enthalpy for the compositions produced, given in Table S1 of the supplementary materials and plotted in the \( \delta-\Delta H_{\text{mix}} \) map of Figure 3. We distinguish between three cases; compositions with an amorphous as-quenched state, compositions with a crystalline state composed of borides, silicides and intermetallic phases (labeled as multiphase alloys), and compositions containing only FCC or BCC phases. For the latter ones, it is not known at this moment if the B and Si atoms could be inside the FCC or BCC structures or accumulated in a small fraction of intergranular amorphous phase not detectable by X-ray diffraction. The results confirm the general
criteria in the case of the FeCoCrNi alloy, as reported previously [17], and the amorphous compositions. The alloys with B and/or Si that show crystalline FCC or BCC solid solutions in their as-quenched states fall in the amorphous region although close to the border with the solid solution region. The multiphase compositions do not follow any clear trend as they appear mostly in the amorphous region but also outside the expected ranges for either amorphous, intermetallic or solid solution formation. Therefore, the general criteria to distinguish between HEAs and HEMGs are only approximately valid in these compositions, probably due to the presence of large contents of metalloid atoms.

As introduced above, this work will focus on the study of the crystallization process of the alloys with glass-forming ability. Compositions (FeCoCrNi)$_{80}$B$_{20}$ and (FeCoCrNi)$_{80}$B$_{10}$Si$_{10}$ were selected to perform a detailed study of the microstructural evolution, from now on labeled as AB and ABSi respectively. The thermal stability of the AB and ABSi HEMGs was studied by means of DSC and the results are shown in Figure 4. Both curves show a glass transition followed by two endothermic processes. The partial substitution of B by Si causes the increase of both the glass transition temperature and the temperature of the first crystallization event, while lowers the temperature of the second crystallization, that become almost overlapped with the first one. As it is common for as-quenched Fe-based metallic glasses, the structural relaxation while heating at constant rate is seen as an exothermal process expanding along a wide range of temperatures below the glass transition.

**Figure 4.** DSC patterns of (FeCoCrNi)$_{80}$B$_{20}$ and (FeCoCrNi)$_{80}$B$_{10}$Si$_{10}$ at a heating rate of 20 K min$^{-1}$.
The glass transition \((T_g)\) and onset of the first crystallization event \((T_{x1})\) temperatures are determined from the DSC curves and are shown in Table 1. The uncertainty in these temperatures is estimated to be less than 1 K. The glass forming ability (GFA) of these HEMGs can be assessed from the supercooled liquid region \(\Delta T_x = T_{x1} - T_g\) and the reduced glass transition temperature \(T_{rg} = T_g / T_m\) where \(T_m\) is the melting temperature. These parameters are also reported in Table 1 and show almost equal \(T_{rg}\) that precludes the production of these alloys in bulk shape; bulk formation roughly appears at \(T_{rg}\) values equal or higher than 0.6. The increase of the supercooled liquid region, \(\Delta T_x\), after the addition of Si reveals that the presence of this metalloid enhances the thermal stability of the amorphous phase in this family of alloys.

Table 1. The glass transition temperature \((T_g)\), onset of the first crystallization event temperature \((T_{x1})\), melting temperature \((T_m)\), supercooled liquid region \(\Delta T_x\) and reduced glass transition temperature \((T_{rg})\) for the \((\text{FeCoCrNi})_{80}\text{B}_{20}\) and \((\text{FeCoCrNi})_{80}\text{B}_{10}\text{Si}_{10}\) alloys (all temperatures with an uncertainty < 1 K).

<table>
<thead>
<tr>
<th>Alloy</th>
<th>(T_g) (K)</th>
<th>(T_{x1}) (K)</th>
<th>(T_m) (K)</th>
<th>(\Delta T_x) (K)</th>
<th>(T_{rg})</th>
</tr>
</thead>
<tbody>
<tr>
<td>((\text{FeCoCrNi})<em>{80}\text{B}</em>{20})</td>
<td>744</td>
<td>788</td>
<td>1395</td>
<td>44</td>
<td>0.53</td>
</tr>
<tr>
<td>((\text{FeCoCrNi})<em>{80}\text{B}</em>{10}\text{Si}_{10})</td>
<td>753</td>
<td>810</td>
<td>1449</td>
<td>57</td>
<td>0.52</td>
</tr>
</tbody>
</table>

3.2. Microstructural evolution during annealing

In order to study the evolution of the amorphous and crystalline phases during annealing, a series of heat treatments were applied to the as-quenched samples. These treatments were chosen in accordance with the DSC curves in order to shed light on the microstructure at the different stages of their transformation: before the glass transition temperature, at the beginning and at the end of the first crystallization event and at the end of the second crystallization event. Figure 5 shows the XRD diffractograms for the AB alloy annealed at temperatures between 673 and 973 K.
Annealing at 673 K, below the glass transition temperature, does not induce any crystallization and the diffractogram still shows the broad peak characteristic of the amorphous structure. However, the diffractograms at 723 and 773 K show the appearance of broad crystalline peaks, i.e. the formation of nanometer-sized crystals, coexisting with an amorphous structure. This crystallization corresponds to the first process with onset at \( T_{x1} \) (Figure 4). The presence of the crystalline phases is detected by X-ray diffraction in samples annealed at temperatures below the \( T_{x1} \) value determined by DSC at 20 K min\(^{-1}\) (Table 1); this is because of the temperature shift due to the different heating rates as the annealing protocols were performed at 6 K min\(^{-1}\). These nanocrystalline peaks can be identified as a M\(_3\)B phase, where M stands for metal and could be any combination of Fe, Co or Ni as the phases Fe\(_3\)B, Ni\(_3\)B and Co\(_3\)B present peaks compatible with the observed ones (the JCDPS cards used are detailed in table S2 in Supplementary Materials). It is worth to mention that the Ni and Co borides present an orthorhombic structure while the iron boride is tetragonal, showing the complexity of the crystalline phase that leads us to identify it as M\(_3\)B. Although the first crystallization products in many Fe-based metallic glasses are typically BCC-Fe or the Fe\(_{23}\)B\(_6\) phase, it is not unusual to find the precipitation of Fe\(_3\)B in some Fe-Si-B metallic glasses [18,19]. In the diffractograms of the samples annealed at 773 and 823 K an FCC phase begins to grow. Therefore, as a consequence of the first...
crystallization event $M_3B$ and FCC phase appear in the AB alloy. The $M_3B$ phase is not stable as it disappears before the second crystallization, as can be seen in the diffractogram above 873 K. At these higher temperatures the main peak corresponds to the FCC structure and the smaller peaks can be clearly identified as $M_2B$. In a similar way than the $M_3B$ phase, this boride can be identified with a Co$_2B$, a Fe$_2B$ and a Ni$_2B$ phase, all with tetragonal structure. Thus, the second crystallization event induces the formation of a $M_2B$ phase while the FCC phase continues to grow.

Figure 6 shows the XRD diffractograms for the ABSi alloy annealed at the same temperatures. Below 773 K, the diffractogram shows completely amorphous samples and at 773 K some nanocrystals begin to form that can be assigned to a BCC phase together with a peak that can be ascribed to a $M_2(B,Si)$ phase, that remains visible at higher annealing temperatures including the fully crystallized sample. In this case, the Si can be incorporated in the structure of the boride but can also be present in a Ni$_2$Si phase. Annealing at 823 K yields the formation of FCC phase together with a new boride, the $M_2(B,Si)$ phase that continues to grow at higher temperatures. At this temperature the peaks corresponding to the BCC phase are still present. Further annealing induces the disappearance of the BCC phase and the growth of the FCC and $M_2(B,Si)$ phases.

A selection of the most representative Mössbauer spectra of the studied samples are shown in Figures 7 and 8 for AB and ABSi alloys respectively, the spectra of the remaining samples can be found in Figures S2 and S3 of the supplementary materials. The as-quenched ones and the annealed ones up to 673 K show a typical wide doublet characteristic of paramagnetic amorphous phases. To take into account the structural disorder, these spectra have been fitted using a distribution of quadrupole splitting ($\Delta$) plotted in the insets of the figures. At 723 K the crystallization begins being noticed in both samples although, as already said, the crystallization path and products are different. For the AB alloy, a sextet of a ferromagnetic phase appears with a value of the hyperfine magnetic field (BHF) of 24.4 T. This phase grows in the sample annealed at 773 K, diminishes at 823 K and completely disappears at 873 K. Therefore, taking into account the XRD results and the hyperfine values (with $\Delta=0.09(8)$ mm s$^{-1}$ and isomer shift $\delta=0.03(4)$ mm s$^{-1}$, the magnitude in parenthesis corresponds to the standard deviation obtained from the fitting software) this ferromagnetic phase can be ascribed to a $M_3B$ structure (the remaining hyperfine parameters are given in Table S3 of the supplementary materials).
sextet corresponding to the M$_3$B phase has a large width (around 1.2 mm s$^{-1}$) to take into account the different metals (Fe, Co or Ni) that can enter in the structure and, thus, change the BHF value. We cannot use a distribution of hyperfine fields due to the fact that the available version of the fitting program does not allow using simultaneously a distribution of quadrupole splittings and BHF.

Figure 6. XRD patterns of (FeCoCrNi)$_{80}$B$_{10}$Si$_{10}$ alloy after annealing at different temperatures. The crystalline peaks are identified and correspond to an FCC, BCC and M$_3$(B, Si) phase.

Moreover, at 773 K, besides the amorphous and the boride phase, a new paramagnetic doublet appears that corresponds to the FCC phase (with $\Delta=0.54(1)$ mm s$^{-1}$ and $\delta=0.00(3)$ mm s$^{-1}$).
Figure 7. Experimental Mössbauer spectra (blue dots) and their fits (red lines) for the \((\text{FeCoCrNi})_{80}\text{B}_{20}\) alloy at three different representative stages of the crystallization process. In colored lines there are the subspectra fitted for the different phases (purple for the amorphous phase, blue and cyan for the FCC phase and orange and dark red for the borides). The insets show the distribution of quadrupole splittings (for the as-quenched samples) or hyperfine magnetic fields (for the annealed ones) needed for the fitting.
Figure 8. Experimental Mössbauer spectra (blue dots) and their fits (red lines) for the (FeCoCrNi)$_{80}$B$_{10}$Si$_{10}$ alloy at three different representative stages of the crystallization process. In colored lines there are the subspectra fitted for the different phases (blue and cyan for the FCC phase and orange and dark red for the BCC and borides). The insets show the distribution of quadrupole splittings (for the as-quenched samples) or hyperfine magnetic fields (for the annealed ones) needed for the fitting.

At 823 K there is still a remnant of the amorphous phase fitted with a distribution of quadrupole splittings and the paramagnetic crystalline phase can be fitted using two doublets with very
different values of the quadrupole splitting ($\Delta=0.57$ mm s$^{-1}$ and $\Delta=0.27(2)$ mm s$^{-1}$). The first doublet has been fitted with fixed hyperfine parameters in order to disentangle its contribution from the one corresponding to the amorphous phase with similar values of the hyperfine parameters. The two doublets for the crystalline phase are necessary for two different reasons. On the one hand, at 823 K are needed to keep the amount of amorphous phase below its amount at 773 K as it would be unphysical that the amorphous phase grows with the annealing temperature. On the other hand, at higher annealing temperatures, they are necessary to be able to account for the different intensities of the two absorption peaks in the central part of the spectrum. As in the XRD diffractograms only one FCC structure can be identified, this result indicates that the crystalline structure of the FCC phase presents a distribution of different chemical environs surrounding the Fe atoms. This is different than what is observed in the FCC phase of the HEA FeCoCrNi (alloy A in this work) where all the elements are randomly distributed in the structure and the Mössbauer spectrum (Figure 9) cannot be fitted with two doublets. In this case it is necessary to use a distribution of quadrupole splittings to take into account the random chemical ordering surrounding the Fe nuclei and characteristic of HEA alloys. The inset of Figure 9 shows this spread distribution over a wide range of $\Delta$ values, whereas the AB alloy annealed at 823 K only have two main contributions.

From 873 K to 973 K the spectra are similar, with two doublets for the FCC phase (with similar hyperfine parameters than the doublets at 823 K) and one BHF distribution for the ferromagnetic phase with an average hyperfine field of 28.6 T and zero quadrupole splitting and isomer shift. According to XRD results, this ferromagnetic phase can be associated to a M$_2$B phase. Although the M$_3$B and M$_2$B phases can present several subspectra according to the different positions that the Fe atoms can occupy in the structure and the number and types of elements surrounding it, such a detailed fitting model has not yielded good results and we opted for a general approach in which we are not able to precisely identify the effect of Co, Cr and Ni on the structure but we can identify and quantify the several phases that appear.
Figure 9. Mössbauer spectrum of the as-quenched FeCoCrNi HEA in ribbon form (blue dots) together with the best fitting (red line) to the experimental data. The inset shows the distribution of quadrupole splittings.

Figure 10 shows the evolution of the at% of Fe atoms in each phase obtained from the fitting of the Mössbauer spectra. These at% have an uncertainty of ± 0.5 %, as estimated from the fitting software. It is clearly shown how the amorphous phase firstly decomposes into an FCC plus a M$_3$B phases that coexist until 873 K, and at this temperature part of the FCC phase and the M$_3$B phase decomposes into a M$_2$B phase. The inset of the figure shows the evolution of the total ferromagnetic and paramagnetic phases demonstrating that in the fully crystallized sample there is the same amount of both magnetic orderings.

Figure 10. Variation of the at% (with a statistical fitting error of ±0.5 %, smaller than the symbol) of the different phases of the (FeCoCrNi)$_{80}$B$_{20}$ alloy as a function of the annealed temperature calculated from the analysis of the Mössbauer spectra. The inset shows in blue (red) the atomic percentage of the total paramagnetic (ferromagnetic) phases as a function of the annealed temperature.
For the ABSi alloy the fitting of the spectra can be performed similarly as in the previous AB samples, although some of the crystalline phases that appear are different. In this case, the first crystallization at 723 K corresponds to a phase that can be ascribed to a BCC phase close to BCC-Fe (with hyperfine field value of 34.1 T and zero quadrupole splitting and isomer shift) and that disappears at 873 K. The appearance of the FCC phase is delayed until 823 K, where the two doublets with similar hyperfine parameters than in the AB samples appear together with the formation of a new boride phase that would correspond to $M_2(B, Si)$ (with hyperfine field value around 15 T and zero quadrupole splitting and isomer shift). Thus, in this composition we also have the double distribution of environs in the FCC phase. The boride phase was fitted using a BHF distribution in an analogous way than the $M_2B$ phase in the AB alloy. However, the presence of Si in this phase diminishes the average BHF in the distribution if compared with the $M_2B$ phase. It is worth to mention that at 823 K the BCC phase has been fitted using a discrete wide sextet while the borides have been fitted with a distribution of hyperfine fields. This has been done in this way in order to be able to differentiate between the two ferromagnetic phases and keep track of their atomic percentages during the transformation. The evolution of all the phases is presented in Figure 11 with the inset showing that the fully crystalline sample contains more ferromagnetic (~64 at%) than paramagnetic phases (~36 at%). Therefore, the substitution of B by Si, besides changing the crystallization products, also favors the presence of ferromagnetic components. The crystallization path of both HEMGs can be summarized in the following way:

$$\text{AB amorphous} \rightarrow M_3B \rightarrow \text{FCC} + M_3B \rightarrow \text{FCC} + M_2B$$

$$\text{ABSi amorphous} \rightarrow \text{BCC} + M_2(B, Si) \rightarrow \text{FCC} + \text{BCC} + M_2(B, Si) \rightarrow \text{FCC} + M_2(B, Si)$$
Figure 11. Variation of the at% (with a statistical fitting error of ±0.5 %, smaller than the symbol) of the different phases of the (FeCoCrNi)$_{80}$B$_{10}$Si$_{10}$ alloy as a function of the annealed temperature calculated from the analysis of the Mössbauer spectra. The inset shows in blue (red) the atomic percentage of the total paramagnetic (ferromagnetic) phases as a function of the annealed temperature.

A more detailed study of the chemical ordering in the crystalline phases of both AB and ABSi alloys, in order to evaluate the effect and the quantity of the dilution of the Co, Cr and Ni atoms in them, is currently being performed by means of Mössbauer Spectra taken at a lower velocity range.

Figure 12 shows the SEM images of the interior of the AB and ABSi alloys at room temperature and after annealing at different temperatures up to 973 K. The as-quenched samples show a smooth and homogeneous cross section characteristic of the amorphous materials. Although, as detected by Mössbauer the crystallization process begins at 723 K, the formed crystals are too small to be noticed in the SEM images. In samples annealed at 823 K a clear crystalline structure, uniformly distributed, is observed with a typical grain size that continuously grows from 923 K to 973 K. Comparing the last row of Figure 12 it can be concluded that the presence of Si hinders the growth of the grains resulting in a sample with a smaller crystals compared to the AB sample.
Figure 12. SEM images of the HEMGs alloys (FeCoCrNi)$_{80}$B$_{20}$ (left column) and (FeCoCrNi)$_{80}$B$_{10}$Si$_{10}$ (right column) in their as-quenched state (first row) and after annealing at 823, 873 and 973 K.

To further study the effect of Si in the microstructure, the grain size distribution of both alloys as a function of the annealing temperature was computed from the SEM images (see Figure 13). The average grain size of the AB alloy (Figure 13 top) grows from ~69 (14) nm at 823 K to ~185
(65) nm at 973 K. The magnitudes in parenthesis corresponds to the standard deviation. In all the
temperatures the width of the distribution is large, especially after 823 K, indicating a
microstructure without a well-defined characteristic length. In contrast, Figure 13 (bottom)
shows the grain size distribution for the ABSi alloy, with a lower average grain size that grows
from ~37 (7) nm at 823 K to ~135 (60) nm at 973 K and with a narrower width below 973 K.
Therefore, the presence of Si instead of B in the microstructure not only reduces almost to a half
the average size of the crystals but also produces a more uniform microstructure.

![Graph of grain size distribution](image)

**Figure 13.** Distribution of grain sizes in (FeCoCrNi)$_{80}$B$_{20}$ (top) and (FeCoCrNi)$_{80}$B$_{10}$Si$_{10}$ (bottom) after annealing at different temperatures.

The devitrification of metallic glasses in order to obtain metallic glass / nanocrystalline
composites is a well-known strategy to produce materials with superior mechanical properties,
such as high hardness and wear resistance. It is also a common way to modify their magnetic properties. Metallic glasses based on the (FeCoCrNi)-(B,Si) compositions offer large possibilities to produce new materials with tuned properties depending on B-Si content and the annealing protocol. The effect of the annealing treatments on the mechanical and magnetic properties of the AB and ABSi alloys will be presented in future work.

4. Conclusions

In the present work, several compositions of high entropy metallic glasses have been produced: (FeCoCrNi)$_{80}$B$_{20}$, (FeCoCrNi)$_{80}$B$_{15}$Si$_{5}$, (FeCoCrNi)$_{75}$B$_{10}$Si$_{15}$ and (FeCoCrNi)$_{80}$B$_{10}$Si$_{10}$, the three last ones reported for the first time. The crystallization and microstructural evolution of two of them, (FeCoCrNi)$_{80}$B$_{20}$ and (FeCoCrNi)$_{80}$B$_{10}$Si$_{10}$, have been studied by means of X-ray diffraction, Mössbauer Spectroscopy and scanning electron microscopy. In both compositions the crystallization begins with the precipitation of a metastable boride (M$_3$B) or a BCC phase that disappears at higher temperatures to form stable M$_2$B or M$_2$(B,Si). The crystallization of these borides is accompanied by the appearance of a paramagnetic FCC phase that according to the Mössbauer results presents a distribution of different chemical environs surrounding the Fe atoms. Moreover, the presence of Si substituting some B in the alloys changes the crystallization path in a way that the fully crystalline sample has a larger ferromagnetic component and refines the microstructure with smaller and more uniform grains. The partial nanocrystallization of amorphous alloys is a well-known strategy to improve some of their mechanical and magnetic properties. The detailed knowledge of the crystallization route of these new HEMGs, presented in this work, opens the possibility to tailor their microstructure and to optimize their properties by applying appropriate thermal treatments.

Acknowledgements

L. Panahi acknowledges the financial support from Generalitat de Catalunya through a FI grant 2018FI_B_00502. P. Bruna and E. Pineda acknowledge the financial support from MINECO grant FIS2017-82625-P and from Generalitat de Catalunya grant 2017-SGR-42. X-ray diffraction experiments were performed at MSPD beamline at ALBA Synchrotron with the
collaboration of ALBA staff. The authors acknowledge the priceless help of Dr. Trifon Trifonov at the facilities of the Barcelona Research Center in Multiscale Science and Engineering.

Data Availability

The raw/processed data required to reproduce these findings cannot be shared at this time due to technical or time limitations.

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Figure
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Figure

Different phases are indicated with different symbols and colors. The peaks at 2θ = 40, 50, and 60 degrees correspond to specific crystallographic planes (111), (200), and (220), respectively. The phase notation includes FCC, BCC, and $M_2(B, Si)$. The intensity scale is shown on the y-axis, and the temperature scale is given on the right side of the graph for each set of peaks.
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All the authors equally contributed to the design, development, analysis and writing of the paper.
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