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Structure of some CoCrFeNi and CoCrFeNiPd multicomponent HEA alloys by diffraction techniques

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ABSTRACT

The structure of $CoCrFe_yNi$ (y = 0, 0.8 and 1.2) and $CoCrFeNi\text{-}Pd_x$ (x = 0.0, 0.5, 0.8, 1.0, 1.2 and 1.5) High Entropy Alloys has been investigated by neutron and standard X-ray as well as by high-energy X-ray diffraction techniques. The alloys were produced by arc melting and afterwards heat treated under several different conditions. It has been concluded that the CoCrFeNi alloy in as-cast condition is, contrary to what is claimed in the literature, not single-phase but consists of at least two different phases, both of fcc type. The difference in lattice constant between the two phases is close to 0.001 Å. Diffraction patterns measured by X-ray and neutron diffraction have shown that the structure of the alloy is not affected by 3 h heat treatment up to 1100 °C. Changing the amount of Fe has no drastic effect on alloy structure. The Pd-containing alloys have also all been found not to be single-phase but to consist of at least four different phases, all being of fcc type. The lattice constants for all phases increase with Pd content. The relative amounts of the different phases depend on Pd concentration. Furthermore, heat treatments of 3 h duration at different temperatures have a significant effect on the alloy phase composition. It is suggested that HEAs should be considered as multicomponent alloys presenting "simple" diffraction patterns, e.g. consisting of one or several lattices of fcc, hcp or bcc type with very close lattice parameters.

1. Introduction

Multicomponent metallic alloys of the type usually called High Entropy Alloys (HEAs) have recently raised considerable attention because of their attractive physical properties [1–6] such as high hardness, outstanding wear resistance, good high-temperature strength and thermal stability. A HEA was originally defined as an alloy consisting of 5 or more components of relative compositions in the range 5–35 at.% forming single and simple close-packed crystalline structures of solid solution type [7]. However, there are very few, if any, HEAs that are truly single phase. Many of the alloys taken to meet the current definition of a HEA alloy are in reality multiphase with in most cases one main phase and one or several minor phases [8,9]. Thus, the original definition of a HEA has to be reconsidered and several approaches to this have been made (see for example [10,11]). From the literature and the authors' own experience HEAs should be considered as multicomponent alloys presenting "simple" diffraction patterns, e.g. consisting of one or several lattices of fcc or bcc type with very close lattice parameters. The alloys that are discussed below correspond to this definition and will irrespective of their actual compositions, be denoted as HEAs.

Numerous publications have been devoted to finding rules by which it is possible to predict whether an alloy of a certain composition forms a HEA upon solidification. Suggested models based on semi-empirical approaches have considered both electronic quantities such as the elemental electronegativities, concentrations of valence electrons and the itinerant electron concentrations d-orbital energy levels and also thermodynamic ones such as the enthalpy and the entropy of mixing of the binaries that can be formed by the elements [12–21]. The parameters have been combined with the atomic size mismatch of the elements in

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order to predict if an alloy is of HEA type via statistical methods, see [22–25] and references therein. Furthermore, CALPHAD [5,10,26–28], DFT and *ab initio* [29–31] calculations have been used for the same purpose. The main difficulty met for the validation of models and calculations is that measured structures and microstructures and also physical properties published in the literature show a considerable spread. This circumstance suggests that the alloys in many cases have not been adequately characterized in terms of possible small contents of intermetallic phases and grain size distributions depending on different production techniques and thermal treatments. In order to resolve this situation it is obviously necessary to use different complementary experimental techniques covering a length scale from a tenth of a nanometer to several microns.

One well reported family of HEAs is based on the four component CoCrFeNi (below denoted CCFN) alloy to which has been added one, two or three elements in different proportions, either separately or in combination, including Al, Cu, Mn, Ti, Pd, Sn, Ru, W, etc. Many different techniques have been used to characterize the structures of the resulting alloys, as well as their physical properties. Nevertheless, the understanding of why some of these alloys form simple close-packed structures and some additional intermetallic phases is still lacking. Also the mechanism behind the composition-property relationships is largely unclear.

The base CCFN alloy, even though it contains only four elements, presents the characteristics of a HEA as its diffraction pattern is apparently very simple. It has been extensively studied during the last ten years and has been reported to be single-phase and a true

Table 1
Experimental parameters for the different diffraction measurements. The wave vector Q is given by $Q = 4\pi/\lambda\sin(\theta)$ where λ is the wavelength of the incident radiation and 2θ the scattering angle. T denotes transmission geometry and R reflection, respectively.

	Neutron diffraction (ND) (ILL)		High-energy X-ray diffraction (HEXRD) (ESRF) ID22	Standard X-ray diffraction (XRD) (GPM)
	D20	D2B		
Wavelength of incident radiation (Å)	1.123	1.595	0.400913	1.78897, 1.79285
Resolution (ΔQ/Q) at Q = 3 $Å^{-1}$ (%)	~1	~0.2	~0.03	~0.2
Measurement geometry	T (fixed sample)	T (rotating sample)	T (rotating sample)	R (fixed sample)

Table 2
List of alloys in different conditions investigated by the experimental techniques used in the present work. (T0) corresponds to an alloy in as-cast condition allowed to cool in the Cu mold while (T1), (T2) and (T3) denotes the temperatures 1100 °C, 400 °C, and 700 °C, respectively, at which the alloy was kept during 3 h (q) indicates that the alloy after annealing has been dropped into ice water and (s) that the alloy was allowed to cool in the furnace. All measurements were performed at ambient temperature.

CCF_yNPd_x		Nominal alloy composition	ND (ILL)		HEXRD (ESRF)	XRD (GPM)
y	x		D20	D2B		
0.8	0	$Co_{26.3}Cr_{26.3}Fe_{21.1}Ni_{26.3}$	T0, T1(q), T1 (s), T2(q), T3(q)			
1.0	0	$Co_{25}Cr_{25}Fe_{25}Ni_{25}$	T0, T1(q), T1(s), T2(q), T3(q)		T0	T0, T1(q), T1(s), T3(q), T3(q), T1(q) + T3(q)
	0.5	$Co_{22.2}Cr_{22.2}Fe_{22.2}Ni_{22.2}Pd_{11.1}$			T0	T0
	0.8	$Co_{20.8}Cr_{20.8}Fe_{20.8}Ni_{20.8}Pd_{16.7}$	T0, T1(q), T3(q)			
	1.0	$Co_{20}Cr_{20}Fe_{20}Ni_{20}Pd_{20}$	T0, T1(q), T3(q)	T1(q), T1(s)	T0	T0, T1(q), T3(q), T1(q) + T3(q)
	1.2	$Co_{19.2}Cr_{19.2}Fe_{19.2}Ni_{19.2}Pd_{23.1}$	T0, T1(q), T3(q)			
	1.5	$Co_{18.2}Cr_{18.2}Fe_{18.2}Ni_{18.2}Pd_{27.3}$			T0	T0
1.2	0	$Co_{23.8}Cr_{23.8}Fe_{28.6}Ni_{23.8}$	T0, T1(q), T3(q)		T0	

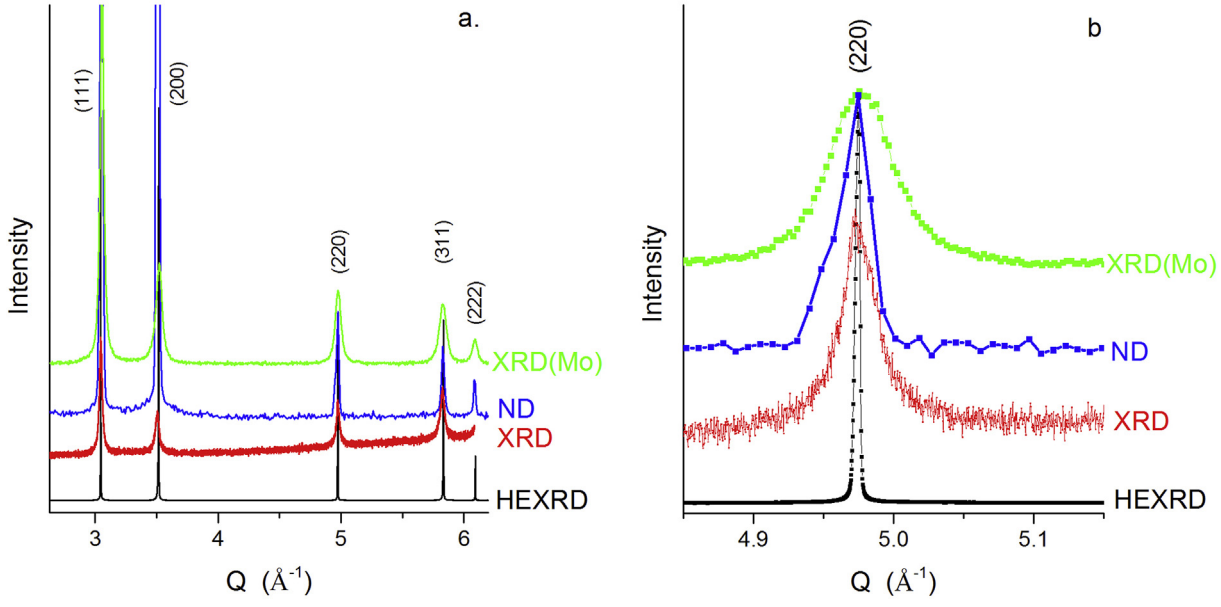

Fig. 1. (a) Measured diffraction patterns for a CCFN alloy by different experimental techniques. (b) The fcc (220) peak on an enlarged scale. Patterns are measured by HEXRD (bottom curve), XRD (1st middle curve), ND (2nd middle curve) and XRD(Mo) (top curve). The corresponding Miller indices are shown in a).