

Undercooling studies and growth velocity measurements on multi-component FeCuNi{X} alloys

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Abstract

High entropy alloys or complex concentrated alloys have recently gained wide attention due to their excellent high temperature properties. New alloys are also being explored for functional properties towards magnetic and thermoelectric applications. Unlike conventional alloy design, exploration of high entropy alloys involves the central region of the phase diagram. Microstructures of these alloys processed through melt route have shown multiple phases which challenge their designation as high entropy alloys. Undercooling is a possibility to obtain metastable microstructures. Solidification studies on undercooled alloys of this class are limited to only a few in the open literature. In this work, undercooling studies were carried out on FeCuNi{X} series of alloys where {X} = {Co, Sn}. Microstructure evolution was correlated to the extent of undercooling. A maximum undercooling of >200 K was achieved in these studies. During solidification, high speed video imaging was employed to measure the recalescence growth velocity as a function of undercooling. The growth velocity showed sluggish compared to Ni based alloys below 175°C undercooling temperature.

Introduction

Multicomponent alloys with equatomic compositions have attracted many research groups for the last few years. These alloys can be called with different designations like high entropy alloys (HEAs) [1], complex concentrated alloys [2], etc. High entropy alloys with remarkable properties are reported in literature [2]. This category of alloys can be a potential candidates in different sectors such as high temperature applications [3 4], cryogenic applications [5], functional applications [6], structural applications [7] etc. For the application, the behaviour of these alloys at different processing conditions and understanding of its physical metallurgy is required. Presently different processing techniques are employed to manufacture HEAs, which include conventional castings, mechanical alloying with sintering and induction melting, etc. The study of solidification behaviour of these alloys under different conditions is limited and needed to be explored.

There are a few undercooling studies reported on HEAs such as CoCrCuFeNi [8,9] and WMoTa NbZr [10]. These studies shown the liquid phase separation phenomenon could

be occurred at undercooling conditions in CoCuFe containing alloys. Liquid phase separation was reported in as cast condition of HEAs which violates the concept of HEA phase formation [11]. In case of WMoTaNbZr alloys shows stable BCC phase at all levels of undercooling [10]. HEAs behaviour at different undercooling conditions is yet to be explored. Sn added HEAs were reported to be good at corrosion properties in NaCl solution while compared to 304 stainless steel [12]. In this present study FeCoNiCuSn₅ HEA was taken for undercooling studies. The microstructure variation and observed growth velocity was correlated with different undercooling temperatures.

Experimental Details

As cast samples in the form of button with a weight of 20 gm were prepared by using vacuum arc melting technique with a non consumable tungsten electrode. The pure elements (>99.9%) was weighed based on the atomic proportion and melted in the argon atmosphere. The samples were melted for six times to get a homogeneous distribution of alloying elements and after each melting, cast buttons were flipped. The arc melted button was cut in to required quantity by using electrical discharge machining and the cut samples were polished to remove the oxide layer. The undercooling experiments were carried out using melt fluxing technique and boron tri oxide was used as a flux during experiments. Temperature data with respect to time was captured using two colour infrared pyrometer with an accuracy of $\pm 5^{\circ}\text{C}$. The high speed imaging of solidification process was captured by using Photron FASTCAM[®] high speed camera with 1 lakh frames per second and the data was analysed by using Photron FASTCAM[®] Viewer software. The as cast and undercooled samples were characterised by using back scattered electron imaging with EDS attachment using Quanta 400[®]. Structural characterisation was done by XRD using X'pert Pro PANalytical[®] with Cu-K α ($\lambda = 0.154056$ nm) radiation, operated at 45 kV and 30 mA, with a step size of $2\theta = 0.017$ deg. Transmission electron microscopy studies were done on Technai-FEI[®] to identify phases in as cast samples.

Results and discussion

As cast microstructure

The as cast sample consists of 3 major phases such as FeCoNi rich phase, Cu rich phase and CuNiSn rich phase. Since Cu having immiscibility with Fe and Co, it will segregate in the interdendritic region. Figure 1 shows the existence of three phases in the present alloy.

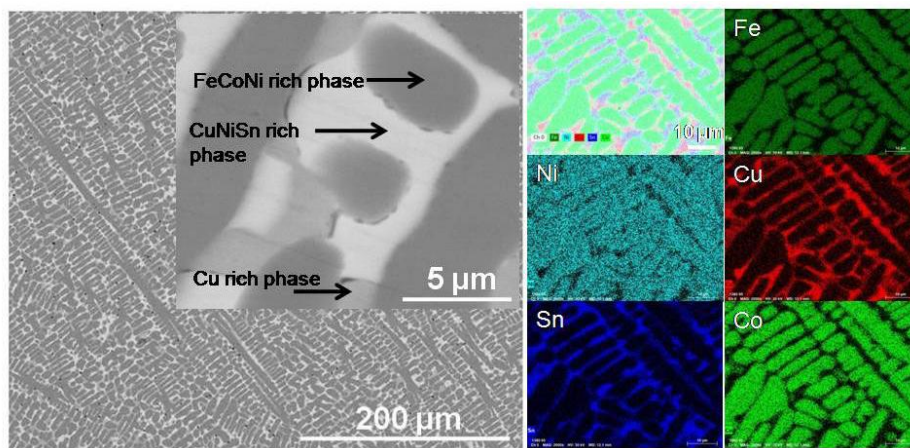


Figure 1: BSE SEM image of as-cast sample and its EDS mapping

From the BSE low magnification image, it is clear that the FeCoNi phase is the primary dendritic phase with Cu rich and CuNiSn rich phases formed in the interdendritic regions. It is evident from the EDS mapping that the Fe and Co are almost absent at the interdendritic region where as Ni distribution is less in the interdendritic region but not completely depleted. TEM analysis shown in figure 2 confirms that the major phase in the alloy is disordered FCC.

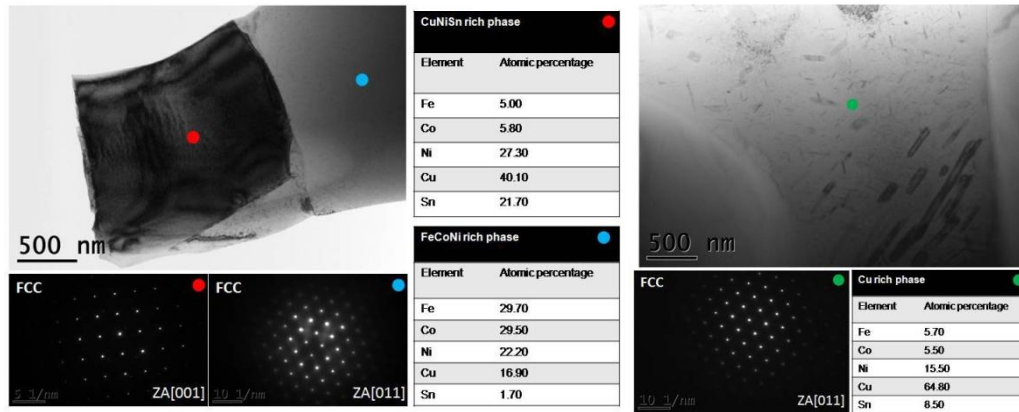


Figure 2: TEM micrograph and EDS quantification of as cast sample

From EDS spot analysis in TEM, it is clearly shown that the primary phase formed is FeCoNi rich and it also confirms that Ni is distributed in Cu rich and CuNiSn rich phases. The CuNiSn rich phase consists of a major amount of Cu and Ni. The TEM reveals formation of fine precipitates in the Cu rich region which may be due to the immiscible nature of Cu with Co and Fe leading to precipitation or segregation.

Time temperature characteristics

The typical temperature variation with respect to time for the alloy chosen is shown in figure 3. The liquidus of the studied alloy is 1363°C marked in the figure 3. The undercooling temperature is taken as the difference between the recalescence temperature and liquidus temperature. The curve shows a primary recalescence event which corresponds to the formation of FeCoNi rich primary dendritic phase and slope change around 950°C shows the formation of CuNiSn rich phase. The studied alloy shows a maximum undercooling of $0.15T_L$.

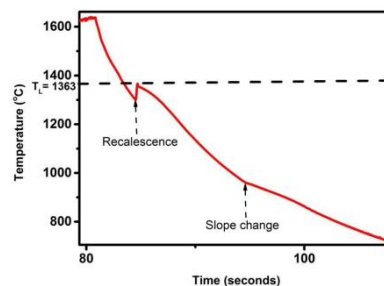


Figure 3: Typical time temperature characteristics of FeCoNiCuSn₅ during undercooling experiments

Undercooled microstructure

SEM-BSE image shown in figure 4 confirms the variation of undercooled samples compared to as cast. It is clear that all phases are present in all level of undercooling and also confirms that with increasing level of undercooling there is a refinement in microstructure. There are reports on liquid phase separation of Fe and Cu rich region in Fe-Cu-Sn system at different undercooling conditions [13]. The studied alloy shows no liquid phase separation and no macro segregation at all level of undercooling.

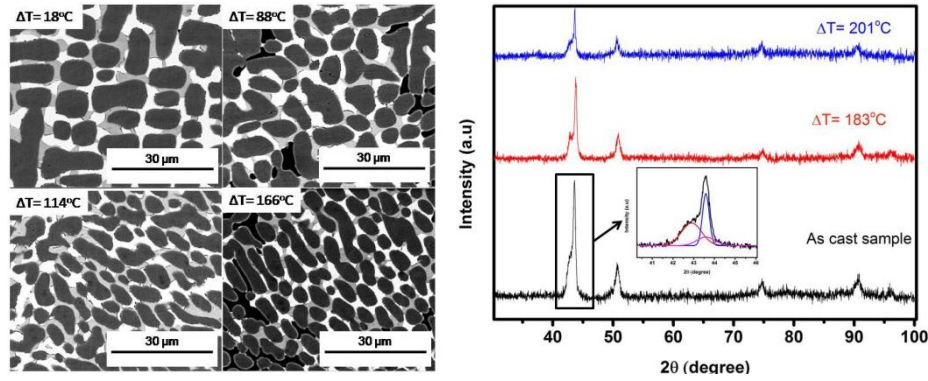


Figure 4: SEM-BSE images and XRD pattern of undercooled sample

The XRD analysis confirms that the phases are stable even at deeper undercooling in the studied HEA. The deconvolution in the first peak reveals that the presence of 3 phases which are having close lattice parameters. The XRD confirms that there is no major peak shifting and also the strain due to undercooling in this system is negligible.

Growth velocity

Figure 5 shows the growth velocity calculated from the high speed video imaging confirms that the growth velocity increases with the undercooling temperature. The velocity order shown here is sluggish (at undercooling below 175°C) compared to the pure metals and conventional Ni based alloys. In the higher undercooling regime (above 175°C) the observed growth velocity is more than 5 m/sec (not shown in figure 5) may attributed to the deep undercooling achieved. The red curve shown in figure 5 confirms that the velocity variation with respect to undercooling temperature increasing non-linearly in the range of undercooling below 175°C. The dependence of growth velocity with undercooling temperature in the system can be written as

$$\text{Growth velocity (V) (m/sec)} = 1.1346 \times 10^{-7} (\Delta T)^{2.95815}$$

The growth velocity in the current system was sluggish compared to the Fe-Co binary systems [14] and comparable to the commercial tool steels [15]. The velocity domain is comparable with the reported HEAs such as CoCrCuFeNi and WMoTaNbZr. The observed velocity was comparable to intermetallic compounds [16] and lower than Ni based alloys [17]. The growth velocity of Fe-Cu-Sn system which has shown liquid phase separation [13] was lower than the studied HEA

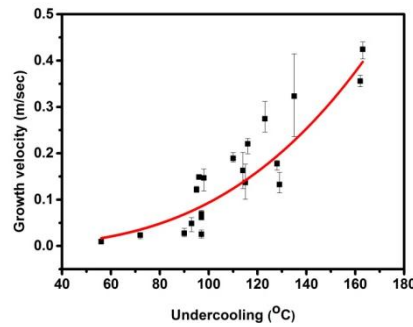


Figure 5: Growth velocity Vs. undercooling temperature

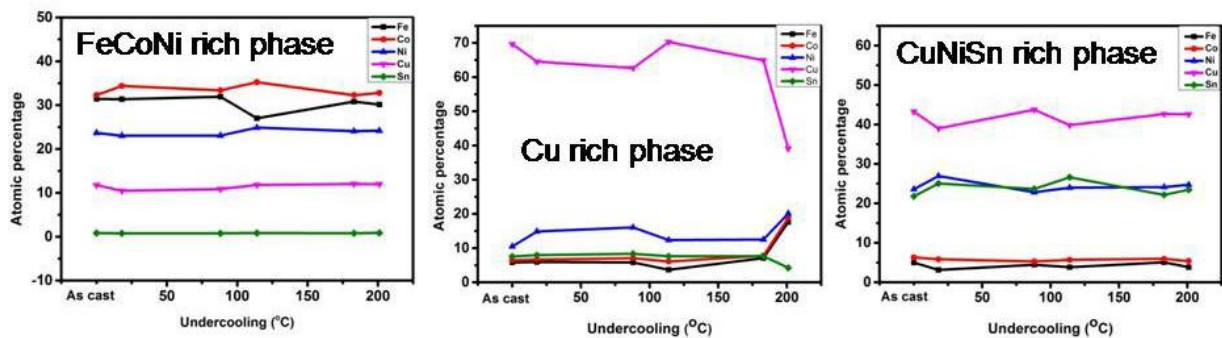


Figure 6: Compositional variation of individual elements in different phases

The EDS analysis of individual elements in different phases plotted in figure 6. It shows that the individual element atomic fraction is almost equal in FeCoNi rich phase at all levels of undercooling. The Cu and Sn are slightly increasing with increase in undercooling confirms there is no significant solute trapping in the primary dendritic phase. The dip in Cu concentration in Cu rich phase at highest undercooling may be due to solute trapping in this regime. This might be the reason for high velocity in that domain.

Summary

Undercooling studies on FeCoNiCuSn₅ alloy was carried out and obtained a maximum undercooling temperature of 0.15T_L. The studies confirm that the phase stability of studied HEA in deep undercooling conditions. There is no metastable phase formation in this system at all levels of obtained undercooling. The growth velocity increasing non-linearly in the range of undercooling temperature below 175°C. EDS results confirms that there is no significant solute trapping with respect to undercooling in the studied alloy.

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