Magnetism in $CoCrFeNiZr_x$ eutectic high-entropy alloys: the influence of microstructure on the properties of a multiphase HEA

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In recent years the alloy design strategy called *high-entropy alloys (HEAs)* [1] has gained popularity and it enables one to synthesize novel multicomponent alloys, in which the dominant phase is a simple solid solution, e.g. bcc or fcc, consisting of five or more principal elements (elements in similar concentrations, from 5 at.% to 35% each). Besides the interesting properties and potential applications [2], HEAs also provide some unique challenges from the perspective of basic physics: a) their physical properties are not obvious as they are random mixtures of a large number of elements; b) their properties, e.g. superconductivity [3], may be influenced by the nanostructure; c) most high-entropy alloys are not "ideal" single solid solutions but "real" multiphase materials, whose microstructure may be a coexistence of two different solid solutions, a coexistence of a solid solution and an intermetallic, etc. This contribution will tackle this last challenge and by analysing the magnetism of $CoCrFeNiZr_x$ eutectic HEAs with regard to their microstructure, we will at least partially address the open question whether the physical properties of a "real" multiphase HEA can be obtained as a simple composition-weighted average of the structural phases' properties.

For the case of eutectic $CoCrFeNiZr_x$ HEAs, it was previously reported [4] that they are phase-segregated mixtures of three different phases, an fcc solid solution, a C15 Laves phase and Ni_7Zr_2. Our investigation into these HEAs [5] correlated magnetic, electrical resistivity and specific heat measurements with the microstructure as obtained by XRD and SEM. For our composition range of $x = 0.4 – 0.5$, XRD and SEM (see Fig. 1) show two dominant structural phases occurring in the $CoCrFeNiZr_x$ HEAs: a) a Zr-free random solid solution of Co, Cr, Fe and Ni and b) a cubic C15 Laves phase isostructural to $MgCu_2$, with the Mg site populated exclusively by Zr and the other sites by a Co-Cr-Fe-Ni mixture. The C15 Laves phase occurs solely in the fine lamellas of the eutectic matrix. Meanwhile, the Co-Cr-Fe-Ni solid solution also appears as fine lamellas in the eutectic matrix, but additionally it appears in the $x = 0.4$ and $x = 0.45$ samples as bulky dendrites. The magnetic measurements indicate – via a decomposition of the dc magnetization, peaks in the ac magnetization and the widths of the *M(H)* hysteresis loops – that two magnetic structures are appearing in the samples, see Fig. 2: a) a disordered ferromagnetic (F) component consisting of small ferromagnetically polarized domains and b) a superparamagnetic-like (S) component. We report that the most tempting and seemingly obvious mapping of one structural phase (C15 Laves, fcc solid solution) to one magnetic component (F, S) does not work in the eutectic $CoCrFeNiZr_x$ HEAs as the resulting compositional average fails to properly describe the large variation of magnetic properties with the relatively small variation of volume fraction of structural phases. As an alternative, we offer a different explanation of the magnetism of $CoCrFeNiZr_x$ HEAs, which also incorporates the notion that a long-range ordered ferromagnetic structure can only occur in the bulk of a sufficiently large and sufficiently ordered crystal. Due to the small size of the lamellas (both C15 Laves and fcc solution) in the eutectic matrix, the spins there cannot order ferromagnetically and constitute the superparamagnetic (S) component. On the contrary, the bulky fcc dendrites and perhaps some larger fcc lamellas are large enough for their spins to order ferromagnetically and constitute the F component. Thus, the amount of bulky dendrites is the predominant factor determining the amount of magnetic F-component – just as observed experimentally, where the x = 0.4 sample has by far the largest amount of both dendrites and F-component.

At this point, let us provide some additional data on the physical properties for our colleagues' future reference. The transition temperatures are ≈ 160 K for the F-component and ≈ 40 K for the S-component, with the frequency-dependent shifts in the ac mag. susceptibility (see Fig. 2) indicating slowing-down dynamics for both transitions. The possibility of the S-component being spin-glass or mictomagnetic was explored and discarded. The electrical resisitivities increase from 91 μΩcm at 2 K to 109 μΩcm at 390 K.

To sum up, the magnetism of $CoCrFeNiZr_x$ eutectic HEAs is a problem of a multiphase "real" HEA, where simple compositional averages are not sufficient and the situation is severely complicated by the microstructure. The take-away message is that one might need to be careful to include or at least consider the microstructure in interpretations of physical properties of multiphase "real" HEAs.

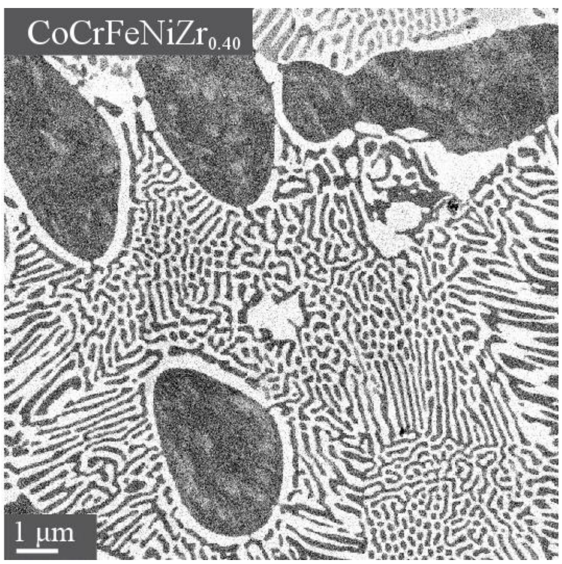

Figure 1. SEM BSE image of the $CoCrFeNiZr_{0.40}$ sample. The darker blobs are small parts of the bulky dendrites. Note that there are only two phases in the image, the darker fcc solution (dendrites, dark eutectic lamellas) and the lighter C15 Laves (light eutectic lamellas only).

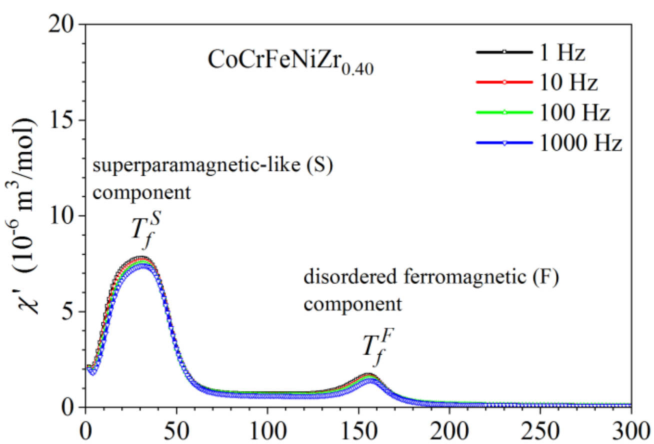

Figure 2. AC magnetic susceptibility for the $CoCrFeNiZr_{0.40}$ sample. The idea that the F component must be either the dark or the light phase in Figure 2 and the S component the other one, doesn't work! See text.

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