The effect of cerium in Ce-Gd-Tb-Dy-Ho hexagonal high-entropy alloy

S. Vrtnik[1], P. Koželj[1], A. Jelen[1], Z. Jagličić[2], M. Feuerbacher[3], J. Dolinšek[1]

[1]*Jožef Stefan Institute and University of Ljubljana, Faculty of Mathematics and Physics, Jamova 39, SI-1000 Ljubljana, Slovenia*

[2]*Institute of Mathematics, Physics and Mechanics and University of Ljubljana, Faculty of Civil and Geodetic Engineering, Jadranska 19, SI-1000 Ljubljana, Slovenia*

[3]*Institut für Mikrostrukturforschung, Forschungszentrum Jülich, D-52425 Jülich, Germany*

stane.vrtnik@ijs.si

High-entropy alloys (HEAs) were first introduced in 2004 and represent a novel field in materials science [1]. HEAs are metallic alloys composed of multiple principal elements (5 or more) in equimolar or near-equimolar ratios and are conceptually different from conventional alloys, which are typically based on one principal element. According to this concept, high entropy of mixing can stabilize disordered solid solution phases with simple structures, like a body-centered cubic (bcc), a face-centered cubic (fcc), and a hexagonal close-packed (hcp) structure. The elements are randomly distributed on the crystal lattice, and therefore HEAs represent a new class of metallic materials between ordered crystals and metallic glasses.

Among HEAs, rare-earth (RE) based hexagonal high-entropy alloys containing elements from the heavy half of the RE series (from Gd to Lu) are special. They are considered as *prototypes of an ideal HEA* with completely random distribution of the elements on an almost undistorted hexagonal close-packed lattice [2].

This contribution will present a study of the Ce-Gd-Tb-Dy-Ho hexagonal HEA (HEA-Ce), where a light-RE element Ce is alloyed with four heavy-RE elements [3]. Since the binary mixing enthalpies of Ce with these elements are all zero, random mixing of the elements and an ideal solid solution can be expected. Contrary to these expectations, a two-phase structure forms in the HEA-Ce, consisting of the majority hcp matrix plus rhombohedral precipitates that occupy a significant fraction of the sample's volume, with both phases having very similar composition (Fig. 1).

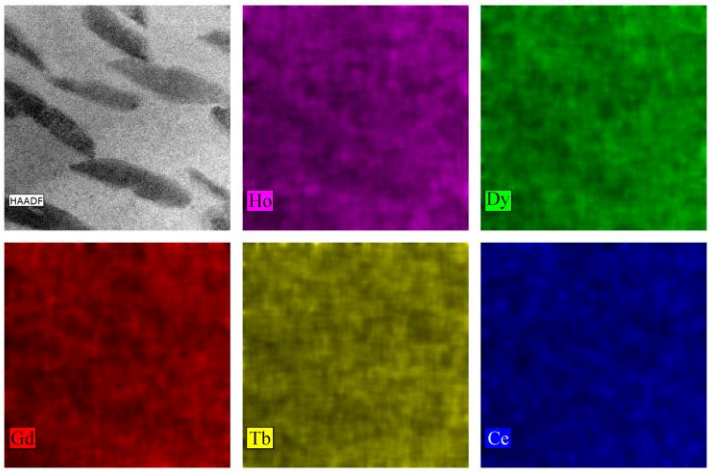

Figure 1. EDS elemental maps of the HEA-Ce sample.

The "ideality" of the HEA-Ce solid solution is very likely compromised by the fact that the crystal structure of Ce is different (fcc for γ-Ce and double-layered hcp (dhcp) for β-Ce) from the structures of other elements (hcp) in the HEA-Ce.

We have determined the magnetic state of the HEA-Ce by performing measurements of the magnetic properties, the specific heat and the electrical resistivity in a magnetic field. The DC magnetization (Fig. 2), the AC susceptibility and the $M(H)$ curves show that the moments in the HEA-Ce undergo a 2nd-order thermodynamic phase transition to a ferromagnetic (FM) state. The $M_{zfc} < M_{fc}$ inequality below T_C is a sign of nonergodicity and high degeneracy of the collective spin state. The zfc magnetization is zero at the lowest measured temperature T = 2 K, indicating that the magnetic structure upon cooling in zero field breaks up into FM-polarized domains that orient randomly, so that the vector sum of the domains' moments is zero. This is further supported by the low-temperature specific heat measurements (Fig. 3) where field-dependent linear-in-T contribution is present, as is commonly found in strongly disordered magnetic systems. Summing up, the magnetically ordered state of the HEA-Ce can be described as a disordered FM state with a 2nd-order thermodynamic FM phase transition at T_C = 140 K.

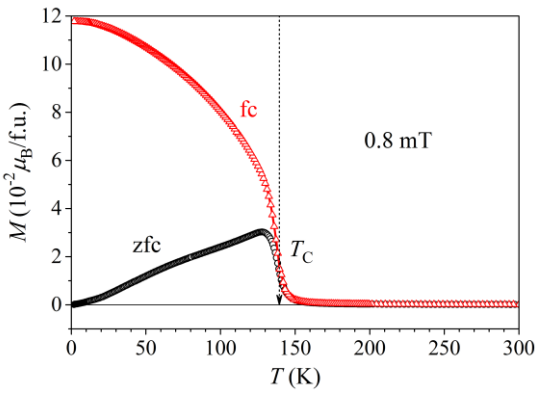

Figure 2. DC magnetization measured for the zfc and fc protocols.

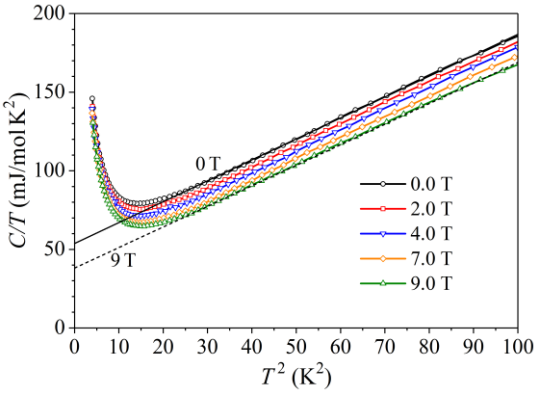

Figure 3. Low-temperature specific heat in magnetic fields up to 9 T shown in a C/T versus T^2 plot.

While investigating the effect of Ce on the magnetism of RE-based HEAs, it is interesting to compare it with magnetic properties of equimolar Y-Gd-Tb-Dy-Ho hexagonal HEA, which is a single-phase material with rich magnetic field-temperature (H,T) phase diagram – containing a long-range-ordered periodic (helical) antiferromagnetic state, a field-induced FM state and a low-temperature spin-glass state [4]. In contrast, introduction of the Ce light-RE element into the matrix of the same four heavy-RE elements changes the crystal structure (a two-phase structure forms) and long-range-ordered periodic magnetic structures do not form anymore.

The introduction of Ce did not yield any of the exceptional phenomena that are characteristic for the Ce-containing alloys and compounds (mixed valence, heavy-fermion or unconventional superconductivity).

1. J.W. Yeh, S.K. Chen, S.J. Lin, J.Y. Gan, T.S. Chin, T.T. Shun, C.H. Tsau, *et al.*, *Adv. Eng. Mater.*, **6**, (2004), 299.

2. M. Feuerbacher, M. Heidelmann, and C. Thomas, *Mat. Res. Lett.*, **3**, (2014), 1.

3. S. Vrtnik, J. Lužnik, P. Koželj, A. Jelen, J. Luzar, Z. Jagličić, A. Meden, *et al.*, *J. Alloys Compd.*, **742**, (2018), 877.

4. J. Lužnik, P. Koželj, S. Vrtnik, A. Jelen, Z. Jagličić, A. Meden, *et al.*, *Phys. Rev. B*, **92**, (2015), 224201.