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Phase formations in low density high entropy alloys

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ABSTRACT

Phase formations in high entropy alloys (HEAs) with at least two light elements in literature are predicted by CALPHAD (CALculation of PHAse Diagrams) thermodynamic calculations and the results are compared with experimental observations. The comparison suggests that the applicability of traditional CALPHAD calculations depends on the manufacturing processes of HEAs. Factors such as solute trapping, energies of defects need to be considered while predicting phases in HEAs prepared by non-equilibrium processes. The effects of light elements (Al, Ti, Si, alkali and alkaline earth metals) on the phase formations in HEAs are discussed. Especially, intermetallics predicted for Si-containing HEAs by traditional CALPHAD calculation can be suppressed in rapid solidification process, due to the solute trapping effect. Mg or other alkali and alkaline earth metals can lead to the formations of various intermetallics in HEAs prepared by conventional casting, but could be dissolved into solid solutions by non-equilibrium processes such as mechanical alloying. It is proposed that non-equilibrium processes may be an effective way to introduce light elements Si, alkali and alkaline earth metals into HEAs.

1. Introduction

High entropy alloys (HEAs) have opened up an exciting area for new alloy design and development [1,2]. Different from conventional alloys, like Al, Fe, Ti-based alloys or TiAl intermetallics, HEAs usually contain five or more principal elements and the content of each is between 5 and 35 at% [1]. They are reported to have promising mechanical, chemical and magnetic properties, such as high strength, high wear resistance, high oxidation resistance, etc. [2]. Primarily due to the high entropy effect, the microstructures of HEAs usually exhibit single solid solution like body-centered cubic (BCC), face-centered cubic (FCC), hexagonal close packed (HCP), mixture of the above, or predominant solution with minor intermetallics.

Several criteria are used to predict the formation of a solid solution. One of the criteria is the classical Hume-Rothery rule based on atomic size, crystal structure, valence and electronegativity. Another group of criteria introduce thermodynamic parameters such as enthalpy of mixing and entropy of mixing, topological parameter describing the effect of atomic size [3,4], or mismatch entropy [5]. In recent decades, CALPHAD (CALculation of PHAse Diagrams) approach has been increasingly used in alloy design, within an Integrated Computational Materials Engineering (ICME) framework [6]. Through phase diagrams and phase stabilities calculated from multi-component thermodynamic databases, it is more convenient to establish phase relationships [7–11], which can accelerate the development of HEAs. Zhang et al. [7] discussed the entropy of mixing on the stability of solid solution and the use of CALPHAD approach in the development of HEAs. Zhang et al. [8] investigated the effects of each element in the AlCoCrFeNi alloys on the FCC/BCC structure transition and the simulation from thermodynamic database agrees well with the experimental results. Zhang et al. [9] employed the CALPHAD approach to investigate the phase stability and phase transformation within the Al-Co-Cr-Fe-Ni system. Raghavan et al. [10] used a CALPHAD approach to predict the phase formations of a number of alloys in literature and concluded that the prediction of BCC structure is more accurate than that of FCC. Senkov et al. [11] developed a method to rapidly screen a large number of alloy systems using CALPHAD modeling, and found that the probability of solid solutions decreases as the number of elements increases because the configurational entropy rises slowly while the probability of at least one pair of elements favoring formation of intermetallics increases more rapidly.

So far, most research has been aiming at developing HEAs with exceptional mechanical properties, while only a few investigations focus on low density HEAs [12–20]. Since HEAs generally consist of 4 or more elements, except AlLiMgScTi alloy [13], it is usually necessary to introduce heavier element with density higher than 5 g/cm^3, like Fe, Co, Ni. In order to reduce the density, one way is to increase the content of lighter element while maintaining the mechanical properties, such as Al content in the classical AlCoCrFeNi alloys. Another way is to add two or more light elements [13–20]. In the

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Table 1
Phase formations of the HEAs prepared through solidification processing.

Ref.	Alloys	Method	Phase (Exp. in literature)	Major Phase (Scheil Cal.)	Phases (mole percent > 0.1% after rounding) Scheil Cal.(as cast) or Equil. Cal. (as annealed)
[32]	CoCrFeNi-Ti	AM	Fcc	Bcc	Bcc_B2(0.65), Bcc_A2(0.036), Fcc(0.314)
	CoCrFeNi-TiAl0.5	AM	Bcc_A2, Bcc_B2, Laves	Bcc	Bcc_B2(0.887), Fcc(0.112), Laves_C15(0.001)
	CoCrFeNi-TiAl1	AM	Bcc_A2, Bcc_B2, Laves	Bcc	Bcc_B2(0.975), Bcc_A2(0.005), Fcc(0.016), Laves_C15 (0.003)
	CoCrFeNi-TiAl1.5	AM	Bcc_A2, Bcc_B2	Bcc	Bcc_B2(0.998), Fcc(0.001), Laves_C15 (0.001)
	CoCrFeNi-TiAl2	AM	Bcc_A2, Bcc_B2	Bcc	Bcc_B2
[33]	CoCrFeNi-Al	AM	Bcc_A2, Bcc_B2	Bcc	Bcc_B2(0.74), Bcc_A2(0.171), Fcc(0.089)
	CoCrFeNi-AlTi0.5	AM	Bcc, Laves	Bcc	Bcc_B2(0.909), Bcc_A2(0.041), Fcc(0.05)
[34]	CoCrFeNi-AlTi0.5	IM	Bcc_B2, Bcc_A2	Bcc	Bcc_B2(0.909), Bcc_A2(0.041), Fcc(0.05)
	CoCrFeNi-AlTi0.5	IM+750 °C, 10 h	Bcc_B2, Bcc_A2, Sigma	–	Bcc_B2(0.738), Sigma(0.262)
[35]	CoCrFeNi-Al	AM	Bcc	Bcc	Bcc_B2(0.74), Bcc_A2(0.171), Fcc(0.089)
	CoCrFeNi-AlTi0.5	AM	Bcc1, Bcc2	Bcc	Bcc_B2(0.909), Bcc_A2(0.041), Fcc(0.05)
	CoCrFeNi-AlTi1	AM	Bcc1, Bcc2	Bcc	Bcc_B2(0.975), Bcc_A2(0.005), Fcc(0.016), Laves_C15 (0.003)
	CoCrFeNi-AlTi1.5	AM	Bcc1, Bcc2, Laves	Bcc	Bcc_B2(0.987), Bcc_A2(0.005), Laves_C15(0.005), Fcc(0.003)
[36]	CoCrFeNi_Al	AM, IM	Bcc	Bcc	Bcc_B2(0.74), Bcc_A2(0.171), Fcc(0.089)
	CoCrFeNi_AlSi0.2	AM, IM	Bcc	Bcc	Bcc_B2(0.576), Bcc_A2(0.18), Fcc(0.224), Cr_3Si(0.02)
	CoCrFeNi_AlSi0.4	AM, IM	Bcc	Bcc	Bcc_B2(0.541), Bcc_A2(0.135), Cr_3Si(0.074), Fcc(0.246), Co_2Si(0.003)
	CoCrFeNi_AlSi0.6	AM, IM	Bcc, δ(Cr, Si rich)	Bcc	Bcc_B2(0.521), Cr_3Si(0.15), Bcc_A2(0.079), Fcc(0.235), Co_2Si(0.014)
	CoCrFeNi_AlSi0.8	AM, IM	Bcc, δ(Cr, Si rich)	Bcc	Bcc_B2(0.509), Cr_3Si(0.187), Bcc_A2(0.103), Co_2Si (0.054), Fcc(0.147)
	CoCrFeNi_AlSi1	AM, IM	Bcc, δ(Cr, Si rich)	Bcc	Bcc_B2(0.49), Cr_3Si (0.181), Co_2Si(0.128), Bcc_A2(0.162), Fcc(0.039)
[37]	Co-CrFeNi-AlTi0.5	AM	Bcc1, Bcc2	Bcc	Bcc_B2(0.909), Bcc_A2(0.041), Fcc(0.05)
	Co1.5-CrFeNi-AlTi0.5	AM	Bcc, Fcc	Bcc	Bcc_B2(0.808), Fcc(0.174), Laves_C15(0.018)
	Co2-CrFeNi-AlTi0.5	AM	Bcc, Fcc	Bcc	Bcc_B2(0.694), Fcc(0.265), Laves_C15(0.041)
	Co3-CrFeNi-AlTi0.5	AM	Bcc, Fcc	Bcc	Bcc_B2(0.525), Fcc(0.415), Laves_C15(0.059)
[38]	CoCrFeNi-Al0.3	AM	Fcc	Fcc	Fcc(0.988), Bcc_A2(0.01), Al_3Ni_5(0.001)
	CoCrFeNi-Al0.3Ti0.1	AM	Fcc	Fcc	Fcc(0.927), Bcc_B2(0.073)
	CoCrFeNi-Al0.3	AM+700 °C, 144 h	Fcc, Bcc_B2	–	Fcc(0.589), Bcc_B2(0.287), Sigma(0.124)
	CoCrFeNi-Al0.3Ti0.1	AM+700 °C, 144 h	Fcc, Bcc_B2	–	Fcc(0.370), Bcc_B2(0.241), Sigma(0.237), Fcc_L12(0.152)
[39]	Co1.5CrFeNi1.5-Ti0.5	AM	Fcc, $(Ni,Co)_3Ti$	Fcc	Fcc(0.836), $(Ni,Co)_3Ti$ (0.064), Bcc_B2(0.1)
	Co1.5CrFeNi1.5-Ti0.5Al0.2	AM	Fcc, $(Ni,Co)_3Ti$	Fcc	Fcc(0.835), Bcc_B2(0.152), $(Ni,Co)_3Ti$ (0.012), Fcc_L12(0.001)
	Co1.5CrFeNi1.5-Ti	AM	Fcc, $(Ni,Co)_3Ti$	Fcc	Fcc(0.555), $(Ni,Co)_3Ti$ (0.099), Bcc_B2(0.346)
	Co1.5CrFeNi1.5-TiAl0.2	AM	Fcc, $(Ni,Co)_3Ti$	Fcc	Bcc_B2(0.491), Fcc(0.504), $(Ni,Co)_3Ti$ (0.005),
[40]	CoCrFeNi-Al2Si	LC	Bcc_B2, Bcc_A2	Bcc	Bcc_B2(0.822), Cr_3Si(0.152), Cr_5Si_3(0.015), FeSi(0.008)
[41,42]	CoCrFe6Ni-AlSiTi	LC	Bcc_A2	Bcc	Bcc_B2(0.824), Laves_C14(0.159), Co_2Si(0.006), G_PHASE(0.009), Cr_3Si(0.001), Fcc(0.001)
		LC+500 °C, 5 h	Bcc_A2	–	Bcc_B2#1(0.474), Laves_C14(0.226), Bcc_B2#2(0.21), Cr_3Si(0.073), G_PHASE(0.017)
[43]		LC+500 °C, 5 h	Bcc_A2, Bcc_B2	–	Bcc_B2#1(0.474), Laves_C14(0.226), Bcc_B2#2(0.21), Cr_3Si(0.073), G_PHASE(0.017)
		LC+750 °C, 5 h	Bcc_A2, Bcc_B2	–	Bcc_B2#1(0.55), Bcc_B2#2(0.22), Laves_C14(0.23)
		LC+1000 °C, 5 h	Bcc_A2, SiTi, Bcc_B2	–	Bcc_B2#1(0.644), Bcc_B2#2(0.156), Laves_C14(0.2)
		LC+1150 °C, 5 h	Bcc_A2, SiTi, Si_2Ti, Bcc_B2, $D0_3$, unknown phase	–	Bcc_B2(0.836), Laves_C14(0.164)
[44]	CrCuFeNi-AlTi	AM	Bcc1, Bcc2, Fe_2Ti	Bcc	Bcc_A2(0.136), Bcc_B2(0.517), H_L21(0.201), Fcc(0.145)
[45]	CoCuFeNi-Al	AM	Bcc, Fcc	Bcc	Bcc_B2(0.855), Fcc(0.145)
	CoCuFeNi-AlSi	AM	Bcc, Fcc	Bcc	Bcc_B2(0.606), Co_2Si(0.298), Ni_2Si(0.002), Bcc_A2(0.094)
	CoCuFeNi-AlTi	AM	Bcc, Fcc	Bcc	Bcc_B2(0.7), Laves_C14(0.148), Fcc(0.148), H_L21(0.003)
[46]	CoCrCuFeNi-AlTi	AM	Bcc1, Bcc2, Fcc	Bcc	Bcc_B2(0.802), Bcc_A2(0.026), H_L21(0.05), Fcc(0.122)
[47]	CoCrCuFeNi-AlTi0.5	AM	Bcc1, Bcc2, Fcc, intermetallics	Bcc	Bcc_B2(0.754), Bcc_A2(0.073), Fcc#1(0.16), Laves_C14(0.005), Fcc#2 (0.001), H_L21(0.008)
	CoCrCuFeNi-AlTi1	AM	Bcc1, Bcc2, Fcc, intermetallics	Bcc	Bcc_B2(0.802), Bcc_A2(0.026), H_L21(0.05), Fcc(0.122)
[48]	CoCrFeNi-AlTi0.5	AM	Bcc1, Bcc2	Bcc	Bcc_B2(0.909), Bcc_A2(0.041), Fcc(0.05)
	Cu0.25-CoCrFeNi-AlTi0.5	AM	Bcc1, Bcc2	Bcc	Bcc_B2(0.789), Bcc_A2(0.1), Fcc#1(0.082), Laves_C14(0.006), Fcc#2 (0.021), H_L21(0.001)
	Cu0.5-CoCrFeNi-AlTi0.5	AM	Bcc1, Bcc2	Bcc	Bcc_B2(0.760), Bcc_A2(0.101), Fcc(0.129), Laves_C14(0.007), H_L21 (0.004)
[49]	Cu0.5-CoCrFeNi-Ti0.5Al0.5	AM	Fcc, Bcc1, Bcc2	Bcc	Bcc_B2(0.477), Bcc_A2(0.071), Fcc#1(0.413), Laves_C14(0.003), Fcc#2 (0.035)
	Cu0.25-CoCrFeNi-Ti0.5Al0.75	AM	Bcc1, Bcc2	Bcc	Bcc_B2(0.699), Bcc_A2(0.091), Fcc#1(0.164), Fcc#2(0.044), Laves_C14 (0.002)
[50]	CoCrNi-AlSi	GTAW	Bcc_B2	Bcc	Bcc_B2(0.58), Cr_3Si(0.214), Co_2Si(0.2), $(Cr,Ni)_4Si_3$(0.001), Ni_2Si(0.003), FeSi(0.001), NiSi(0.001)
[51]	CoFeNi-Al0.2Si0.2	AM, IM	Fcc, BCC_B2, Bcc_A2	Fcc	Fcc(0.996), Bcc_B2(0.001), Co_2Si(0.003)
[52]	CoCrNi-Al0.5Ti0.5	AM	Bcc_A2, Bcc_B2, Fcc, Sigma	Bcc	Bcc_B2(0.76), Bcc_A2(0.058), Fcc(0.154), Sigma(0.026), Laves_C15 (0.003)
		AM+500 °C, 24 h	Bcc_A2, Bcc_B2, Fcc, Sigma	–	Bcc_B2(0.485), Fcc_L12(0.267), Sigma(0.161), Bcc_A2 (0.087)

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