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Progress in High-Entropy Alloys

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Driven by scientific curiosity and the demand for high-performance materials, research in high-entropy alloys (HEAs) has attracted worldwide interest in the fundamental understanding and applications of their structure/processing/property relationship[1–4] since the first few papers were published.[5,6] As mentioned in Ref. 1, other names have also been used for HEAs, including multicomponent alloys, multiprincipal element alloys, equimolar alloys, equiatomic ratio alloys, substitutional alloys, compositionally complex alloys, etc. In fact, they all refer to, or are derived from, the same concept that the ideal configurational entropy of mixing reaches the maximum (namely, $R \times \ln(N)$, where R is the ideal gas constant and N is the total number of components) when the molar composition for all components in solid solution is the same. Although single-phase HEAs are usually thermodynamically stable only at high temperatures, their composition, temperature, and pressure dependences can vary greatly depending on the individual system. At low temperatures, however, they will decompose to phases with lower entropies as long as kinetics allows. At zero temperature, the entropy of all phases must diminish to zero. Furthermore, research has demonstrated that arbitrary mixing of elements ($N \geq 5$) in equal molar ratio will often not produce single-phase HEAs, while only carefully chosen compositions with balanced enthalpy and entropy properties will.[2,7,8] As pointed out in Ref. 3, practical applications of HEAs often require manipulation of the microstructure to contain more than one phase; therefore, the name of HEAs now has been extended greatly beyond what was originally referred to as single-phase multicomponent solid solution in equal or near-equal molar ratios.

This topic consists of a total of 12 invited papers. There are three overview papers, and the other nine are regular research reports. Due to the extreme importance in the field, the rules for HEA formation have been studied extensively mainly as a function of alloy composition. The major rules are enthalpy of mixing (ΔH_{mix}) and atomic size difference (δ) as suggested in Ref. 9. In light of recently published results, these rules were reexamined independently by Wang et al. and Liu et al. The valence electron concentration was also reexamined as an indicator for crystal structure type. Guided by binary phase diagrams, Takeuchi et al. were able to fabricate nearly single-phase HEAs with a hexagonal close-packed (HCP) structure in YGdTbDyLu and GdTbDyTmLu, confirming formation of HCP HEAs based on rare earth elements as suggested in Ref. 1. To explore the compositional dependence of forming face-centered-cubic (FCC) HEAs and the mechanical properties, Tasan et al. studied two non-equiatomic alloys, $Fe_{40}Mn_{27}Ni_{26}Co_5Cr_2$ and $Fe_{37}Mn_{45}Co_9Cr_9$. They reached two interesting conclusions: (I) The requirement for the equal-atomic ratio can be more relaxed, suggesting a fairly broad FCC phase field in the alloy system they studied; and (II) the mechanical properties of heavily alloyed HEAs at room temperature are only marginally improved compared with binary Fe-Mn alloys. Serration behavior has been observed in various HEAs during plastic deformation, and the fundamental understanding of this phenomenon was first studied by Antonaglia et al. who compared the predictions of a slip-avalanche model with slow compression and tension tests from cryogenic to elevated temperatures. The good agreement between the model prediction and experiments is very encouraging.

Aiming for developing lightweight HEAs for the aerospace and transportation and defense industries, alloys with low-density elements such as Al, Mg, Li, Ti, etc. were studied independently by Yang et al. and Hammond et al. The empirical $\Delta H_{\mathrm{mix}} - \delta$ rules were used to guide their alloy design. Although single-phase, low-density HEAs were not achieved, Yang et al. discovered that the dominant phase in $Al_{80}Li_5Mg_5Zn_5Sn_5$ and $Al_{80}Li_5Mg_5Zn_5Cu_5$ was solid solution FCC Al, and Hammond et al.

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demonstrated the importance of ball milling + large plastic deformation using equal-channel angular extrusion in producing bulk AlFeMgTiZn. Their pioneering work will be very useful for future computational and experimental research in this important area. To develop high-temperature alloys that are superior to Ni-based alloys, Senkov et al. studied the microstructure and mechanical properties of Al-containing refractory HEAs. The addition of Al was to improve the strength and oxidation resistance and lower the density.

Powder metallurgy remains an important route in manufacturing HEAs, and Zhang et al. successfully synthesized bulk $CrCuFeMnMo_{0.5}Ti$ using mechanical alloying and sintering. The main phase of the alloy has a body-centered cubic structure. Lin et al. applied an HEA binder (i.e., $Co_{1.5}CrFeNi_{1.5}Ti_{0.5}$) in liquid phase sintering with TiC and found that it is much superior to two traditional binders (Ni and $Ni_{13}Mo_7$). The HEA binder resulted in excellent wettability, a much finer grain structure, and an improved hardness–toughness combination. Laser-induced rapid solidification has the advantages of enhanced solid solution and lower cost, and thus, it could be an important route to fabricating single-phase HEAs and to studying their properties. In this regard, Zhang et al. reviewed the microstructure and mechanical and chemical properties in laser-induced rapidly solidified HEAs in comparison with conventional Co- and Ni-based alloy coatings. On the other hand, a comprehensive review of the formation of high-entropy bulk metallic glasses (BMGs) and their properties was done by W.H. Wang. Strategies in designing high-entropy BMGs with excellent glass-forming ability were discussed. An importance in atomic size difference was emphasized, and unique physical and mechanical properties of high-entropy BMG can be obtained.

The following papers being published under the topic of "Progress in High-Entropy Alloys" provide excellent details and research on the subject. To download any of the papers, follow the url http://link.springer.com/journal/11837/66/10/page/1 to the table of contents page for the October 2014 issue (vol. 66, no. 10):

- "Phase Selection in High Entropy Alloys: From Non-equilibrium to Equilibrium" Zhijun Wang, Sheng Guo, and C.T. Liu
- "The Phase Competition and Stability of High-Entropy Alloys" W.H. Liu, Y. Wu, J.Y. He, Y. Zhang, C.T. Liu, and Z.P. Lu
- "High-Entropy Alloys with a Hexagonal Close-Packed Structure Designed by Equi-Atomic Alloy Strategy and Binary Phase Diagrams" Akira Takeuchi, Kenji Amiya, Takeshi Wada, Kunio Yubuta, and Wei Zhang
- "Composition Dependence of Phase Stability, Deformation Mechanisms, and Mechanical Properties of the CoCrFeMnNi High-Entropy Alloy System" C.C. Tasan. Y. Deng, K.G. Pradeep, M.J. Yao, H. Springer, and D. Raabe
- "Temperature Effects on Deformation and Serration Behavior of High-Entropy Alloys (HEAs)" J. Antonaglia, X. Xie, Z. Tang, C.-W. Tsai, J.W. Qiao, Y. Zhang, M.O. Laktionova, E.D. Tabachnikova, J.W. Yeh, O.N. Senkov, M.C. Gao, J.T. Uhl, P.K. Liaw, and K.A. Dahmen
- "Phase Stability of Low-Density, Multiprincipal Component Alloys Containing Aluminum, Magnesium, and Lithium" X. Yang, S.Y. Chen, J.D. Cotton, and Y. Zhang
- "Equal-Channel Angular Extrusion of a Low-Density High-Entropy Alloy Produced by High-Energy Cryogenic Mechanical Alloying" Vincent H. Hammond, Mark A. Atwater, Kristopher A. Darling, Hoang Q. Nguyen, and Laszlo J. Kecskes
- "Microstructure and Properties of Aluminum-Containing Refractory High-Entropy Alloys" O.N. Senkov, C. Woodward, and D.B. Miracle
- "Synthesis and Characterization of $CrCuFeMnMo_{0.5}Ti$ Multicomponent Alloy Bulks by Powder Metallurgy" Kuibao Zhang, Guanjun Wen, Hongchuan Dai, Yuancheng Teng, and Yuxiang Li
- "New $TiC/Co_{1.5}CrFeNi_{1.5}Ti_{0.5}$ Cermet with Slow TiC Coarsening During Sintering" Chun-Ming Lin, Che-Wei Tsai, Sheng-Min Huang, Chih-Chao Yang, and Jien-Wei Yeh
- "Application Prospects and Microstructural Features in Laser-Induced Rapidly Solidified High-Entropy Alloys" Hui Zhang, Ye Pan, Yi-Zhu He, Ji-Li Wu, T.M. Yue, and Sheng Guo
- "High-Entropy Metallic Glasses" W.H. Wang

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