High-Performance High-Entropy Alloys

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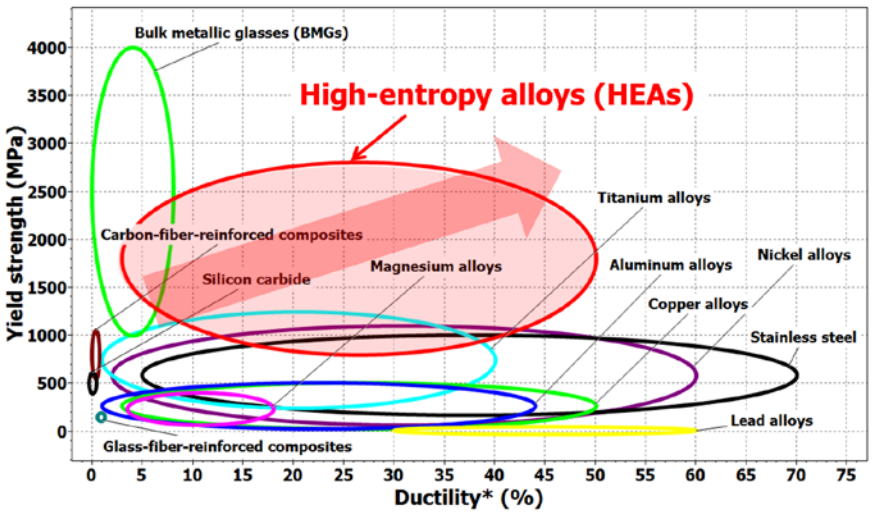
I. Executive Summary

High-performance high-entropy alloys (HEAs) have great potential in replacing existing materials in harsh environment owing to their enhanced thermodynamic stability and reduced atomic diffusion resulting from the unusually large configurational entropy in the solid solution structure. HEAs typically contain 5 or more principal elements in equal molar ratio, and HEAs in simple face-centered cubic (FCC), body-centered cubic (BCC) and hexagonal-close packed (HCP) structures have been reported. Literature has shown that HEAs are superior to existing materials such as composites, ceramics, metallic alloys and bulk metallic glasses in the yield strength-ductility relationship and other properties.



* Ductility combines both tensile and compressive deformations at room temperature.

In order to enhance the efficiency of existing coal-fired power plants and a variety of other industries such as transportation and defense sectors, developing high-performance materials such as HEAs has been carried out at NETL utilizing HPCEE. The HEAs under development include densities ranging from 3.0 to over 10.0 g/cm^3. The HEA composition can be tailored according to the target application especially the temperature: room temperature, intermediate temperature (<600°C), high temperature (600-1200°C), or ultra-high temperature (>1200°C). A super wide range of elements are included in the alloy design, such as all transition metal elements including rare earth elements and refractory metals, alkaline earth metals, and semi-metals. Compositions in 4-, 5-, 6-, 7-, 8-, 9- and 10-component systems are all considered. The new alloys are designed to possess: enhanced thermal stability; reduced weight; increased strength; acceptable ductility; excellent oxidation resistance; enhanced creep performance.

First-principles density functional theory (DFT) calculations, molecular dynamics, and Monte Carlo simulations have been performed to screen potential HEA compositions that will meet or exceed the target materials properties. All these simulations are done at HPCEE. HPCEE allows us to virtually design materials chemistry without limitations on the number of alloys in simulations. Quantum mechanical simulations only require atomic number as input. Screening through hundreds and even thousands of alloys can be done in much shortened timeframe with the powerful HPCEE. Only alloys of promising success are recommended for experimental

verification. Save in materials cost, time and manpower is tremendous if compared to traditional trial-and-error type laboratory work. Several conference presentations, journal papers and patent applications have resulted.

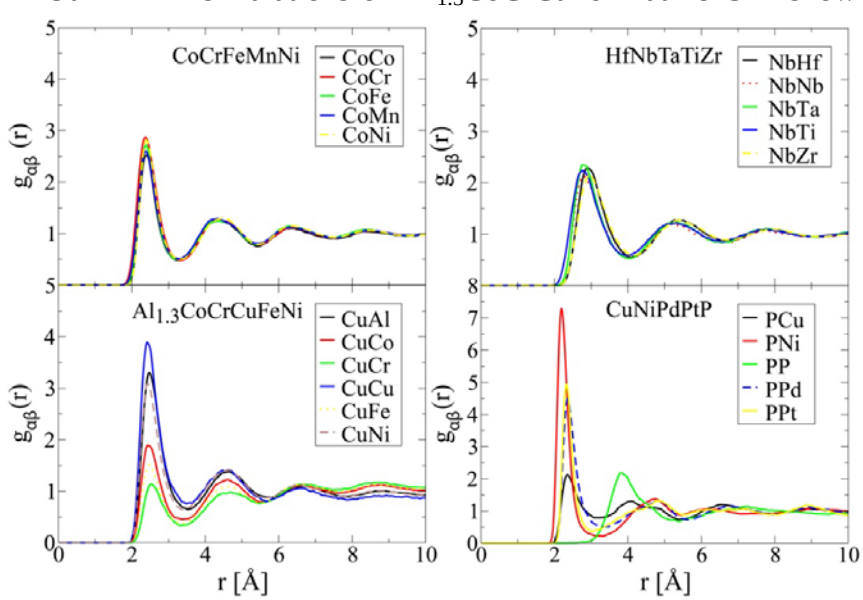
II. Problem(s)

Existing alloys are vulnerable to environmental degradation at high temperatures, which causes rapid oxidation, loss of strength, undesirable phase transformations, rapid microstructure coarsening, accelerated creep, and thus much shortened lifetime. Consequently, there is urgent need in developing new materials with significantly improved properties (mechanical, thermal, and environmental) to be operated at higher temperature and higher pressure where environmental degradation is more severe for a wide array of industrial applications that demand high efficiency and long lifetime as well as lower cost. In addition, transportation industry and defense sectors have everlasting strong demand for light-weight high-strength materials.

III. Results

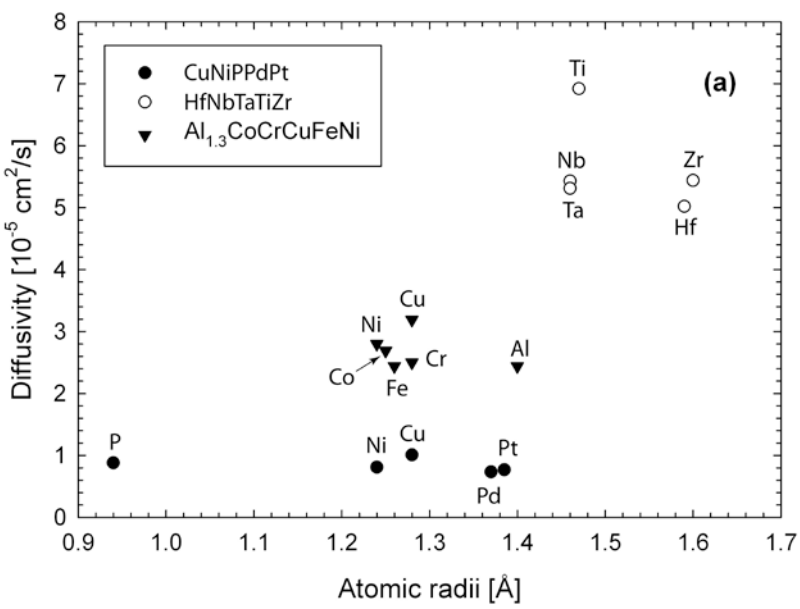
Design of high entropy alloys is not obvious; random mixing of elements in the periodic table in equal molar ratio does not result in formation of single-phase HEAs. As a matter of fact, to date there have been only a handful of single-phase HEAs reported. The approach we have used in our study is to combine DFT calculations, AIMD and Monte Carlo simulations, and CALPHAD (acronym of CALculation of PHAse Diagrams) modeling. Our AIMD simulations show that single-phase HEAs (e.g., CoCrFeMnNi and HfNbTaTiZr) lack strong tendency in short-range ordering and clustering in the liquid state. Multi-phase alloys (e.g., $Al_{1.3}CoCrCuFeNi$) and amorphous alloys (e.g., CuNiPdPtP) exhibit a preferential atomic pair distribution function (PDF).

Our AIMD simulations on $Al_{1.3}CoCrCuFeNi$ at 1873 K show that the preferred correlation for both Al and Ni is the Al-Ni pair, the Cr-Fe pair for both Cr and Fe, the Co-Cr pair for Co, and the Cu-Cu pair for Cu. These results suggest the existence of preferred short-range ordering of Al-Ni, Co-Cr and Cr-Fe pairs in the liquid. These structural features in liquid are consistent with experimental



observation of formation of B2-NiAl and Cr-Co-Fe rich phase during solidification. The preferred Cu-Cu pair correlation suggests Cu tends to segregate in the liquid. This leads to the formation of a Cu-rich phase during solidification, which is also consistent with experimental observations.

The atomic diffusivity can also be predicted from the slope of the mean square displacement plots obtained from AIMD simulations. The plot compares atomic diffusivity in $Al_{1.3}CoCrCuFeNi$, HfNbTaTiZr and CuNiPPdPt at T = 1,873, 2,273, and 1,200 K, respectively. The difference in self-diffusion constants among these three alloys is dictated by the simulation temperatures. Higher temperatures correspond to higher diffusivity. For $Al_{1.3}CoCrCuFeNi$, Cu is the fastest diffusion species and its diffusivity is about 31% higher than Al or Fe. Cu segregation enhances Cu diffusivity, while strong correlation between Al and the transition metals (Ni, Co, Cu) and large atomic size of Al make contributions to slower diffusion rate of Al. For HfNbTaTiZr, the trend in the diffusion constants in the descending order (Ti > Nb ~ Zr > Ta > Hf) seems to follow the order of the atomic size and weight of the constituent elements, further confirming lack of strong chemical ordering or segregation. For CuNiPPdPt, P has the smallest atomic size but its diffusivity is noticeably smaller than Cu which has the highest diffusivity. This is a direct consequence of strong bonding between P and metals. The close correlation between short-range ordering and segregation in liquid and phase formation during solidification demonstrates the important role of liquid structure in HEA formation. In other words, single-phase solid solution HEAs are promoted by compositions in which preferred short-range ordering and segregation are absent in the liquid structure. Therefore, AIMD simulations have been carried out for hundreds of compositions to examine their possibility to form single-phase solid solution HEA as the first screening step.



Our following steps include DFT calculations in the solid state to determine the entropy sources, enthalpy of formation, electronic, vibrational and elastic properties of model HEA compositions that are down-selected from CALPHAD calculation and AIMD simulations. In particular, a hybrid AIMD/Monte Carlo simulation has been adopted to simulate the disordered structure as well as using the special quasi-random-structure (SQS) method. These tasks are being actively undertaken at NETL in particular searching for light-weight HEAs and oxidation-resistant HEAs.