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Viewpoint article

Materials selection considerations for high entropy alloys

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ABSTRACT

Increased interest in high entropy alloys (HEA)s has led to significant activity in the development of new equimolar multicomponent metal systems. The present viewpoint article suggests applying a lens of practicality related to alloy economics and resource usage issues. A framework for HEA materials selection is presented to assist the metallurgical community as it searches for HEAs with feasible implementation possibilities, by identifying unsuitable alloying elements based on price or metrics of supply availability. For some metrics, such as price volatility, the elemental diversification in HEAs could prove beneficial, while for others, such as recyclability, elemental breadth introduces significant challenges.

1. Introduction

The concept of high entropy alloys (HEA)s has ignited renewed interest in fundamental thermodynamics, processing, and characterization approaches for multicomponent alloys. In just a decade, the literature on high entropy alloys has increased 500 fold, as the community debates what defines an HEA and what properties can be obtained from equi-proportion combinations of multiple components that may or may not exhibit high configurational entropy [1]. Recent interest in HEAs has covered a significant space of characterization and processing approaches [2], theoretical work leveraging ab initio methods to screen for promising alloys [3], and statistical approaches to mine for promising properties [4,5]. Most HEA research focuses on two main compositional domains, namely those based on refractory elements and those based on commodity metals. The latter typically involve metals such as Cr, Co, Fe, Ni, Mn, and Cu, and the resulting HEAs are often compared with stainless steel [6]. The former use metals such as V, Cr, Ti, Mo, Nb, Ta, W, Zr, and Hf and are compared with refractory metals [7,8]. The compound forming elements Al and Ti are often added to both families [9].

Missing from these discussions to date is a quantitative framework to evaluate the feasibility of scale-up and manufacture of potential HEAs. Such a framework could help focus the space in a manner reminiscent of how Ashby charts focused the process of materials selection for mechanical design [10]. This article takes the initial steps towards such a framework for resource-efficiency evaluation applied to HEAs. In addition to structural or functional properties, price, manufacturability, and resource use are key features that should be considered; this paper presents some initial discussion on each of these points. This evaluation is fundamentally different for HEAs compared with conventional alloys because HEAs lack a base metal. An HEA has significant concentrations of five or more elements, so that even a basic metallurgical palette of 12 elements gives 3302 different HEA bases, motivating the need for intelligent ways to reduce the selection space.

We frame this analysis from two different quantitative perspectives. First, we perform elemental screening on material price, price volatility, and resource availability (geographic concentration and coupled production). We also present analysis of these metrics once the constituent elements are mixed into a multi-component alloy. Finally, we comment on the recyclability of these materials based on the thermodynamics of separation. For some of these metrics the equi-molar concept provides a stabilizing effect, while for others the impact is negative. Through this analysis we illustrate several practical considerations that should factor into HEA design.

2. Analysis

In what follows, we provide commentary on material price, price volatility, materials availability, and recyclability metrics to address the potential for HEAs to compete successfully with incumbent alloys. For each metric, we first provide the method used in the analysis followed by the results for that metric. For the present analysis, we limit the discussion to equimolar alloys only, although in some cases the lessons of this analysis argue for a significant departure from that recipe in future HEA design. We emphasize that while metrics of economics, materials availability, and recyclability should ultimately be considered as part of dynamic systems whose values would be influenced by each other (correlated), the present general static framework can be applied to inform element selection and HEA design.

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2.1. Material price

We first provide insight into materials price as a metric for HEA feasibility. Only material price was considered for a proposed HEA (we do not add costs incurred in alloy processing), and we consider published materials price, rather than cost, so that we can refer to publicly available information. It is important to remember that a manufacturer incurs a cost, rather than a price, but for the purposes of describing our data and methods, one can envision the price as contributing to an incurred manufacturing cost relative to incumbent alloys.

When available, we used prices for commodity metals traded on the London Metal Exchange (LME) available from Thomson Reuters Datastream, as these are updated at least monthly (Ni, Al, Cu, Zn, Sn, Fe, Ag, Au, Ir, Pd, and Pt). Otherwise, annual price data were obtained from the United States Geological Survey (USGS) historical statistics for mineral and material commodities [11] from 1964 to 2014. For metals not reported on the LME, we note some limitations in the available price data. For example, prices for some minor metals (Nb and Sc, for example) remain constant for several years because there are not data available from open transactions. Another example of a data limitation is found for the case of Y; the reported price was based on metal oxides before the year 2000, but the basis for reporting changed into pure metals afterwards.

First, we categorize the elements that have been mentioned across the HEA literature of the last decade in terms of 50 year historic average price of the element. We will refer to these categories for the subsequent analysis of materials price and price volatility. These can be broken down in the following four categories where price is shown on a per mole basis (since this is how HEA compositions are typically framed):

- Very high price: Au, Sc, platinum group metals (50 yr average >$1000 per mole)
- High price: Ag, Ga, Ge, Hf, In, La, Ta (50 yr average ~$100 per mole)
- Intermediate price: Be, Bi, Cd, Co, Mo, Nb, Sn, Te, W, Y, Zr (50 yr average ~$5 per mole)
- Low price: Al, Cr, Cu, Fe, Li, Mg, Mn, Ni, Pb, Sb, Si, Ti, V, Zn (50 yr average ~$0.5 per mole)

One way to consider the domain of HEAs by economic constraint is to systematically calculate all possible price combinations for any hypothetical equimolar alloy, in comparison with incumbent alloys. We have conducted that combinatorial investigation, the results of which are summarized in Fig. 1. Fig. 1a presents the range of alloy price as a function of number of elements (N) in an alloy considering the price categorization above (only Sc, Pd and Ru are included from the very high price category). For N ranging from 1 to 6, we calculate an equimolar alloy for all possible combinations of elements, and for each N we generate the box and whisker plots that show (from bottom up) the 10th, 25th percentile, median, 75th and 90th percentiles of the full distribution of calculated alloy prices.

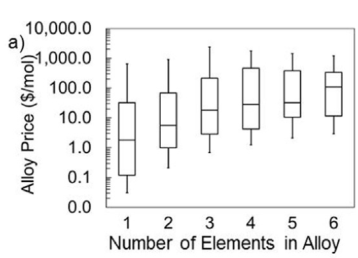
There are several interesting trends revealed in Fig. 1a. First, we note that the median price of alloys increases as the number of constituents rises, by about an order of magnitude by the time a six-component system is reached; mixing elements raises the average price because there is a higher likelihood of a combination including an element from the higher price groups. This suggests that if alloy design is conducted without considering price, the resulting HEAs are likely to be expensive compared with even current specialty metals. However, the lower tails of the curves in this figure offer a more optimistic view, as some equimolar combinations even out to $N = 6$ exhibit prices below the median $N = 2$ price, with values near the “intermediate” price range as defined above.

Second, as the alloy complexity level rises, the spread of possible alloy prices drops considerably, from almost five orders-of-magnitude at $N = 1$ to about two by $N = 6$. Diversification of the elemental mix thus tends to narrow the tails of the distribution. This trend is examined in more detail in Fig. 1b, which shows at which number of constituents a highly priced element has to participate in a finished alloy to have its cost “diluted” by the other elements in the system to become cost competitive with other specialty alloys. For a simple set of benchmarks, we use current market prices for Ni- and Ti-based alloys, as lower bounds on the more costly advanced alloys. Prices for incumbent alloys were obtained from Granta Design's CES selector [12] and converted to a per molar basis and averaged for comparison. We explicitly compare these incumbent alloy prices to the price-weighted mole fraction for each element (the mole fraction, and therefore price, decreases as the number of constituents increases). Clearly, there are significant limitations of final alloy cost based on the elements that are being considered for HEA systems. We can see that even Ta, which has been considered in several refractory HEA works, needs to be used in a cocktail of 15 constituents (equimolar) to achieve cost parity with Ti-based alloys. By the same token, virtually any HEAs that consider Au, Hf, Ge, In, Sc or platinum group metals (Ir, Pd, Pt, Rh, and Ru) will face considerable challenges in competing with incumbent alloys and will have to, therefore, demonstrate extraordinarily significant performance improvements.

Conversely, alloys containing Mo, Nb, Bi, or Sn fall into the range of Ni- or Ti-based alloys (between $1 and $5/mol) for at least 5 element HEAs. Alloys containing these elements in equimolar proportions would have challenges competing economically with less expensive advanced alloys (than Ni- and Ti-based) without significant performance improvements. The practicality of working with N equimolar constituents becomes much more dubious from both a processing standpoint as well as a supply chain perspective as N rises. On the other hand, Co, Cd, W, Zr and all the elements within the low price group listed above appear price competitive even in 5 or less constituent HEAs, all other things being equal.

2.2. Price volatility

The economic analysis in Fig. 1 was based on average 2014 price, but metal prices change significantly over time, so we also present an assessment of price volatility from 1964 to 2014. Volatility is of interest



b)

Element	Av. Ni-based ($1.70/mol)	Av. Ti-based ($3.14/mol)
Te	8	5
Ga	15	8
Ag, Ta	30	15
In, Hf	50	25
Ge	80	40
Ru	300	200
Ir, Pd	1000	600
Au, Pt, Rh, Sc	> 3000	> 1500

Fig. 1. Price analysis a) range in alloy price in ($/mol) as number of elements increases (including Pd, Ru and Sc from the very high price group). Box and whisker from bottom up shows 10th, 25th percentile, median, 75th and 90th percentile. b) Minimum number of elements necessary to be economically competitive with Ni and Ti-based alloys. Full price list in $/mol shown in the supplemental information.

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