Development of Complex Concentrated Alloys (CCAs) Utilizing Scrap to Preserve Critical Raw Materials †

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Abstract: The research and development of high-entropy alloys (HEAs) and complex-concentrated alloys (CCAs) are growing rapidly, focusing on the enhanced properties of these alloys. However, so far, their manufacturing has not exceeded the laboratory scale. To meet this challenge, a combination of the processing characteristics and methods along with their sustainable production must be ensured. Moving towards a circular economy, this includes the utilization of low-cost, widely available scrap for the manufacturing of CCAs. Changing the raw materials, can ensure a cost-efficient production and paves the way to surpass major limitations in the industrial manufacturing of CCAs. Examples of a novel lightweight CCA design approach will be presented in this work.

Keywords: high-entropy alloys; complex concentrated alloys; scrap; raw materials; sustainability; lightweight alloys

1. Introduction

Metallic materials are metals at the focal point of the European Union’s circular economy initiatives [1–3]. It is of utmost importance to provide solutions and close the loop of wasted materials. Numerous endeavors to outline existing issues and prevent Europe’s metals from being deposited to landfills, incinerated or exported without guarantee of proper treatment have been deployed [4–6]. Nevertheless, it is too early to foresee if the ambition of the European Commission’s Action Plan will be translated into reality. The following years will be pivotal to implement strong environmental regulations on the metallurgy sector and cross over into more eco-friendly, resource-efficient material design approaches [4].

Traditional alloy design is based on the selection of one main element, with the addition of alloying elements, in order to achieve the properties required for a specific application. Consequently, knowledge of the alloys near the corners of a multicomponent phase diagram is well developed. However, there is a knowledge gap regarding the behavior of alloys near the center of the phase diagram [7]. The traditional alloy design has imposed many restrictions in exploring the full range of feasible alloys, since there are many more potential compositions positioned at the center of a multicomponent phase diagram comparing with the corners. Thus, utilizing only a major alloying element and other minor elements additions for properties enchantment is a restrictive practice.

From that knowledge gap, the concept of high-entropy alloys (HEAs) has emerged. This idea is based on the theory that an increasing number of alloying elements would
increase the configurational entropy, and as a result, solid-solution structures would be promoted [8]. The invention of HEAs has been characterized as "a renaissance in physical metallurgy" [9].

It is worth underlining that to date, there has not been a complete definition for HEAs. This fact allows the research community to explore the field with a relative degree of flexibility [10]. However, the first widely accepted definition for HEAs is that they have to be multi-component alloys with each element’s concentration varying between 5–35 at. %, developed on the high-entropy effect in order to generate single solid-solution structures [11]. Since then, the HEA field has rapidly evolved and is not only limited by single-phase SS microstructures. The HEA field has developed and now that it contains multiphase alloys, the interchangeable terms of compositionally complex alloys [12] and most recently of complex concentrated alloys (CCAs) [13,14] were also introduced in order to describe them. To this extent, compositionally complex alloys are the alloys with a complex composition, while containing a large number of alloying elements, but not definitely in a big proportion for each element, which can be described as CCAs [12]. Contrarily, complex concentrated alloys are the alloys with a higher concentration of component elements [15]. Furthermore, it has been found that the unique performance and characteristics of these alloys can be found in a 2–3 principal alloying element system. Thus, the broader term of multi-principal alloys/multi-principal element alloys (MPAs/MPEAs) to describe this category of alloys has been introduced. Alloys fall into the MPEAs category when they consist of a large number of alloying elements in high concentrations, whereas at least two of them act as the principle-base elements [16]. These new definitions do not create any implications neither to the effect nor to the importance of configurational entropy [14,16]. In this paper, the authors use the most recently developed definition of CCAs.

These type of alloys (HEAs, CCAs and MPEAs) are manufactured by vacuum arc melting (VAM) and vacuum induction melting (VIM) techniques in an Ar or N\textsubscript{2} protective atmosphere and casting in a water-cooled copper mold [17]. These techniques are chosen due to the high melting point of various raw materials. The materials were remelted several times, in order to achieve high homogeneity in the alloys structure. The governing principles of manufacturing HEAs are reported in the work of Kumar et al. and Jablon-ski et al. [18,19]. In spite of the high-cost casting process, HEAs and CCAs are susceptible to some castability and liquidity issues and the desired compositional homogeneity is not always achieved. This is due to the high concentrations of multiple alloying elements. Additionally, the melting point for some of those elements (i.e., Cr, Fe, Ti, Nb, etc.) can be higher than the boiling point of other alloying elements (such as Mg, Li or Zn), which can promote evaporation losses and subsequent undesired casting defects, such as porosity. Thus, in order to upscale into the industrial scale, the understanding and the tuning of the parameters in the manufacturing of HEAs, MEAs and CCAs has become the new challenge due to the high complexity of the process [20,21].

Using high-purity raw materials, the bulk level of an industrial plant is accompanied with very high acquisition expenses. This poses an obstacle acknowledged by most of the industry [21,22]. There is an emerging trend, following the circular economy, for creating additional value from waste/scrap material in cases where the cost of separating co-mingled alloy flows is prohibitively high [23]. The scenario of implementing lower-purity raw materials, containing some ppm of various elements, has to be examined for cost reduction. Since the bottom line for most commercial alloys manufacturing is the cost of the product, the focus point of the current study is to examine the economic viability of the discussed concept.

2. Complex Concentrated Alloys: Types and Trends

This new field of multicomponent alloys has emerged and shows a great future potential of material properties, both physical and mechanical. Complex concentrated alloys are deployed as a mixture of at least four alloying elements in high proportions.
High mixing entropy derives from the high concentration of elements, which usually favors formation of simple solid-solution structures [24].

It is clear that there is a vast field of possible combinations of elements that can be utilized for synthesizing CCAs. Thus, some selection criteria have been stipulated for elements, which can be used for producing CCAs with certain properties [25]. There was the early hypothesis that phase evolution and stability and the exceptional properties in HEAs and CCAs are attributed to the four core effects [26]. In order to design new alloys, it is necessary to keep under consideration the four core effects describing these alloys, since using different alloying elements expands the field of diversity, and we can obtain various properties [13,27].

These four effects are the following.

1. **High-entropy effect**

   Based on the use of high number of elements, configurational entropy ($\Delta S_{\text{mix}}$) increases, which tends to reduce $\Delta G_{\text{mix}}$ and formation of simple solid-solution structures becomes more likely [28].

2. **Lattice distortion**

   This category of alloys is characterized by high lattice strains and induced stresses, which are attributed mainly due to the different atomic radius of each element [29].

3. **Sluggish diffusion**

   There is the generic propose that sluggish diffusion in HEAs/CCAs tends to decrease the diffusion rate of atoms and that induces slower rates of phase transformation in the multi-element matrix. Subsequent formation of new phases from old phases requires the cooperative diffusion of different kinds of atoms in order to be accomplished [30].

4. **Cocktail effect**

   Cocktail effect is a term usually used to refer to the fact that there can be unexpected properties acquired after mixing various alloying elements in a system, which would not be possible to obtain from any single element [31].

   However, those four effects as depicted in Figure 1 are not fully researched or backed up by sufficient evidence [30,32].

![Figure 1](image-url) The four core effects of CCAs [27,30].

Figure 2 illustrates the classification of the seven CCAs categories as defined by Miracle and Senkov in their work [13].
Figure 2. Illustration of the studied CCAs categories sorted by elemental groupings as Senkov et al. defined in their work [13].

The very first category consists of alloys built on the transition metals (i.e., Al, Co, Cr, Fe, Mn, Ni, Ti, V). This category is thoroughly researched. In recent years, many publications describing alloys containing Co, Cr, Fe, Ni, Fe have been derived [13].

The second category is also very known and consists of refractory CCAs. Refractory CCAs were designed based on the concept of developing new high temperature structural metallic materials. Conceivably, this represents the foremost endeavor to conceive a completely new CCA group to meet a specific set of requirements. Such alloys contain at least four out of the nine refractory elements (i.e., Cr, Hf, Mo, Nb, Ta, Ti, V, W, Zr) and some non-refectory elements such as Al and Si for enhanced properties and decreased density [13,33].

The third category includes light metals, such as Al, Be, Li, Mg, Si, Sc and Zn. In the case of the main driving force is the urgent need for designing low-density, lightweight alloys, while maintaining the least level of mechanical properties [18,34]. A wide range of melting and boiling points for each element in this group makes development difficult, in such a way that mechanical alloying or careful selection of master alloys is taken into consideration in primary processing [13,35].

The fourth category is based on 4f transition metals, such as Dy, Gd, Lu, Tb, Tm and Y. These elements combined have interesting effects and the focus is shifted toward creating a single-phase structure of hexagonal close-packed (HCP) solid solutions [14].

The fifth category is of high interest, since the already-known conventional brass and bronze alloys are altered in order to enhance their strength and improve their machinability [36].

For the sixth CCAs categories, precious metals are utilized. The scope of creating this category of CCAs is to substitute high-cost Pd and Pt with Au, Ru, Co, Cr, Cu and Ni and reduce the high total alloy cost [14].

Lastly, there is a special category of CCAs containing B, C and N. Alloys in this family contain elements from the 3D transition metal group or the refractory metal CCA category. Additions of B, C and N have a dramatic effect on the presented phases and evolved microstructures, and subsequently on properties. A majority of alloys in this category include N, whereas alloys with C or B are limited. Most of the alloys are produced as thin films, and alloys often contain several atom percentages of O [13].

The diagram in Figure 3 represents a direct comparison of the CCAs categories and conventional alloy, i.e., Al, Fe, Ni, Mg, Ti-based alloys [15]. Various CCAs classes can emerge among a wide range of conventional alloys. It worthy to mention that interesting new design capabilities can present from light metal CCAs, which are found in the gap.
between Mg- and Al-based alloys. Enhanced properties, such as yield strength, can be correlated to the microstructure of these alloys, thus CCAs can be seriously considered as new type of materials, which can compete and potentially replace known conventional alloys [15].

There is tremendous research effort to be put in the field of CCAs. First of all, this field proposes a vast range of different chemical compositions and various microstructures. Considering the 72 elements that are not labelled as toxic or radioactive, neither the noble gases, the total achievable number of five-element systems expands to 13,991,544 and the number of systems with more than three and less than six elements rise up to 171,318,882. Moreover, there is a big gap in libraries containing new materials data. New ways to approach the vastness of CCAs are required for materials libraries, which can compromise with the large number of alloying elements. As Senkov stated, the major driving question for metallurgists is “what conventional structural materials exist for which no parallel CCA activity exists?”. An attempt to answer this question must be the leading direction for future research [13].

3. Approach and Discussion

So far, it is evident that the manufacturing process of these alloys is characterized by high expenses. Moreover, typical production of aluminum alloys consists of high-purity raw materials and implementation of scrap as well. Examples of that case are the alloys of 5xxx series. Their production requires two categories of raw materials at different ratios. The melt pool usually consists of 70% high-purity raw materials (such as A-class scrap, master alloys, elemental materials, etc.) and approximately 30% of it is common scrap. On the contrary, CCAs have the potential to be a realistic alternative in the cost-reduction and recyclability aspect, since our concept is to exclusively utilize common scrap for their production. A compositionally complex alloy offers flexibility and presents the potential to be produced exclusively from varying and intermingled flows of end-of-life alloys [23].
Regarding our study, we choose chemical compositions as shown in Table 1. The lightweight HEA and CCA used were designed and studied by Y. Qiu et al., X. Huang et al. [37,38] and D. Mitrica et al. [39].

Table 1. Chemical composition of A-CCA and B-CCA.

| Alloy/Elements | A-CCA ¹ | B-CCA ¹ |
|----------------|--------|--------|
| Al             | (25) 15.18 | (20) 12.95 |
| Mg             | -     | (20) 11.67 |
| Zn             | -     | (20) 31.39 |
| Si             | -     | (20) 13.48 |
| Cu             | -     | (20) 30.51 |
| Cr             | (25) 29.25 | -         |
| Ti             | (25) 26.92 | -         |
| V              | (25) 28.65 | -         |

¹ Number in parenthesis is at. %, whereas without parenthesis is wt.%.

The chosen CCAs are focused on containing an increased amount of lower density elements, in order for the final material to be considered as lightweight, since this is the latest trend from European Union regarding materials design [40–45]. Thus, Al, Mg and Si are added in higher quantities. Table 2 shows the direct comparison of raw materials cost between those two alloys and the fact that CCAs with common scrap offer a promising alternative in order to reduce materials production costs. Note that the H symbol is used for the manufactured CCA with high-class scrap, whereas the L symbol is used in the case of lower quality scrap.

Table 2. Comparison of cost for CCAs produced by high- and low-quality scrap.

| Alloy/Elements (wt.%) and Cost (USD/Ton) | AH-CCA | AL-CCA | BH-CCA | BL-CCA |
|-----------------------------------------|--------|--------|--------|--------|
| Al                                      | 398.32 | 258.91 | 339.8  | 220.88 |
| Mg                                      | -      | -      | 178.73 | 116.17 |
| Zn                                      | -      | -      | 953.94 | 620.06 |
| Si                                      | -      | -      | 312.93 | 203.4  |
| Cu                                      | -      | -      | 2973.96| 1933.08|
| Cr                                      | 2636.68| 1713.96| -      | -      |
| Ti                                      | 2366.3 | 1538.07| -      | -      |
| V                                       | 4295.05| 2791.78| -      | -      |
| Total                                   | 9696.35| 6302.72| 4759.36| 3093.59|

The equation used for calculating the cost of each alloying element is:

\[
\text{Cost of alloying element} = [\text{used wt. %}] \times [\text{1 ton price in USD}] \quad (1)
\]

where USD/ton is approximately the price of London Metal Exchange (LME) and other known price market analysts for A-quality scrap, whereas for lower-purity scrap the price is calculated as 65% of LME’s and pure metals price [46–52]. Total cost of the alloys for 1 ton of produced material is concluded by summing up each alloying elements price.

Finally, it is evident that lower quality scrap can offer a viable alternative in terms of cost reduction, since AH-CCA’s cost is USD 9696.35 for 1 ton of produced materials, whereas the proposed lower-purity scrap AL-CCA would cost approximately USD 6302.72 per ton. Additionally, price per ton for BH-CCA and BL-CCA would be USD 4759.36 and USD 3093.59, respectively. In this approach, a cost reduction of USD 3393.63 and USD 1665.77 was achieved. It is important to underline that such lower quality scrap would come with a higher level of impurities. Although, it is unknown if those small amounts of impurities, typically limited to some ppm, will affect the final properties of the as-cast material, since the range of different combinations of concentrations is too vast. Thus, future endeavors...
utilizing CALPHAD methodologies to screen out compositions designed with low-purity scrap are needed and small-scale trial melts are required for examining the divergence of materials properties. Finally, it is important to design proper heat treatments, since the majority of CCAs are only studied in the as-cast condition.

4. Conclusion-Outlook

This preliminary work can be briefed into the following conclusions and future outlooks:

(1) Complex concentrated alloys (CCAs) present a relatively new category of metallic alloys, which are based on the concept of multi-component systems and elements being present on high proportions, similar to the previous high entropy alloys (HEAs) and multi-principal element alloys (MPEAs) concepts/definitions. In our case, where CCA was used, a lower number of elements, at lower concentrations and intermetallic compounds, is acceptable.

(2) CCAs are competent of having equal or enhanced characteristics and properties for a comparable or lower raw materials selection cost.

(3) Lower purity scrap utilization for the production of CCAs is a promising new strategy, which enables higher levels of sustainability and cost-efficiency.

(4) Elimination of high-cost raw materials (i.e., master alloys) makes CCAs an even more appealing alternative.

(5) Future research efforts should be shifted towards alloys that are either Al-rich or Mg-rich. Such alloys would contain large amounts of desirable solute elements, which might dissolve into the solid solution and additionally promote the formation of beneficial phases (i.e., precipitates, particles, secondary phases, etc.), while capitalizing the high-entropy concept, while offering lower density alternative alloys.

(6) Initial designing and casting trials need to be carried out in order to examine the current concept’s feasibility from the scope of physical metallurgy.

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References

1. Treating Waste as a Resource for EU Industry: Analysis of Various Waste Streams and the Competitiveness of Their Client Industries | Internal Market, Industry, Entrepreneurship and SMEs. Available online: https://www.google.com/url?sa=t&rct=j&q=&esrc=s&source=web&cd=&ved=2ahUKEwi138n9h6L0AhWZ8LsIHT_XBAMQFnoECAIQAQ&url=https%25253A%2 (accessed on 31 July 2021).

2. European Circular Economy Stakeholder Platform. Available online: https://circulareconomy.europa.eu/platform/en/knowledge/metal-recycling-factsheet-euric (accessed on 31 July 2021).

3. Recycling Circular Economy. Available online: https://www.european-aluminium.eu/policy-areas/recycling-circular-economy/ (accessed on 31 July 2021).

4. Hagelüken, C.; Lee-Shin, J.; Carpentier, A.; Heron, C. The EU Circular Economy and Its Relevance to Metal Recycling. Recycling 2016, 1, 242. [CrossRef]

5. McKinsey. Available online: https://www.mckinsey.com/industries/chemicals/our-insights/the-european-recycling-landscape-the-quiet-before-the-storm?fbclid=IwAR1v8c60GlwA_66xea0KLOUmGqzoFyzhzLwCP1sIoU_ra_KV1dPtuG_ki8# (accessed on 31 July 2021).

6. EURACTIV. Available online: https://www.euractiv.com/section/circular-materials/news/metals-recycling-in-eu-could-collapse-under-new-rules-companies-say/?fbclid=IwAR0NEJ9Xru7bAEAzfUL3_t80b4SKxa5QIExjamam-Yiggs-AeektE6a3Hs (accessed on 31 July 2021).

7. Cantor, B. Multicomponent and High Entropy Alloys. Entropy 2014, 16, 4749–4768. [CrossRef]
39. Mitrica, D.; Badea, I.C.; Olaru, M.T.; Serban, B.A.; Vonica, D.; Burada, M.; Geanta, V.; Rotariu, A.N.; Stoiciu, F.; Badilita, V.; et al. Modeling and Experimental Results of Selected Lightweight Complex Concentrated Alloys, before and after Heat Treatment. *Materials* 2020, 13, 4330. [CrossRef] [PubMed]

40. European Commission. Available online: https://cordis.europa.eu/article/id/406955-multi-material-lightweight-components-for-use-in-cars-and-aircraft (accessed on 30 July 2021).

41. European Commission. Available online: https://cordis.europa.eu/article/id/169500-highperformance-lightweight-nanoreinforced-alloys (accessed on 30 July 2021).

42. European Commission. Available online: https://cordis.europa.eu/article/id/423150-integrated-lightweight-and-sustainable-aircraft-components (accessed on 30 July 2021).

43. European Commission. Available online: https://cordis.europa.eu/article/id/150459-lightweight-alloys-forging-future-flight (accessed on 30 July 2021).

44. European Commission. Available online: https://cordis.europa.eu/project/id/606156 (accessed on 30 July 2021).

45. LIGHTME. Available online: https://www.lightme-ecosystem.eu/about.html (accessed on 30 July 2021).

46. London Metal Exchange: Non-ferrous. Available online: https://www.lme.com/Metals/Non-ferrous#tabIndex=0 (accessed on 30 July 2021).

47. Chromium Price Chart, China Chromium Price Today-Shanghai Metals Market. Available online: https://price.metal.com/Chromium (accessed on 30 July 2021).

48. Roskill. Available online: https://roskill.com/news/titanium-prices-continue-strong-performance-in-2021/ (accessed on 30 July 2021).

49. INN. Available online: https://investingnews.com/daily/resource-investing/battery-metals-investing/vanadium-investing/vanadium-outlook/ (accessed on 31 July 2021).

50. Daily Silicon Price, Lme Comex Shfe Price of Silicon Live|SMM-China Metal Market. Available online: https://www.metal.com/Silicon (accessed on 31 July 2021).

51. Higher Demand, Firm Costs Lift China’s Magnesium Prices. Available online: https://www.argusmedia.com/en/news/2231091-higher-demand-firm-costs-lift-chinas-magnesium-prices (accessed on 31 July 2021).

52. Silicon Price Rises Boost European Producers. Available online: https://www.argusmedia.com/en/news/2187058-silicon-price-rises-boost-european-producers (accessed on 31 July 2021).