Sustainable Low-Cost Method for Production of High-Entropy Alloys from Alloy Scraps

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Abstract
In this communication, we propose a sustainable way to produce high-entropy alloys (HEAs) from alloy scraps called “alloy mixing”. We successfully demonstrate the method’s feasibility at a lab scale using a near-equimolar CrCuFeMnNi HEA. Alloy scraps (304L stainless steel (SS), Nichrome 80, and electrical wire grade Copper) obtained from various sources were melted together using vacuum arc melting along with minor additions of Mn and Cr to achieve the equiatomic composition. The alloy was characterized using X-ray diffraction (XRD) and scanning electron microscopy (SEM), which confirmed that the alloy produced through “alloy mixing” exhibits a microstructure similar to that of the alloy with the same composition produced through conventional melting of pure elements. Property calculation module on ThermoCalc was used to compare the yield strength of the conventional alloy and the alloy with impurities which indicated a 50% increase in yield strength. An uncertainty quantification analysis with 1000 alloy compositions with varying impurity contents indicates that the yield strength is strongly dependent on the impurity content. The cost analysis revealed that “alloy mixing” would lead to a significant reduction in fabrication costs. The results of this study are promising in the context of the commercialization of HEAs.

Graphical Abstract

Keywords Scraps · Recycling · Sustainability · High-entropy alloys

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Introduction

The data published by the US Environmental Protection Agency [1] indicated that Municipal Solid Waste (MSW) in the US alone included 34.69 million tons of metallic scraps in the year 2018, of which only 34.9% was recycled. Recycling has been shown to reduce cost [2] and energy consumption [3] significantly as the primary metal production process is both cost- and energy-intensive in nature. In recent years, there have been several efforts to recycle metallic materials, especially in the steel industry. However, large quantities of metallic scraps remain as waste. Hence, we need more avenues for recycling metallic alloy scraps.

High-entropy alloys (HEAs) are a new class of alloys with five or more elements in near equal proportions. [4, 5] This new class of materials has attracted the alloying community due to its marked deviation from established norms of alloy design based on a single principal element. Over the years, researchers have found that HEAs can be tailored to possess several unique properties such as excellent fracture toughness [6], corrosion resistance [7], and catalytic properties [8]. Despite these developments on the alloy design front, the real-life application of these alloys is limited by their high cost as they are typically produced by vacuum melting of pure elements. One of the possible ways to significantly reduce the cost would be the usage of metallic scraps available.

According to the fact-sheet released by the World Steel Association [9] on scraps, the usage of metallic scraps would also reduce the production cost indirectly by enhancing the (i) conservation of energy, (ii) conservation of resources (through a reduction in consumption of ores used in primary metal production) and (iii) curbing CO₂ emissions. This is advantageous in terms of both economic and environmental sustainability. According to Li et al. [10], conventional steelmaking process consumes 2.8 times more raw materials (ores and fluxes) and releases 7.7 times more CO₂ when compared to 100% scrap-based electric-arc steelmaking.

The challenges of extending the usage of scraps in industrial-scale production of HEAs are (i) preservation of the unique alloy microstructure and (ii) mitigation of possible negative impact due to the presence of impurity elements. Hence, it is essential to understand the effect of using metallic scraps in producing HEAs at a lab scale before upscaling the production to industrial scale. In this work, we use a strategy named "alloy mixing" using metallurgical alloy scraps to produce HEAs that can solve the problems mentioned above. We melted alloy scraps together instead of melting pure metals to produce HEA, thereby reducing the cost of production significantly while enabling the recycling of metallic scraps. We evaluate the feasibility of this technique by analyzing the impact of using scraps on the microstructure of the alloy and the effect of impurities on the yield strength of the alloy.

We demonstrate the feasibility of this technique using an equiatomic CrCuFeMnNi HEA; the composition was chosen due to the easy availability of raw materials, and it has already been produced through the conventional process with its microstructure being well characterized. Moreover, this alloy has been identified as a candidate alloy for semisolid processing [11], which would help in the near-net-shape production of components by thixoforming or rheocasting. The alloy is also expected to exhibit a good balance of strength and ductility due to a multi-phase microstructure [12].

Materials and Methods

The precursor materials (scraps) used in this study are 304L stainless steel (from “broken” tensile bars from a laboratory), Nichrome 80 (from “used” furnace coil), and electrical grade Cu (from Cu wires). In addition to this, small quantities of 99.9% Mn and Cr were used to achieve the equiatomic composition. The alloys sourced from scraps were mechanically abraded on a belt grinder to remove any surface contamination and they were further cleaned on an ultrasonic cleaner in three solutions atleast three times (ethanol, acetone, and de-ionized water) to remove any other impurities present on the surface of the scrap.

An ingot weighing 30 g was melted under a high vacuum (10⁻⁵ bar) in a Ti-gettered Ar atmosphere on a lab-scale vacuum arc furnace with a Tungsten electrode. The sample was re-melted atleast five times to ensure chemical homogeneity.

XRD analysis using a Cu-Kα source was performed for the as-cast sample for phase identification. The sample was metallographically prepared, and the microstructure was characterized using a SEM with a field emission gun (FEG). In order to study the partitioning of elements between different phases, energy-dispersive spectroscopy (EDS) analysis was performed during the characterization under the SEM.

To evaluate the effect of impurities from the scrap on the yield strength of the alloy, the yield strength model included in the ThermoCalc (Version 2021b) property calculation module. We compared the yield strength of the alloy without any impurities (conventionally fabricated alloy) with the yield strength of alloy with impurities at 25 °C. In this study, we considered Si and C as the main impurities present in the alloy fabricated by alloy mixing. The nominal composition of the alloy with impurities is given as the mean composition in Table 1. We also created 1000 variations in impurity concentration about the mean alloy composition using the uncertainty quantification function available on
ThermoCalc. The input parameters used to create the variation is listed in Table 1. The main purpose of this analysis was to ascertain the effect of variability in scrap composition on the yield strength of the alloy.

During this study, we considered the face-centered cubic phase as the matrix phase, as it is the phase with the highest volume fraction as known from the data on alloy with the same composition fabricated using conventional route [13]. We used a constant grain size of 200 μm for both pure and impure variants as they are fabricated under the same solidification conditions. (i.e., vacuum arc melting).

We also performed a cost analysis to compare the prices of the pure elements and the scrap to demonstrate the economic impact of this new technique.

Results and Discussion

The XRD analysis shows that the as-cast alloy has three constituent phases (2 face-centered cubic phases and a body-centered cubic phase) (Fig. 1). When we compare this pattern with the one reported by Li et al. [13] for the alloy with the same composition fabricated by the conventional method, the peaks for different phases match well, clearly indicating that our method preserves the microstructure of the alloy. This is further confirmed by the SEM micrograph (Fig. 2) of the alloy fabricated by alloy mixing, which captures the features such as flower-pot morphology of the 2nd phase and inter-phase boundary precipitation of the 3rd phase, which are well documented for the alloy fabricated through the conventional route with the same composition.

The EDS analysis (Fig. 3) can be corroborated with the XRD data to ascertain the identity of each of the 3 phases present in the material. The matrix phase-α (with a phase fraction of 57%) is an FCC phase with the presence of all elements except Cu. The β phase with the flower-pot morphology enriched with Cr is likely the BCC phase as Cr is known to stabilize the BCC structure over the FCC. The α’ phase on the phase boundaries enriched with Cu is likely the second FCC phase as Cu has a tendency to segregate due to its positive enthalpy of mixing with the other alloying elements [14].

Several studies [11, 12, 15–18] have described the phase formation in Cu-based cantor HEA variants including CoCr-CuFeMn and CrCuFeMnNi (the alloy used in the current study). They have consistently concluded that the microstructure consists of 2 FCC phases and a BCC phase. They

| Alloying element | Mean composition (in wt%) | Δ Min/Max |
|------------------|---------------------------|-----------|
| Fe               | 19.08                     | 0         |
| Cr               | 18.24                     | 0         |
| Ni               | 20.59                     | 0         |
| Mn               | 19.28                     | 0         |
| Cu               | 23.20                     | 0         |
| Si               | 0.5                       | 0.4       |
| C                | 0.02                      | 0.03      |

Fig. 1 XRD pattern showing peaks corresponding to different phases present in the microstructure of the as-cast CrCuFeMnNi HEA fabricated using alloy mixing method. α FCC peaks were compared to Ni-FCC peaks (JCPDS-ICDD No.4-480), α’ FCC peaks were compared to Cu-FCC peaks(JCPDS-ICDD No. 4-836) and β BCC peaks were compared to Cr-BCC peaks(JCPDS-ICDD No. 6-694)

Fig. 2 SEM secondary electron image (x3500) showing the microstructure of the as-cast CrCuFeMnNi HEA fabricated through alloy mixing; the green arrow shows the β phase with flower-pot morphology, and the red arrow shows the α’ phase on the phase boundary (Color figure online)
also noted that phase selection agrees with the established critical parameters for HEAs. The presence of the BCC phase has been ascribed to the presence of significant Cr in this alloy. Moreover, Ren et al. [15] used values of Ni-equivalent (\( \text{Nieq} = X_{\text{Ni}} + 0.20X_{\text{Mn}} + 0.20X_{\text{Cr}} \), where \( X_i \) is the atomic fraction of component) and Cr-equivalent (\( \text{Creq} = X_{\text{Cr}} + X_{\text{Fe}} \), where \( X_i \) is the atomic fraction of component) and the relation between them to predict the possible phases. For our alloy, \( \text{Nieq} = 0.29 \) and \( \text{Creq} = 0.4 \), this combination predicts the presence of FCC + BCC microstructure. The presence of an additional FCC phase has been rationalized based on the positive binary enthalpy of mixing by Campo et al. [11].

The yield strength predicted by the ThermoCalc software for the alloy without impurities (the pure alloy) is found to be 135.55 MPa, while the alloy corresponding to the mean impurity concentration is 190.21 MPa which is 50% higher than the pure alloy. The difference can be fully attributed to the difference in solid solution strengthening between the two variants of the alloy, as we do not have any precipitation in both cases, and the grain size is assumed to be the same for both alloys. We should be careful in interpreting these results because we would have a difference in work hardening between the pure and impure variants, and we should also consider the effect of the impurity elements (i.e., Si and C) on the ductility of the alloys. However, we have results from the literature showing that Si improves work hardening rate by decreasing the Stacking fault energy (SFE) [19], and it also leads to uniform elongation and slightly enhanced ductility by the formation of refined dislocation cell structure during plastic deformation [20, 21]. The effect of carbon would be insignificant as it is present in very small amounts. Therefore, the impure alloys are expected to exhibit increased ultimate tensile strength along with good tensile ductility.

The results from the uncertainty analysis are presented below as a histogram (Fig. 4a). It is interesting to note that the yield strength shows a large variation for small variation in the impurity content, which demonstrates the importance of controlling compositional variability in the scrap. In the steel industry, end-of-waste criteria [22] for metallic scraps have been established to ascertain whether a particular scarp is “usable” for steelmaking. Similar criteria should be established for HEAs for successful upscaling of the “alloy mixing.” Detailed studies must be undertaken to establish the standard protocols, which is out of the scope of this study.

It should be noted that some of the impure variants have a lower yield strength compared to that of the pure alloy, which shows that we should be careful in controlling the scrap composition. We plotted the yield strength as a function of Si content (Fig. 4b), which shows that the yield strength varies linearly with Si content. This is interesting because Si, which is present as an impurity, helps in strengthening, indicating that impurities are not necessarily detrimental to the mechanical properties of the alloy. It is
likely that Si improves the yield strength by solid solution strengthening. We did not observe a clear trend with respect to the variation in Carbon content. It is due to the very low carbon content in the raw material. While the results from the strengthening model available in ThermoCalc are reliable, we need to conduct further experiments to get a complete understanding of the phenomena. However, these results are extremely useful in the context of guiding future experiments.

Table 2 lists the market price for the alloy scraps and pure elements [23, 24]. It is evident that alloy scraps are 100 times cheaper than pure elements. The bar chart given in Fig. 5 compares the price of HEA manufactured...
by “alloy mixing” and HEA produced from pure elements. It is pertinent to note that, this work being a lab-scale study using scraps as the precursor for HEAs, there was no cost incurred in pre-treatment of scrap. On the other hand, when the process is implemented at a plant scale, pre-treatment of scraps (including sorting, classification and purification) would be necessary, and there would be a cost associated with it. However, based on techno-economic models for scrap-based processes used in the steel industry [25, 26], the scrap-based processes are highly profitable even after accounting for the additional cost incurred in the pre-treatment of scraps. Hence, it is reasonable to conclude that scrap-based “alloy mixing” would be economically beneficial for the mass production of HEAs.

Conclusions

- Alloy mixing using scraps preserves the microstructure of the alloy as confirmed by characterization using XRD and SEM.
- The yield strength of the impure alloy was 50% higher than the conventionally manufactured alloy, indicating possible additional impact on the solid solution strengthening from the impurity elements, especially Si.
- The uncertainty quantification with respect to variation in impurity content indicated that the yield strength showed a large variation (nearly 100 MPa) as a function of impurity concentration. It also revealed that if we do not control the scrap composition properly, we may end up degrading the properties.
- Our cost analysis revealed that alloy mixing could lead to a significant reduction in fabrication costs.

Hence, Alloy mixing serves as a promising sustainable and cost-effective method for the fabrication of HEAs, which would enable the commercialization of HEAs while serving as a feasible avenue for alloy scrap recycling. It is hoped that this study would encourage industries to take up further interest in the commercialization of HEAs using metallic scraps as a precursor. Future research must focus on (i) establishing protocols for sorting the incoming scraps, (ii) high-throughput screening of impurities in incoming scraps and, and (iii) establishing end-of-waste criteria for scraps.

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Declarations

Conflict of interest The authors declare that they have no conflict of interest.

References

1. United States Environmental Protection Agency (2021) Advancing sustainable materials management: 2018 tables and figures assessing trends in material generation and management in the US; 2021 ASI 219-6.
2. Broadbent C (2016) Steel’s recyclability: demonstrating the benefits of recycling steel to achieve a circular economy. Int J Life Cycle Assess 21:1658–1665. https://doi.org/10.1007/s11367-016-1081-1
3. Manabe T, Miyata M, Ohnuki K (2019) Introduction of steelmaking process with resource recycling. J Sustain Metall 5(3):319–330. https://doi.org/10.1007/s40831-019-00221-1
4. Yeh J, Chen S, Lin S, Gan J, Chin T, Shun T, Tsau C, Chang S (2004) Nanostructured high-entropy alloys with multiple principal elements: novel alloy design concepts and outcomes. Adv Eng Mater 6(5):299–303. https://doi.org/10.1002/adem.200300567
5. Cantor B, Chang JTH, Knight P, Vincent AJB (2004) Microstructural development in equiatomic multicomponent alloys. Mater Sci Eng A 375:213–218. https://doi.org/10.1016/j.msea.2003.10.257
6. Li Z, Raabe D (2017) Strong and ductile non-equiatomic high-entropy alloys: design, processing, microstructure, and mechanical properties. JOM 69:2099–2106. https://doi.org/10.1007/s11837-017-2540-2
7. Sahu S, Swanson OJ, Li T, Gerard AY, Scully JR, Frankel GS (2020) Localized corrosion behavior of non-equiatomic NiFeCrMnCo multi-principal element alloys. Electrochimica acta 354(1):136749. https://doi.org/10.1016/j.electacta.2020.136749
8. Tomboc GM, Kwon T, Joo J, Lee K (2020) High entropy alloy electrocatalysts: a critical assessment of fabrication and performance. J Mater Chem A Mater Energy Sustain 8(3):14844–14862. https://doi.org/10.1039/d0ta05176d
9. World Steel Association (2021) Use of scraps in the steel industry fact sheet https://worldsteel.org/publications/fact-sheets/, Accessed 12 Feb, 2022.
10. Li X, Sun W, Zhao L, Cui J (2018) Material metabolism and environmental emissions of BF-BOF and EAF steel production routes. Miner Process Extr Metall Rev 39(1):50–58. https://doi.org/10.1080/08827508.2017.1324440
11. Campo KN, de Freitas CC, da Fonseca EB, Caram R (2021) CrCuFeMnNi high-entropy alloys for semi-solid processing: the effect of copper on phase formation, melting behavior, and semi-solid microstructure. Mater Charact 178:111260. https://doi.org/10.1016/j.matchar.2021.111260
12. Oh SM, Hong SI (2018) Microstructural stability and mechanical properties of equiatomic CoCrCuFeNi, CrCuFeMnNi, CoCrCuFeMn alloys. Mater Chem Phys 210:120–125. https://doi.org/10.1016/j.matchemphys.2017.09.010
13. Li C, Li JC, Zhao M, Jiang Q (2009) Effect of alloying elements on microstructure and properties of multiprincipal elements high-entropy alloys. J Alloys Compounds 475:752–757. https://doi.org/10.1016/j.jallcom.2008.07.124
14. Troparevsky MC, Morris JR, Kent PRC et al (2015) Criteria for predicting the formation of single-phase high-entropy alloys. Phys Rev X 5(1):011–041. https://doi.org/10.1103/PhysRevX.5.01104
15. Ren B, Liu ZX, Li DM, Shi L, Cai B, Wang MX (2010) Effect of elemental interaction on microstructure of CuCrFeNiMn high
entropy alloy system. J Alloys Compounds 493:148–153. https://doi.org/10.1016/j.jallcom.2009.12.183
16. Praveen S, Murty BS, Kottada RS (2012) Alloying behavior in multi-component AlCoCrCuFe and NiCoCrCuFe high entropy alloys. Mater Sci Eng A 534:83–89
17. Campo KN, de Freitas CC, Fanton L, Caram R (2020) Melting behavior and globular microstructure formation in semi-solid CoCrCuFeNi high-entropy alloys. J Mater Sci Technol 52:207–217
18. Rogal Ł (2017) Semi-solid processing of the CoCrCuFeNi high entropy alloy. Mater Des 119:406–416. https://doi.org/10.1016/j.matdes.2017.01.082
19. Blinov VM, Bannykh IO, Lukin EI, Bannykh OA, Blinov EV, Chernogorova OP, Samoilova MA (2021) Effect of substitutional alloying elements on the stacking fault energy in austenitic steels. Russ Metall Metally 2021:1325. https://doi.org/10.1134/S0036029521100086
20. Xiong R, Liu Y, Si H, Peng H, Wang S, Sun B, Chen H, Kim HS, Wen Y (2020) Effects of Si on the microstructure and work hardening behavior of Fe-17Mn-11C-xSi high manganese steels. Metals Mater Int 27:3891–3904. https://doi.org/10.1007/s12540-020-00846-y
21. Llewellyn DT (1997) Work hardening effects in austenitic stainless steels. Mater Sci Technol 13(5):389–400. https://doi.org/10.1179/mst.1997.13.5.389

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