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Computational materials design of a corrosion resistant high entropy alloy for harsh environments



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ABSTRACT

The integrated computational materials engineering approach is inherently well suited to explore the vast, multi-dimensional high entropy alloy (HEA) compositional and processing space, and has been adopted in this work, coupled with empiricism, to the design of highly corrosion resistant HEAs. Using the combination of empirical and computational approaches, three non-equimolar HEA compositions were identified for their predicted ability to form a single-phase structure and to exhibit high corrosion resistance. One of them, $\text{Ni}_{38}\text{Cr}_{21}\text{Fe}_{20}\text{Ru}_{13}\text{Mo}_6\text{W}_2$, was successfully synthesized on the lab-scale and homogenized at 1250 °C for 120 h. Exceedingly high corrosion resistance of the Ni-rich HEA was demonstrated in electrochemical testing.

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Corrosion has become an obstacle to achieving many of the identified engineering grand challenges, according to a recent national academy study [1]. Advancement of technological applications and securing engineering operations in our society demands the design of new corrosion resistant alloys (CRAs) that have superior intrinsic corrosion resistance and are able to resist aggressive corrosion attack in harsh service environments. High entropy alloys (HEAs) are a new class of materials that have exhibited promising characteristics to meet this objective. HEAs comprise single phase solid solutions of five or more elements at or near equimolar composition [2,3]. HEAs are distinct from conventional alloys in that they are not based on one single majority host element, such as Fe in steels, Ni in superalloys, and Al in Al-alloys. Instead, they are composed of multiple principle elements, so they overcome barriers in conventional alloy design and offer vast degrees of freedom in alloy compositions and properties. Numerous studies [4–13] have been conducted to investigate various HEAs with potentially high corrosion resistance. It is worth noting that most of the published studies have focused on HEAs that are equimolar or simple substitutional derivatives of equimolar compositions. However, the corrosion performance of HEAs is not necessarily optimized at such compositions as evidenced by the strong dependence of corrosion resistance on alloy composition and surface oxide film chemistry in compositional complex

alloys and even simple binary alloys [14,15]. Therefore, to identify the most corrosion resistant HEAs, it is important to navigate away from the equimolar trial-and-error approach to corrosion and embark on exploratory routes into the vast, non-equimolar compositional space.

The scarcity of corrosion studies on complex non-equimolar HEAs is partly due to the limitations of the conventional empirical approach to CRA design, which is usually costly, incremental and time-consuming. Such drawbacks become more prominent when it comes to designing and synthesizing HEAs, where the myriad possibilities in the multi-dimensional compositional space are too large to tackle by experimental approaches alone. There is clearly a need for an advanced approach to design CRAs and especially corrosion resistant HEAs (CR-HEAs). Integrated computational materials engineering (ICME) is a modern systems-based approach to design materials that meet specific performance criteria by linking computational materials models across multiple length scales [16]. The ICME approach can readily predict many properties for an alloy based on tools such as Calculation of Phase Diagrams (CALPHAD) and Density Functional Theory (DFT), provided accurate databases of materials behavior are available. Thus, ICME is ideally suited to efficiently and exhaustively search for and design CR-HEAs with sought-after attributes. Mechanistic corrosion models for predicting corrosion resistance quantitatively from alloy composition on a fundamental scientific level are currently being actively developed [17], but are not yet mature enough to be incorporated into an ICME framework. However, it is possible to combine empirical corrosion resistance paradigms based on prior knowledge with computational tools to identify promising CR-HEAs [17].

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In this paper, we report a design process using a combination of empiricism and computation that has led to successful identification of several single-phase non-equimolar CR-HEAs showing great potential for superior corrosion resistance. The present study has mainly focused on single-phase HEAs, as the development of homogeneous solid solution alloys with minimization of structural and chemical heterogeneities is the most typical strategy for CRA design with the greatest chance for superior corrosion resistance. One of the designed CR-HEAs has been successfully synthesized and has experimentally demonstrated single phase stability and exceedingly high corrosion resistance, even in very harsh testing environments.

The pitting resistance equivalent number (PREN) [18,19], a linearized fit of the wt% of certain constituent alloy elements to corrosion performance parameters, initially derived for Fe-based CRAs has been considered. Various equations for PREN have been developed from numerical fitting of elemental concentrations in Fe-Cr-Ni alloys to experimentally determined corrosion parameters, such as critical pitting potential and critical pitting temperature [20,21]. PREN is a simple correlation that is useful for predicting corrosion resistance of Fe-based stainless steels. The approach has been extended to Ni base super alloys [22–25] and iron-based metallic glasses [26]. In both cases, a qualitative trend was found, but the database is not extensive enough to establish a strong relationship for wide-ranging compositions. Moreover, PREN lacks a scientific basis for capturing the underlying mechanism that governs the effects of those beneficial alloying elements, making it difficult to apply PREN to alloys that include elements other than those found in Fe-based CRAs (such as those elements found in HEAs). PREN also lacks consideration of microstructure, environment or interactions between alloying elements.

The PREN approach has been used in this work, but discretion has been exercised and additional ICME tools and guidance have been employed complementarily in an attempt to extrapolate PREN beyond the fitted data and into new HEA compositional space. It is possible to design an alloy that has sufficiently high configurational entropy to be considered an HEA, but remains chemically akin to Fe-based stainless steels and Ni-based superalloys (e.g., enriched in Fe or Ni), such that the PREN approach may still be used for semi-quantitative prediction of corrosion resistance. The PREN used in the present work is defined as $PREN = wt. \% Cr + 3.3 (wt. \% Mo + 0.5 wt. \% W)$, a version taking in account the positive influence of W in addition to Cr and Mo on pitting resistance [25,27,28].

Backed by this rationale, two initial HEA compositions, one enriched in Fe and the other enriched in Ni as specified in Table 1, have been conceived based on prior corrosion and metallurgical paradigms: 1) Cr, Mo, W can effectively improve corrosion resistance according to the PREN model; and 2) Ru is useful to effectively suppress topologically closed packed phases and promote single phase formation [29]. These two compositions represent the HEA compositional spaces where the aforementioned corrosion-enhancing elements are combined. Thermo-Calc with the TCHEA2 database [30] was utilized to identify specific HEA compositions that have a wide temperature window over which a single phase is stable with the goal of quenching to a single phase structure at ambient temperature and enabling proper homogenization. This database has been demonstrated to have excellent agreement with the experimental HEA phase stability studies [31].

Table 1

HEAs designed based on prior corrosion paradigm and predicted single phase by CALPHAD in Thermo-Calc software with TCHEA2 database.

Initial compositions (at.%)	Stable phases (at.%)	Structure	ΔS_{conf}	PREN
$Fe_{30}Cr_{20}Mn_{20}Ru_{20}Mo_5W_5$	$Fe_{30}Cr_{25}Mn_{25}Ru_{10}Mo_6W_4$	BCC	1.58R	64
	$Fe_{32}Ru_{30}Cr_{14}Mn_{14}W_6Mo_4$	HCP	1.59R	50
$Ni_{30}Cr_{20}Fe_{20}Ru_{20}Mo_5W_5$	$Ni_{38}Cr_{21}Fe_{20}Ru_{13}Mo_6W_2$	FCC	1.53R	54
	$Ru_{42}Fe_{21}Cr_{15}W_6Ni_4Mo_1$	–	–	–

The thermodynamic properties of the two initial compositions were calculated at 1100 °C, a high temperature assumed high enough to solutionize the HEAs into a single phase. The results indicate that both compositions are unstable at 1100 °C and each will decompose into two stable phases (Table 1). Among the four new phases, one is rich in Ru ($Ru_{42}Fe_{21}Cr_{15}W_6Ni_4Mo_1$) and was therefore excluded from further consideration. The other three are disordered solid solutions of BCC and FCC, enriched either in Fe or Ni, mimicking to some extent the chemistry of stainless steels and superalloys for which PREN has been successfully applied. The predicted structure, configurational entropy, and PREN of those three phases are presented in Table 1. Their ΔS_{config} are all $>1.5R$, a conventional threshold value above which an alloy can be deemed to be an HEA [32], and their PRENs are comparable to those of commercial super stainless steels and nickel-based superalloys. The results above suggest that the three compositions predicted to be stable at 1100 °C all can form single-phase HEAs that potentially possess superior corrosion resistance as reflected by their high PRENs. In particular, the Ni-rich FCC-based HEA, $Ni_{38}Cr_{21}Fe_{20}Ru_{13}Mo_6W_2$, was selected for further CALPHAD evaluations and experimental validation in this study. To assess the ability of this HEA to form a single phase, a pseudo-binary phase diagram was created, as shown in Fig. 1, where Cr content is varied and balanced by Ni. This diagram shows the amount of Cr that can be substituted by Ni at different temperatures while still retaining the single FCC phase, which aids in exploration of non-equimolar HEAs in a single-phase structure. It can be observed that this particular HEA composition space has a fairly broad single phase region in terms of tolerance in Cr variation, along with wide temperature windows (span of 300 °C–400 °C) at various Cr levels, which are indications of ease of solutionizing and good processability. This phase diagram is also useful for identifying a stable composition range over which systematic changes in elemental concentration could be explored (e.g., to study the effects of different elements on corrosion).

To explore the thermodynamic stability of the oxide film formed on the HEA in water of various pH levels under oxidizing and reducing conditions, stability regions of oxides in the electrochemical potential/pH domain for $Ni_{38}Cr_{21}Fe_{20}Ru_{13}Mo_6W_2$ were computed by a modified version of CALPHAD in Thermo-Calc software (Fig. 2). The calculation conditions were 25 °C, 1 atm, 1 kg of H_2O with 0.6 M NaCl, and the total alloy amount was 10^{-2} mol. The databases employed were TCAQ3, AQS2, SSUB3, and TCHEA2 [30]. TCAQ3 plus AQS2 contain most of the aqueous species for the composing elements, except Mo^{3+} . Due to this absence, the stability region of Mo^{3+} was manually incorporated by superimposing the E-pH diagram for pure Mo, which contains an Mo^{3+} region [33], onto the calculated diagram. SSUB3 includes all the six

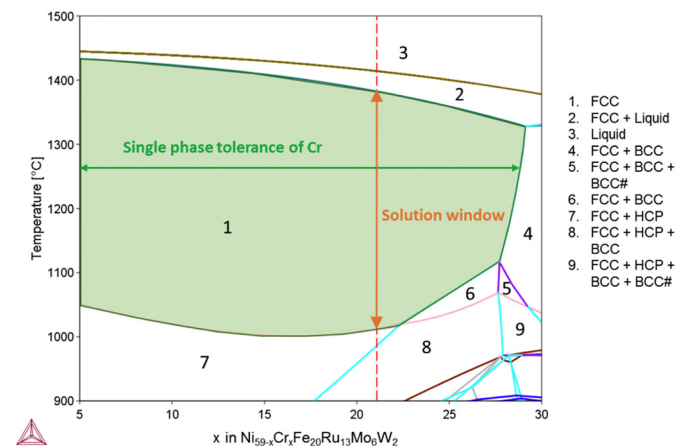


Fig. 1. Pseudo-binary phase diagram of $Ni_{59-x}Cr_xFe_{20}Ru_{13}Mo_6W_2$ calculated in Thermo-Calc with TCHEA2 database. The FCC single phase region is shaded in green. The dashed line corresponds the Ni-rich HEA composition with 21 at.% Cr. BCC and BCC# are two disordered BCC phases with a miscibility gap. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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