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Developing New Type of High Temperature Alloys – High Entropy Superalloys

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Abstract

Novel high temperature alloys – high entropy superalloys (HESA) have been developed by elevating the mixing entropies of Ni-Al-Co-Cr-Fe-Ti systems, these alloys contain stable FCC γ matrix and $L1_2$ γ' precipitates; compositions spaces are outside the scopes of traditional Ni-base superalloys and equimolar high entropy alloys. The thermal stability of high entropy γ' precipitates can be enhanced through alloy design by thermodynamic calculation based on Thermo-Calc. HESAs have potentials to high temperature structural application; alloy densities are below 8.0 g/cm^3 with lower cost of raw materials than those of conventional Ni-base superalloys.

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Introduction

Aerospace, energy, and oil & gas sectors have relied on Ni-based superalloys-made components in order to operate gas turbine engines [1,2]. These superalloys have relied on dispersion of coherent $L1_2$ γ' precipitates in FCC γ matrix for excellent high temperature mechanical properties. Compositions of superalloys have continued to evolve to meet demanding operation conditions [3]. Recently, additions of Re and Ru in superalloys have led to much improvement in creep strength [4-12], however, Re and Ru additions can render alloys to possess higher density and higher cost. Furthermore, the compositions of cast superalloys have to exhibit good castability, however addition of heavy elements (Re,W) tends to cause density inversion and results the formation of casting freckle defects [13]. Traditional alloy design methods that rely on addition of refractory elements have appeared to reach the limit. High entropy alloys (HEAs) are defined to have at least five principal elements with the concentration of each principal element being between 35 and 5 *at%* [14]. There are four core effects associated with HEAs, i.e. (1) high-entropy, (2) sluggish-diffusion, (3) lattice-distortion and (4) cocktail effects [15]. In this paper, a new type of high temperature alloy has been derived from the concept of high entropy alloy and allows the four core effects to be exploited for high temperature applications. These novel alloy systems (density <8.0 g/cm^3) based on non-equimolar Al-Co-Cr-Fe-Ni-Ti systems containing FCC γ matrix with uniform dispersion of $L1_2$ γ' particles have been developed. Since alloy compositions are designed by the high entropy alloy concept, and their microstructures can resemble that of conventional superalloys, hence the term "High Entropy Superalloys (HESA)" has been given.

In our previous work, $Co_{1.5}CrFeNi_{1.5}Ti_{0.5}$ high entropy alloy contain $\gamma' + \gamma + \eta$ phases in its microstructure [16]; this alloy could be fabricated into single crystal by the conventional Bridgeman method, and its single crystal castability is similar to that of conventional Ni-base superalloys. However, η phase is a detrimental phase, and Thermo-Calc (TCNI5 database) has been utilized to perform alloy design to ensure that microstructure can contain mostly γ and γ', Figure 1. Interestingly, this path of alloy design has leaded us into composition spaces that have not really been exploited before. Compositions spaces are actually outside the scopes of traditional Ni-base superalloys and equimolar high entropy alloys, Figure 2.

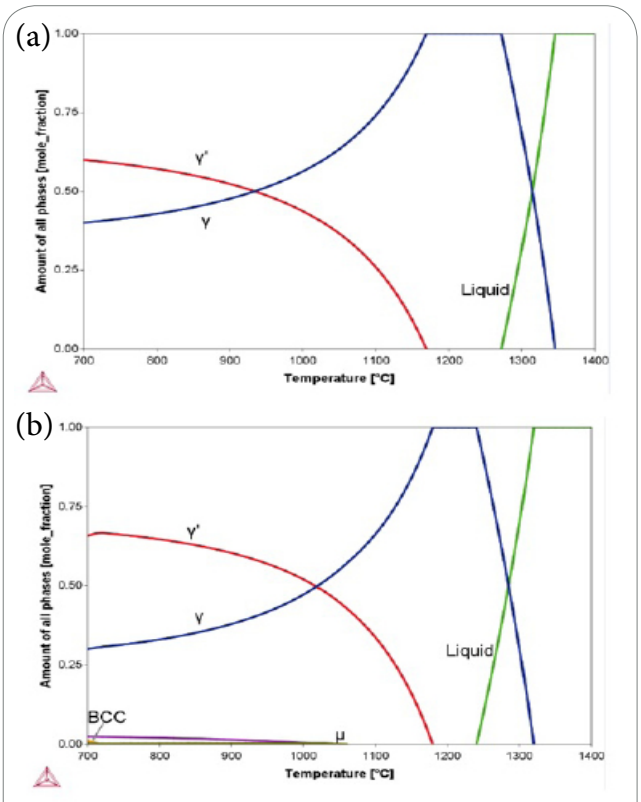

Figure 1: Designing alloy compositions by CALPHAD-base simulations (Thermo-Calc: TCNI5 database) (a) Alloy A, and (b) Alloy C.

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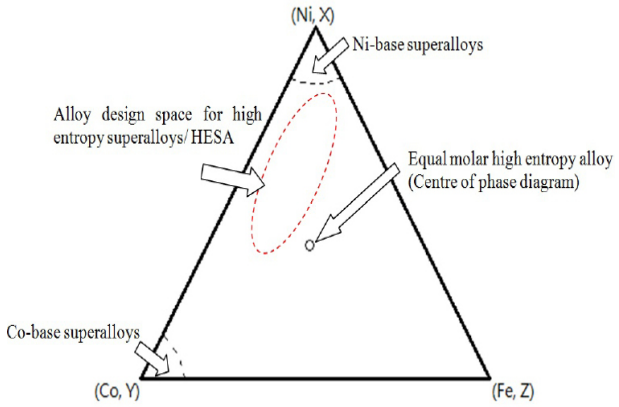

Figure 2: Illustration of the alloy design space for high entropy superalloys.

Table 1 lists three example compositions of HESA; the mixing entropy is calculated by the following equation: $\Delta S_{mix} = -R(X_A ln X_A + X_B ln X_B + \cdots)$, where ΔS_{mix} is the mixing entropy of alloy, R is the gas constant, and X_A means the molar fraction of constituent A in whole alloy, X_B means the molar fraction of constituent B, and so on. Unlike conventional Ni-base superalloys, their densities are below 8.0 g/cm^3 and raw materials cost can be 20% less than that of 1st generation superalloys, such as CM247LC.

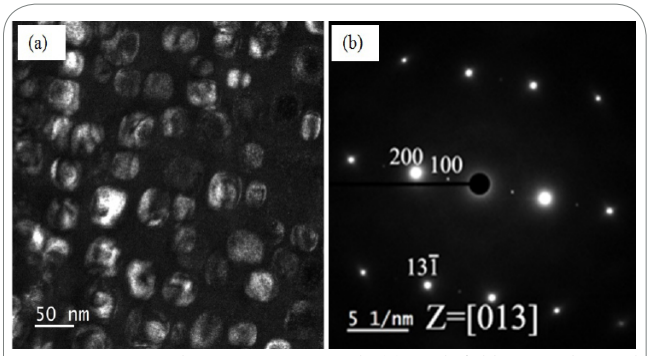

Figure 4: TEM analysis on HESA sample (a) Dark field image shows γ' particles in γ matrix, (b) Diffraction patterns shows the superlattice reflection of γ'.

The high temperature phase stability of HESA is excellent. The γ' solvus temperatures of Alloy A, B and C are measured by differential thermal analysis to be 1,146°C, 1,165°C, and 1,194°C, respectively. After isothermal ageing at 1,050°C for 500 hrs, microstructures of HESA remain stable γ-γ' with no μ, σ, η, δ, β detrimental phase formations, Figure 5. Conventional Ni-Fe base superalloys can only contain $Ni_3(Al, Ti)$ γ' within a fairly narrow range of Al/Ti ratios [1]. As the Al content is increased for a given Ti level in these alloys, the sequence of stable phases includes hexagonal Ni_3Ti (η), $Ni_3(Ti,Al)$ (γ'), cubic Ni_2AlTi (Heussler phase), cubic Ni(Al,Ti) (β). And, among

Alloys	Ni	Al	Co	Cr	Fe	Ti	Ta	Mo	W	ΔS_{mix}	density (g/cm3)
A	50.5	8.9	17.2	9.2	8.2	6.0	--	--	--	-1.46 R	7.68
B	40.7	7.8	20.6	12.2	11.5	7.2	--	--	--	-1.58 R	7.64
C	48.6	10.3	17.0	7.5	9.0	5.8	0.6	0.8	0.4	-1.56 R	7.94

Table 1: The nominal composition, mixing entropy and γ' solvus of some HESA systems (*at%*).

The sample preparation procedure involved making master alloys by the arc-melting process, the mixtures of the constituent elements were with purities higher than 99.5 wt% in an argon atmosphere, and the melting processes were repeated four times to ensure chemical homogeneity of the master alloy. The next process was directional solidification casting, by referring to our previous work [16], 120 *mm* in height and 9 *mm* in diameter directional solidified (DS) bars were fabricated by the conventional Bridgeman furnace with DS seed material of Rene 142 obtained from in-house casting. The withdrawing of the single crystal cast started after the mold temperature was stable at 1,550°C with a withdraw rate of 40 *mm/hour*, and a temperature gradient ~30°C /mm. The as-cast microstructure contains dendritic structure; phase constituents include only FCC γ matrix and coherent $L1_2$ γ' phases, Figure 3. The existence of ordered $L1_2$ γ' phases was proven by the superlattice diffractions in Figure 4.

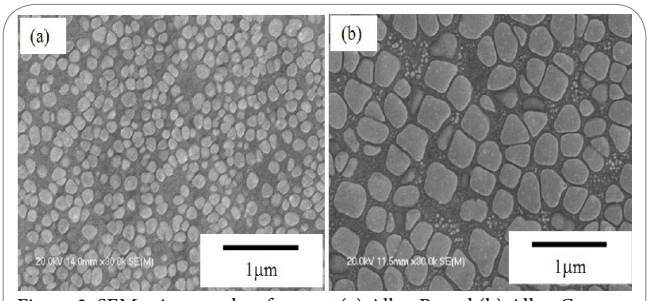

Figure 3: SEM micrographs of as-cast (a) Alloy B, and (b) Alloy C.

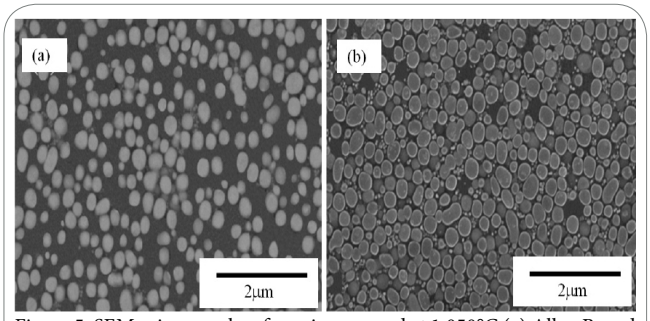

Figure 5: SEM micrographs of specimens aged at 1,050°C (a) Alloy B, and (b) Alloy C.

these phases, only the γ' can provide strengthening, the other phases tend to form coarse platelets. So traditional Ni-Fe base superalloys rely on Ti addition for metastable Ni_3Ti γ' strengthening, however long exposure at temperatures above 650°C can cause γ' to transform to η, and result loss in strength. An alternative to Ti is Nb addition, in the presence of high Nb/(Ti+Al) ratios, a metastable phase Ni_3Nb γ'' can form for effective strengthening, however, after prolong exposures at temperatures beyond 650°C, γ'' can be replaced by Ni_3Nb δ, which is also a coarse platelets. By contrast, HESAs contain moderate Fe content and is able to accommodate sufficient Al content to possess stable phase. Although Fe is known to degrade the phase stability in conventional Ni and Ni-Fe based superalloys [14], high content of Co in HESA appears to stabilize the microstructure for further

Al, Cr, Ti additions without jeopardizing phase stability at high temperature. Although Thermo-Calc predicts the formation of BCC and μ phases in Alloy C at lower temperatures, however, isothermal ageing at 700°C or below conducted so far has not yielded any phase instability, possibly due to very sluggish phase transformation rate in the high entropy alloy system. Hence γ' precipitates can remain stable in HESA for high temperature strengthening purpose.

In Table 2, compositions of individual γ,γ' phase of Alloy B measured by strain ageing are listed in comparison with a 1st and a 4th generation superalloy [17-19]. HESA γ and γ' possess higher degree of randomness in their ordered structures than those of CM247LC and RR2101. Interestingly, from CM247LC to RR2101, the value of entropy in γ' phase has not evolved much, and this is due to the later generations of alloys have relied on γ forming elements to provide strengthening, hence the entropy of γ phase is higher. The potential high temperature strength of HESA can be attributed by high volume fraction of γ' precipitates, high degree of solid solution strengthening due to lattice distortion, and the increase in APB energy. According to JMatPro calculation (Ni alloys database), the APB energy of γ' in Alloy B can reach to 0.25 J/m^2, while that of CM247LC is about 0.19 J/m2, resulting higher energy penalty for dislocation pairs to cut through HESA γ'.

	Cr activity	Al activity	Cr activity	Al activity
	900°C	900 °C	1,100 °C	1,100 °C
Alloy B	0.00466	$5.1165x10^{-8}$	0.00213	$2.38801x10^{-7}$
Alloy C	0.00308	$3.62780x10^{-8}$	0.00148	$2.26364x10^{-7}$
CM247LC	0.00322	$1.421678x10^{-8}$	0.00159	$1.15643x10^{-7}$

Table 3: Cr activity and Al activity calculated by Thermo-Calc (TCNI5 database).

result excellent creep resistances [30]. Furthermore, denser interfacial dislocation network in high misfit alloys can attribute to smaller minimum creep strain rate, since dense dislocation network can hinder pairs of dislocations in γ channel from cutting through the γ'/γ interfaces [31]. Future direction to design HESA should be to enlarge its lattice misfit toward negative, and this can be achieved by addition of various γ and γ' forming elements, not restricted to Al, Co, Cr, Fe, Ni, and Ti.

Comparing to traditional superalloys, HESA contains little or no refractory content, the cost of raw materials is cheaper, HESA has lower density, excellent phase stability, and potentials of high temperature strength, and oxidation resistances.

at%		Ni	Al	Co	Cr	Fe	Ti	Ta	W	Re	Ru	ΔS_{mix}
CM247LC	γ	64.9	8.7	11.0	10.5	-	0.7	0.9	3.1	-	-	-1.17 R
	γ'	69.4	15.5	5.8	3.4	-	1.4	2.3	2.1	-	-	-1.06 R
RR2101	γ	46.0	3.1	26.7	9.5	-	-	0.3	3.6	7.9	2.9	-1.48 R
	γ'	66.1	16.6	8.8	1.4	-	-	2.7	3.0	0.5	0.9	-1.12 R
Alloy B	γ	32.3	4.82	24.7	18.2	16.1	3.88	-	-	-	-	-1.59 R
	γ'	54.4	9.87	13.7	4.3	5.73	12.0	-	-	-	-	-1.39 R

Table 2: Compositions of individual γ, γ' phase, and their $\mathbf{\Delta S_{mix}}$

By calculating the Cr activity and Al activity of HESA (Thermo-Calc TCNI5 database), and make comparisons with those of CM247LC [19], which is known to possess excellent oxidation resistance at high temperatures, we can have some ideas about the potential oxidation resistance of HESA. Values are listed in Table 3, since CM247LC can form continuous protective oxide [19], higher Cr and Al activities in HESAs imply that continuous Cr_2O_3 and Al_2O_3, respectively, can form very rapidly when exposing the alloy to oxidizing environment at high temperatures. After isothermal oxidation at 1,100°C for 5 *hrs*, Alloy C can actually form continuous Al_2O_3, this is an indication that Alloy C can have good oxidation resistance at high temperature, Figure 6.

To further advance HESA, future alloy designs can be conducted to control the coarsening kinetics of γ' phase. Since both Alloy B and C possess spherical γ' after ageing, Figure 5, it is an indication that the lattice misfit between γ and γ' is positive. For advanced superalloys, negative lattice misfit between γ and γ' is desired, because the directional coarsening of the γ' precipitates known as "rafting" is an important microstructural evolution during high temperature creep [20-24]. Rafting is strongly dependent on the sign of applied loading, lattice misfit and elastic constants of γ and γ' phase [25-29]. Lattice misfit (δ) is defined by the following equation, where a γ' is the lattice parameter of γ' and a γ is the lattice parameter of γ phase:

$$\delta = 2(a_{\gamma'} - a_{\gamma})/(a_{\gamma'} - a_{\gamma})$$

With negative sign of δ,γ' can raft in direction perpendicular to the stress axis, effectively hinder the climbing of dislocations and

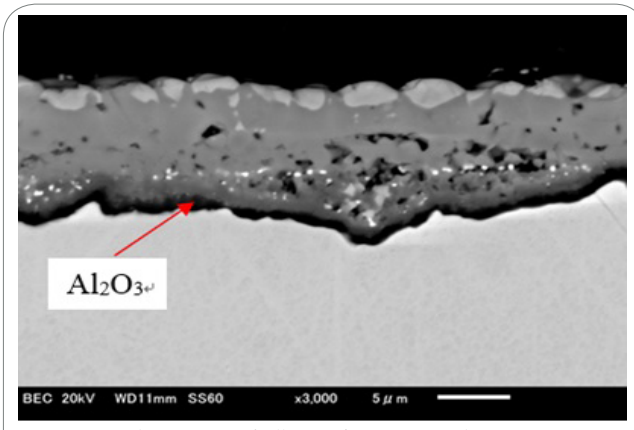

Figure 6: Oxide structure of Alloy C after 1,100°C/5 hrs.

Conclusion

- HESA possess high γ' solvus temperatures and can possess stable γ-γ' microstructures with no μ, σ, η, δ, β detrimental phase formations.
- HESA have potential to exhibit good oxidation resistance.
- HESA has density below 8.0 g/cm^3.
- The cost of raw materials for HESA are lower due to little or no refractory content, hence the cost-performances of HESA can surpass that of some superalloys.

Competing Interests

The authors declare that they have no competing interests.

Author Contributions

All the authors substantially contributed to the study conception and design as well as the acquisition and interpretation of the data and drafting the manuscript.

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