A Promising New Class of High-Temperature Alloys: Eutectic High-Entropy Alloys

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High-entropy alloys (HEAs) can have either high strength or high ductility, and a simultaneous achievement of both still constitutes a tough challenge. The inferior castability and compositional segregation of HEAs are also obstacles for their technological applications. To tackle these problems, here we proposed a novel strategy to design HEAs using the eutectic alloy concept, i.e. to achieve a microstructure composed of alternating soft fcc and hard bcc phases. As a manifestation of this concept, an AlCoCrFeNi2.1 (atomic portion) eutectic high-entropy alloy (EHEA) was designed. The as-cast EHEA possessed a fine lamellar fcc/B2 microstructure, and showed an unprecedented combination of high tensile ductility and high fracture strength at room temperature. The excellent mechanical properties could be kept up to 700°C. This new alloy design strategy can be readily adapted to large-scale industrial production of HEAs with simultaneous high fracture strength and high ductility.

High-entropy alloys (HEAs), or multi-principal-element alloys, emerge as a new research frontier in the metallic materials community1–5. HEAs differentiate with conventional alloys in that they have at least four principal elements, instead of one or two in the latter. It is a breakthrough to the alloy design in the traditional physical metallurgy, and it opens a new arena for explorations of new materials and new properties. Previous studies have indicated that HEAs have a high softening resistance at elevated temperatures5–7, and sluggish diffusion kinetics5. Therefore, HEAs are widely regarded as highly promising high-temperature materials. Before the high-temperature application of HEAs can be seriously pursued, a technical challenge in terms of the mechanical property needs to be tackled. Basically, single-phased HEAs have been found difficult to reach a reasonable balance between strength and (tensile) ductility5–8. Single-phased fcc structured HEAs are ductile but not strong enough8,9. Single-phased bcc structured HEAs, on the other hand, can be very strong but at the price of brittleness9. To the best of our knowledge, there is no report of HEAs possessing an excellent balanced strength and tensile ductility. Naturally, a composite way can be expected to achieve this balance. However, simply introducing a combination of fcc and bcc phases, without a proper structural design, could not solve the problem. Moreover, the inferior castability and compositional segregation, which are common for HEAs, further downgrade their mechanical properties and cast shadow on their engineering applications4,6.

In order to address to these important technical issues that HEAs are currently facing, we proposed here to use the eutectic alloy idea to design HEAs with the composite structure, or it can be said to use the high-entropy alloy concept to design eutectic alloys. Furthermore, we proposed to design the eutectic alloys with a mixture of soft fcc and hard bcc phases, to achieve the balance of high fracture strength and high ductility. Apart from being a new way to obtain the composite structure in HEAs, eutectic alloys are also known to be good candidate high-temperature alloys, because the eutectic solidification structure has the following features: 1) near-equilibrium microstructures that resist change at temperatures as high as their reaction temperature; 2) low-energy phase boundaries; 3) controllable microstructures; 4) high rupture strength; 5) stable defect structures; 6) good high-
temperature creep resistance; 7) regular lamellar or rod-like eutectic organization, forming an in-situ composite\textsuperscript{13}. In addition, eutectic alloys are known to have better castability. Also importantly, since the eutectic reaction is an isothermal transformation and hence there exists no a solidification temperature range, both the segregation and shrinkage cavity can be alleviated. Accordingly, if eutectic HEAs with the composite fcc/bcc structure can be prepared, they are expected to possess the advantageous mechanical properties and castability of eutectic alloys, clearing obstacles for their technological application.

Results

Microstructure and phase constitution. To verify this novel alloy design strategy, an industrial scale AlCoCrFeNi\textsubscript{2.1} ingot of 2.5 kg in weight was prepared, as shown in Fig. 1a. The bulk AlCoCrFeNi\textsubscript{2.1} alloy exhibited an excellent castability with few casting defects, significantly differentiating with other bulk HEAs. The tensile test specimen was machined from the bulk alloy ingot and is shown in Fig. 1b. The cast microstructure of AlCoCrFeNi\textsubscript{2.1} is shown in Fig. 2a. Even in such a bulk cast ingot, a uniform and fine lamellar microstructure characteristic of eutectic alloys was achieved. The inter-lamellar spacing was about 2 \textmu m. The coupled grown two phases showed a clear compositional contrast, with the regions marked by A in Fig. 2b were rich in Co, Cr and Fe, while the regions marked by B were rich in Al and Ni (detailed compositional information given in Table 1). An enlarged microstructure given in Fig. 2c shows that dense nanoscale NiAl-rich precipitates (marked as B\textsubscript{II}) occurred in the CoCrFe-rich region. The X-ray diffraction (XRD) pattern of the alloy is given in Fig. 3a, showing an fcc/B2 dual-phase constitution. The differential scanning calorimetric (DSC) curve given in Fig. 3b shows only one melting event, further evidencing the eutectic composition in this alloy. Correlating the compositional information and the XRD result, the A regions shall correspond to the fcc phase while the B regions (including B\textsubscript{II}) to the B2 phase.

Tensile properties. The eutectic AlCoCrFeNi\textsubscript{2.1} alloy, with an fcc/B2 dual-phase constitution and a uniform and fine lamellar microstructure, exhibited the combination of both high fracture strength and high ductility, which has never been achieved in previously reported HEAs\textsuperscript{1}. The room temperature tensile test showed a fracture stress of 944 MPa and an elongation of 25.6%, from the engineering stress-strain curve given in Fig. 4a. These values converted to 1186 MPa and 22.8% in the true stress/strain condition. Noteworthily, this alloy exhibited an ultra-high strain hardening behavior, having the proof stress (the proof stress is determined by shifting the linear elastic curve to 0.2% strain. We choose to not to call it the yield stress, as the mechanism for such a low elastic limit is still unclear at this stage.) of 75 MPa but reaching the fracture stress close to 1.2 GPa. At elevated temperatures of 600 and 700 \textdegree C (Fig. 4b), the proof stress, fracture stress and elongation were 95 MPa, 806 MPa, 33.7%, and 108 MPa, 538 MPa, 22.9%, respectively, both in the true stress/strain condition. The combination of high strength and high ductility for this EHEA could be maintained at least up to 700 \textdegree C. The mechanical properties of the as-cast EHEA can be further tuned by thermo-mechanical treatments. Figure 5 shows that a simple cold rolling with a thick reduction of 8% can increase the engineering/true proof stress and fracture stress to 275 MPa and 1145 MPa/
1265 MPa, respectively, while remaining a decent ductility of 10.4%/9.9% in elongation.

Technical advantages over conventional high-temperature alloys. To further showcase the excellent balanced mechanical properties of this newly developed EHEA as candidate high-temperature alloys, a comparison between it and NiAl and NiAl/Cr(Mo) eutectic alloys is given in Fig. 6. The reference alloys were chosen because the current EHEA can be regarded as a highly concentrated pseudo-binary NiAl/(Co, Cr, Fe) eutectic alloy, and they are also known to be promising high-temperature alloys, due to the lower density and melting point, much higher thermal conductivity, and excellent oxidation resistance at high temperatures. The major disadvantages for NiAl are the low ductility at room temperature and the low strength at high-temperatures, which also constitute the motivation to develop NiAl/Cr(Mo) eutectic alloys, where the in-situ formed composite structure is expected to improve the mechanical properties of NiAl. As shown in Fig. 6a, compared to NiAl or NiAl/Cr(Mo) eutectic alloys, the EHEA exhibited a much higher fracture strength, and more importantly, a simultaneously much higher ductility at room temperature. Considering the preparation of NiAl and NiAl/Cr(Mo) eutectic alloys often require the expensive processing routes like single crystal growth, directional solidification, and various thermomechanical treatments, that the EHEA prepared using conventional casting and without subsequent processing can have such excellent mechanical properties is indeed groundbreaking. As shown in Fig. 6b, the higher strength of the EHEA over non-EHEAs can be kept at least to 700 °C. It is stressed here that the density of this EHEA was measured to be 7.38 g/cm³, much lower than those of Ni-based superalloys typically with a density of above 8.0 g/cm³. Further optimization of the room-temperature and elevated temperature properties while maintaining this relatively lower density, will certainly enable EHEAs to become competitive high-temperature alloys to Ni-based superalloys. The extraordinary work hardening behavior of the EHEA is reflected when comparing with NiAl-based alloys (Fig. 6c), where the ratios of fracture strength to yield strength (σUTS/σ0.2) are normally in the range of 1−24−26, while the EHEA has a σUTS/σ0.2 (note it is the proof stress here) close to 16. Such a high σUTS/σ0.2 is also far beyond those of conventional alloys, which are in the range of 1−327−29. The unprecedentedly large strain hardening and low yield stress (proof stress) give rise to the unique opportunity of this EHEA in producing ultrahigh strength components after large plastic deformation, which was exemplified by the results given in Fig. 5 and still awaits further investigations. The very large strain hardening for the as-cast EHEA could originate from the fine regular lamellar structure that easily stores dislocations and the alternating soft fcc phases and hard B2-structured NiAl-rich phases. When dislocations pass through soft fcc phases, these hard B2 phases, including the nanoscale B2-structured precipitates within the fcc phases, could pin the movement of dislocations and result in the significant work hardening phenomenon.

Figure 3 | Phase constitution and thermal behavior for the AlCoCrFeNi2.1 alloy. (a), the XRD pattern. (b), The DSC curve.

Figure 4 | Tensile stress-strain curves for the AlCoCrFeNi2.1 alloy. (a), Room-temperature curves. (b), True tensile stress-strain curves tested at 600 and 700 °C, respectively.
As such, our alloy design strategy resulted in the discovery of an EHEA with a fine lamellar fcc/B2 structure and balanced high fracture strength and high ductility. This novel strategy is promising to solve the problems inhibiting the engineering application of HEAs as high-temperature materials, including the inferior castability and compositional segregation, and the conflict between high fracture strength and high ductility. In addition, this novel strategy also brought breakthrough to NiAl-based alloys in significantly enhancing the ductility at room temperature while simultaneously achieving the high strength. The EHEA concept, combining the advantages of both HEAs and eutectic alloys, and at the same time eliminating the disadvantages of these two types of alloys, leads to a promising new class of high-temperature alloys. Using this new alloy design strategy, an industrial scale HEA with uniform organizations and compositions can be prepared by the conventional casting method in a low cost way, allowing for large-scale industrial applications. Further exploration of new EHEAs will be based on previous established physical metallurgy principles to design HEAs, utilizing physicochemical material properties including atomic radius, mixing enthalpy and valence electron concentration. Eutectic alloys compositions can be pinpointed assuming a pseudo-binary multi-component alloy system, and then varying the concentration of one element systematically. Thermodynamics calculations based on the CALPHAD (calculation of phase diagrams) method can also provide an insightful guidance to design EHEAs, on the premise that reliable thermodynamics database for HEAs are to be established and completed.

In summary, here we proposed a novel strategy to design high-entropy alloys (HEAs), i.e., the concept of eutectic high-entropy alloys (EHEAs), to solve the challenging issues for this new type of advanced metallic materials, including the conflict between high fracture strength and high ductility, and the inferior castability and compositional segregation. Based on the new strategy, we successfully designed a highly uniform AlCoCrFeNi2.1 EHEA, with an unprecedented combination of castability, high fracture strength and high ductility. The bulk EHEA ingot of ~2.5 kg in weight was prepared by the conventional casting method using the commercially pure raw materials. The EHEA exhibited a fine lamellar microstructure consisting of coupled grown fcc/B2 phases. Our design strategy is of great significance in both scientific and technical aspects, and can be readily adapted to large-scale industrial production of HEAs.

Figure 5 | Tensile stress-strain curves for the 8% cold rolled AlCoCrFeNi2.1 alloy. The inset shows the microstructure of the cold rolled material.

Figure 6 | Comparison of mechanical properties. (a), The comparison of room-temperature tensile mechanical properties. (b), The comparison of high-temperature strength. (c), The comparison of the ratio of fracture stress to yield stress (proof stress), between the AlCoCrFeNi2.1 EHEA and non-EHEAs, comprising NiAl-base alloys.

Methods
The master alloy of AlCoCrFeNi2.1 was prepared from commercially pure elements (Al, Co, Ni: 99.9 wt.%; Cr, Fe: 99.5 ~ 99.6 wt.%). The raw elements were alloyed in a BN crucible in the vacuum induction melting furnace. The BN crucible was heated to 1500 uC and held for 1 hour to remove the water vapor, before putting into the furnace. The pouring temperature was set to be 1500 uC. Approximately 2.5 kg of master alloys were melted, superheated and poured into a MgO crucible with the length of 220 mm, upper inner diameter of 62 mm and bottom inner diameter of 50 mm. In all cases, the furnace chamber was first evacuated to 6 × 10−2 Pa and then backfilled with high-purity argon gas to reach 0.06 MPa. An IRTM-2CK infrared pyrometer was employed to monitor the temperature with an absolute accuracy of ±2 °C. The microstructure and composition of the alloy were investigated by laser scanning confocal microscope (LSCM), and scanning electron microscope (SEM, Zeiss Supra 55) equipped with an attached X-ray energy dispersive spectrometer (EDS).
phase constitution of the alloy was characterized by the X-ray diffractometer (XRD, Shimadzu XRD-6000) using a Cu target, with the scanning rate of 4°/min and the 2θ scanning range of 20°–100°. The differential scanning calorimetry (DSC, Netzsch STA 449 F3) curve of the alloy was measured from ambient temperature to 1450°C, during both the heating and cooling process, under the protection of a flow argon gas and the heating/cooling rate used was 10 K/min. Room-temperature tensile tests were performed using the Instron 5569 testing machine at a constant strain rate of 0.1 \times 10^{-3}\text{ s}^{-1}. The tensile test specimens cut from as-cast alloys had a diameter of 8 mm and gauge length of 40 mm. High-temperature tensile tests were conducted on a Gleeble 3500 system at a strain rate of 0.005 s^{-1}. In all high-temperature tensile tests, the chamber was first evacuated to 30 Pa and backfilled with high-purity argon gas to reach 0.05 MPa. Tensile tests were also carried out for cold rolled specimens. Plates of the dimension of 100 mm (length) \times 16 mm (width) \times 10 mm (thickness) were machined from the as-cast alloys, and they were sequentially cold rolled with ultimately a thick reduction of 8%. Specimens with a gauge length of 40 mm and a thickness of 3 mm were subject to the room temperature tensile tests, at a strain rate of 2 \times 10^{-3}\text{ s}^{-1}. For the microstructural observations, the alloy was sequentially polished and etched with the 10 vol.% aqua regia - 90 vol.% ethanol solution at room temperature. The density of the cast alloy was measured following the Archimedes’ principle, using the Metter Toledo XS64 density measurement unit.

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Additional information

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