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Editorial: Dual-Phase Materials in the Medium and High Entropy Alloy Systems Al-Cr-Fe-Ni and Al-Co-Cr-Fe-Ni

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Editorial on the Research Topic

Dual-Phase Materials in the Medium and High Entropy Alloy Systems Al-Cr-Fe-Ni and Al-Co-Cr-Fe-Ni

The pioneering work of Yeh et al. (2004) and Cantor et al. (2004) initiated an expansive research activity on high entropy alloys (HEAs), aiming at discovering novel materials in the newly opened compositional spaces. The original concept of entropically stabilized solid solution phases around equimolar alloy compositions with not less than 5 elements has driven the quest for single phase high entropy alloys, as described in a critical update (Streuer, 2020). Recent review articles provide critical assessments of the HEA concept while trying to structure and condense the ample and diverse research results and also provide guidance for future research (Miracle and Senkov, 2017; George et al., 2019; George et al., 2020; Li et al., 2021). Besides continuous research on "*ad litteram*" HEAs which closely follows the original definition, the scope was soon extended as to accommodate multicomponent alloys with lower configurational entropy of mixing, so-called medium entropy alloys, MEAs (i.e., Zhou et al., 2018). Special interest was further focused on alloys that provide pathways to dual-phase or multi-phase microstructures (these alloys are sometimes categorized as compositional complex alloys, CCAs, to differentiate with single phase HEAs/MEAs), thus enabling more options for microstructure engineering.

The alloy systems Al-Cr-Fe-Ni and Al-Co-Cr-Fe-Ni are most attractive in this respect. Both systems host compositional ranges for the design of dual-phase materials composed of a face centered cubic (FCC-A1) and a body centered cubic (BCC-B2) phase following distinct phase transformation pathways. Examples are the alloys $Al_{0.7}CoCrFeNi$ and $AlCrFe_2Ni_2$ (Dong et al., 2016; DeJeer et al., 2017) which pass through a BCC-B2→FCC-A1 solid state phase transformation and the alloys $AlCoCrFeNi_{2.1}$, $Al_{0.9}CrFeNi_{2.1}$ which display eutectic growth following Liquid → BCC-B2+FCC-A1 (Lu et al., 2014; Jin et al., 2019). Importantly, in both alloy systems the Al-rich BCC-B2 phase is prone to spinodal decomposition, which may impact on the overall phase transformation cascade and certainly affect the mechanical properties.

This "Research Topic" was initiated with main focus on dual-phase HEAs and MEAs from the above alloy systems, calling for contributions on a wide range of open issues, including phase transformation pathways, alloy processing by conventional and additive technologies, mechanical and functional properties, i.e., corrosion behavior, and other more. From the perspective of future applications knowledge on all these aspects is required in equal measure. For dual-phase MEAs

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around the composition $AlCrFe_2Ni_2$ this special issue draws on contributions from several partners of the joint European project "NADEA" funded by national agencies in the frame of the M-era. Net program. In fact 7 out of 11 papers relate to this project and capture the progress toward objectives at mid-term. NADEA aims at targeted MEA developments for applications which require a good balance between strength and ductility or toughness along with wear and corrosion resistance in areas commonly served by duplex and superduplex steels. In the following we briefly introduce the individual contributions:

Stryzhyboroda et al. presented key experiments and results from current CALPHAD modeling efforts for the alloy systems Al-(Co)-Cr-Fe-Ni. CALPHAD databases and thermodynamic codes are valuable digital tools for alloy design and ICME modeling, if phase equilibria as well as segregation trends are well described. Currently this is not the case (Gorsse and Senkov, 2018) and more work is required for database modeling and validation specifically also re-assessing entire sub-systems. Kuczyk et al. showed how additive manufacturing by laser metal deposition can provide a fast track to valuable data about phase equilibria, i.e., for validation of CALPHAD databases, using compositionally graded samples. One single sample designed to screen through a selected section plane can be used to accurately measure phase equilibria along one or more isotherms after correspondingly selected annealing treatments. Data were provided for $Al_xCoCrFeNi$ with $x = 0.2$ to1.5 (5–30 at.% Al) at $T = 1350$ K.

Hecht et al. discussed phase transformations in the dual-phase alloy $AlCrFe_2Ni_2$ which are similar to $Al_{0.8}$AlCoCrFeNi and which depend on the cooling rate applied during the BCC-B2→FCC-A1 solid state phase transformation. Apart from the classical Widmanstätten structure obtained upon slow cooling, an ultrafine vermicular microstructure, previously termed noodle-like or worm-like (Dong et al., 2016), was identified for higher cooling rates and associated to a characteristic "duplex spinodal" phase transformation pathway. The related crystal orientation relationship (OR) between FCC and BCC was analyzed in detail, being distinct and different from all well-known ORs established between BCC and FCC phases. Gein et al. further investigated the ultrafine vermicular microstructure in alloys based on $AlCrFe_2Ni_2$ however with minor additions of molybdenum ranging from 1 to 3 at.%. The alloys were prepared by arc melting of large (300 g) buttons and subjected to annealing treatments. For 2 at.% Mo a well-balanced microstructure with promising mechanical properties was reported after annealing at 1,100°C for 1 h with subsequent water quenching. The flexural stress/strain behavior favorably compares to the reference superduplex steel EN 1.4517.

Vogiatzief et al. and Roccio Molina et al. explored additive manufacturing (AM) of an alloy with composition close to $AlCrFe_2Ni_2$, but with 17.5 rather than 16.7 at.% aluminum, using laser powder bed fusion (L-PBF) and laser metal deposition/direct energy deposition (LMD/DED), respectively. Alloy processing required substrate preheating to at least 450°C (LMD/DED) and 700°C (L-PBF), respectively. The applied preheating effectively reduced thermal gradients but also allowed some amount of FCC-A1 to form during the build operation thus mitigating the cracking susceptibility of the spinodally decomposing BCC-B2. The full amount of FCC-A1 was only achieved by post build annealing heat treatments and the annealing temperature and duration was used to tailor microstructure and properties, e.g., the flexural stress/strain behavior. Comparison to a reference superduplex steel EN 1.4517 showed that the target MEA is a promising material with good chances to compete with duplex steels. However, both alloy composition and processing parameters must be further optimized in order to establish a robust AM manufacturing route.

Eshed et al. investigated a casting route for alloy $AlCrFe_2Ni_2$ with main emphasis on microstructure and phase analysis after selected homogenization and annealing treatments. Transmission electron microscope (TEM) and high resolution TEM provided detailed insight into phase constitution. An unexpected carbide phase was observed, which raises questions as to the origin and role of impurities, a subject which calls for further and systematic investigation.

Zollinger and Fleury provided a brief report on the effect of casting texture on the elastoplastic behavior of $Al_{0.8}CrCuFeNi_2$ during uniaxial compression tests. The alloy solidified with a primary FCC-A1 phase and interdendritic BCC-B2 in a hybrid mould with alumina walls and a copper base, thus displaying a morphological transition from a columnar (textured) to an equiaxed (untextured) FCC-A1 phase. When tested under uniaxial compression with the loading axis parallel to the direction of solidification, the columnar microstructure, with a preferred orientation of the fcc phase toward the <100> direction showed remarkably higher yield strength than the equiaxed microstructure. The improved macroscopic behavior of the <100> textured sample was related to confinement of the activated slip system(s) to FCC-A1 dendrites separated from one another by the BCC-B2 envelop. Wang et al. and Godlewska et al. investigated the corrosion behavior of selected Al-(Co)-Cr-Fe-Ni alloys using, among others, potentiodynamic polarization tests and electrochemical impedance spectroscopy.

Wang et al. focused on the alloy $Al_{0.1}CoCrFeNi$ and its behavior in NaCl-containing aqueous solutions of various concentration, while Godlewska et al. probed several alloys around the baseline composition $AlCrFe_2Ni_2$ in a 3.5 wt.% NaCl aqueous solution including for reference three $Al_xCoCrFeNi$ alloys as well as the superduplex steel EN 1. 4517. At room temperature the pitting corrosion resistance and passivation capability of EN 1.4517 are outstanding and unrivaled by $AlCrFe_2Ni_2$-based alloys, irrespective of small Mo-additions. This behavior is due to the Cr-depletion of the BCC phase. The performance in potentiodynamic tests is judged rather similar to lean duplex steels (Siow et al., 2001). The nearly fully FCC alloy tested by Wang and independently confirmed by Godlewska for an alloy with similar composition is the most resistant to pitting corrosion and closely matches the superduplex steel behavior.

Finally, Röhrens et al. addressed dual-phase eutectic alloys prepared by suction casting from ternary, quaternary and quinary eutectic alloys, i.e., $Ni_{48}Fe_{34}Al_{18}$, $Ni_{44}Fe_{20}Cr_{20}Al_{16}$

and $Ni_{34.4}Fe_{16.4}Co_{16.4}Cr_{16.4}Al_{16.4}$. The special merit of the investigation relates to the fact that it incorporates the ternary alloy, originally investigated 20 years ago (Misra and Gibala, 1997; Misra and Gibala, 1999) in an attempt to ductilize the NiAl-B2 intermetallic alloy. This family of alloys could indeed serve as a very good reference for future research on HEA and MEA eutectics for the Al-Co-Cr-Fe-Ni alloy system.

We hope that the reader will find this collection of articles interesting and useful as reference for future research endeavors in this emerging field of alloy design, processing and materials characterization.

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UH and SG wrote the editorial article, while UH, SG, and MW served as editors for this Frontier's research topic.

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