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NANOCRYSTALLINE HIGH ENTROPY MATERIALS: PROCESSING CHALLENGES AND PROPERTIES

FOCUS ISSUE

Introduction

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High-entropy materials (HEMs) are current area of tremendous research interest and activity in materials science and engineering. They include HEAs, as well as entropy stabilized oxides, borides, carbides, and nitrides. The field of metallurgy and materials engineering has seen a renaissance in design and development of novel materials with unprecedented properties, showing promise for potential applications. For thousands of years, alloys have been primarily based on one and rarely two base elements. In a paradigm shift, HEAs are designed to be based on multiple principal elements, having at least five species, expanding compositional space beyond the conventional alloys. With the advent of HEMs, fundamental issues that challenge the proposed theories, models, and methods for conventional alloys emerge, making the systematic investigation on the design of novel microstructure a necessity to drive materials research.

Further properties of these novel multicomponent materials can substantially be improved by making them in nanocrystalline form. However, the inherent nature of the processes utilized for preparation of HEMs via liquid state routes does not lead to nanostructured HEMs. Solid state processing methods, mechanical alloying (MA) followed by sintering, and severe plastic deformation (SPD) are more attractive for obtaining nanocrystalline HEMs in the bulk form. Enhancement of properties will strongly depend on the microstructural length scale; hence, retaining nano-sized grain structure is the utmost requirement in the processing of HEMs in bulk form. This presents many challenges for the materials community to engineer processing techniques to obtain a variety of nanostructures for the betterment of properties. This Focus Issue provides in-depth analyses of the present literature and the future direction of this rapidly advancing field, with invited reviews and articles, along with a large number of contributed articles from experts. The review offers a detailed assessment of the powder metallurgical and SPD routes in synthesizing nanostructured HEMs. Various invited papers dwell on the aspects of synthesis and property estimation of the nanostructured HEMs.

It has widely been known that nanocrystalline microstructure can be obtained by either MA of elemental powders, or SPD of the cast alloys. This Focus Issue contains a large number of papers dealing with processing challenges associated with MA and SPD methods. MA powders are subsequently consolidated using an advanced sintering technique including spark plasma sintering (SPS). Hence, challenges pertaining to retention of nanocrystalline grains and HEA phases in the sintered microstructures have also been deliberated. The review B.S. Murty et al. provides a detailed account of the challenges in obtaining nanocrystalline HEAs obtained via MA followed by SPS route. This review also dwells on the stability of the nanocrystalline phase during consolidation and heat treatment. The major challenges include contamination from the milling media altering the chemistry, oxidation of alloy phases, and grain growth during consolidation. Furthermore, several papers elaborate on the problems in obtaining nanocrystalline multicomponent HEAs consisting of 3d transition metals, as well as refractory HEAs. Vinod Kumar et al. have discussed the alloying and stability of BCC solid solution phase in equiatomic AlCoCrFeNiTi HEA, and have found the HEA phase is stable up to 600 °C. The same group has also provided a detailed report on microstructural evolution and property correlation in AlCuCrFeMn HEA with a variation of W content synthesized via SPS in order to impart high temperature strength. However, such alloying addition leads to the formation of brittle phases; σ, $L1_0$ FeMn as well as B2 intermetallics along with BCC solid solution. The optimum design of the microstructure incorporating these phases is the key for the development of novel nanocrystalline high temperature alloys to achieve high temperature properties. In another interesting study, led by R.S. Kottada, microstructural evolution on refractory CrMoNbTiW via MA and SPS has been reported. As expected, MA of this multicomponent alloy leads to the formation of disorder BCC solid solution, which is stable even after consolidation showing extremely high hardness ~9 GPa. B.B. Panigrahi et al. have shown even it is even possible to achieve full densification of AlCoCrFeNi HEA powder, via pressureless sintering at 1275 °C. The sintered specimen predominantly contains BCC phase with a small fraction of FCC phase. However, retaining nanocrystalline grains in the MA powder is not possible. Similarly, the paper by N.K. Mukhopadhyay et al. demonstrates that the MA route is successful in obtaining nanocrystalline equiatomic AlCoCrFeNiTi HEA exhibiting single BCC phase, which is stable up to 600 °C. However, consolidation of the MA powder indicates the presence of WC, predominantly originated from milling media. Thus, the role of contamination and oxygen in formation and stabilization of nanocrystalline HEA is a fundamental issue requiring more research. Interestingly, nanocrystalline HEA powders synthesized via MA techniques can be used to obtain a hard coating having good oxidation resistance. The paper by R.S. Kottada et al. shows that cold spray can be used as an effective technique to obtain good quality coating of AlCoCrFeNi HEA on Ni-based superalloy. The coating exhibits excellent oxidation resistance due to the formation of protective alumina layer, as well as Mo diffusion from the superalloy substrate.

SPD has been widely utilized by several research groups to obtain bulk nanocrystalline HEAs in various forms. P.P. Bhattacharjee have reported a systematic study on the microstructure and texture evolution in eutectic (B2 + $L1_2$ phase mixture) $AlCoCrFeNi_{2.1}$, during severe warm rolling. The study reveals inhomogeneities in texture evolution. Nonetheless, annealing at 800 and 1200 °C shows that some of the texture components, especially α-fibre is retained for $L1_2$, whereas B2 phase shows strong ND-fibre. However, it is difficult to remove the inhomogeneities of texture upon annealing of the deformed HEA. N.P. Gurao et al. have utilized monotonic and cyclic high pressure torsion (HPT) to obtain nanocrystalline grains to test whether strain path difference can lead to any difference in nanocrystallization. Indeed, cyclic HPT causes strain reversals whereas monotonic HPT leads to the attainment of nanocrystalline grain due to severe grain refinement. H. Choi et al. have reported the deformation behavior of nanocrystalline as well as ultrafine grained CoCrCuFeNi HEA having FCC phases (Cu-rich and CoCrFeNi-rich). The grain boundary strengthening along with lattice distortions have been reported to be the dominant factor deciding the strength and ductility of the deformed HEA. In another study, S. Suwas et al. have reported hot deformation behavior of equiatomic CoCuFeMnNi alloy showing FCC phases (Cu-rich and CoMnFeNi-rich). The deformation in the temperature interval of 850–1050 °C shows strain softening due to dynamic recrystallization along grain boundary, preferentially occupied by Cu-rich phase. Twins have been observed in the DRX grains. The best region of thermo-mechanical processing window is 850–950 °C and strain rate of 10^{-1} s^{-1}.

There are several papers discussing the formation and stability of ultra fine grained HEA phases and their stability via chill mold cast routes. Although chilled molds have been used to obtain bulk HEAs, the nanocrystalline grains cannot be achieved via this route. Nonetheless, it allows investigating phase formation and microstructural evolution under the most conventionally used route. The alloys synthesized can then be used for SPD to obtain nanocrystalline microstructure. Z. Sun et al. have reported the microstructural evolution and associated mechanical properties of ternary CrFeNi due to the addition of Ti. It has been reported that smaller Ti addition leads to the formation of additional BCC phases (Ni, Ti-rich) along with FCC phase. Higher Ti addition (>0.2) leads to the formation of intermetallic phases, including Ni_3Ti and R-phase, leading to improvement of hardness. G. Phanikumar et al. have reported a similar study on Nb addition to FeCoNiCu ternary alloy to obtain polyphase microstructure. Nb-addition leads to effective liquid phase separation between Cu-rich and FeCoNiNb-rich, causing the formation of more Cu-rich spheres. This type of microstructure can provide better mechanical properties and wear resistance. T.P. Yadav et al. have reported the formation of multicomponent Ti–Zr–V–Cr–Ni–Fe Laves phase in the cast and homogenized microstructure. This is an interesting study, showing the formation and stabilization of C14 Laves phase, which is stable up to 1000 °C.

Several papers in the Focus Issue deliberate on the formation and radiation and wear resistance properties of HEAs. The formation of nanocrystalline hexagonal closed packed (HCP) HEAs under extreme conditions (nuclear reactor) has been discussed by R. Devanathan et al. HEA phases consisting of Mo, Te, Ru, Rh, Pd with Ag, Cd, Te in the uranium dioxide fuels has been processed to study whether the radiation induced diffusion can cause alloy formation for nanocrystalline HEAs. The radiation tolerance and stability of nanocrystalline HEAs has been reported by F. Djurabekova et al. It has been shown that HEAs can withstand higher radiation dosage, before nanocrystallinity is lost, opening new application for nanocrystalline HEAs. Lastly, V. Kumar et al. have reported wear behavior of $Al_{0.4}FeCrNi$ alloys with addition of Co. Due to good hardness and plasticity, $Al_{0.4}FeCrNiCo$ reveals excellent wear resistance.

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timely submission and review of the manuscripts. We would like to thank all the authors and reviewers for their sincere effort. The guest editors will feel extremely happy if readers from the materials community take up and advance the concepts found here in their own research in HEMs, widening the field by new ideas and development of novel materials having wider applicability.

On the cover

EBSD grain map for HPT processed equiatomic CuCoFeMnNi high entropy, monotonic HPT by 100° rotation. The color contrast reveals grain orientation.