ABSTRACT

As the grain size of metallic materials is refined from the micrometre to the nanometre scale, their strength increases significantly. However, this enhancement comes with a critical drawback, which is microstructural instability. At elevated temperatures, this instability renders nanocrystalline (NC) metals and alloys unsuitable for practical applications. The focus of this study is to confront that challenge. Notably, the strategic addition of a small amount of specific alloying elements can effectively curb grain growth during elevated temperature exposure.

The work presented here has focused on the development of a bulk NC AlCoCrCuFeNi high entropy alloy (HEA) with enhanced coarsening resistance. The effect of minor alloying additions (1 at. %) with elements having a large atomic size mismatch, i.e., B, Zr, and Y, on microstructural stability has been investigated. The mechanical alloying (MA) route, a well-established technique that not only facilitates significant microstructural refinement but also enables the formation of homogeneous, non-equilibrium solid solutions, has been adapted for synthesis. The solute elements (B, Zr, and Y) have been chosen judiciously, considering their significantly large atomic size mismatch with all six principal alloying elements as well as strong negative mixing enthalpy. While the size mismatch can impart an elastic driving force to trigger segregation, the negative binary mixing enthalpy is expected to promote the formation of ordered phases, which manifest the Zener pinning effect.

The structural stability of the as-milled powders has been evaluated considering the change in grain size, phases(s) and hardness drop by annealing it up to 1173 K (~ 0.75 T_m) for a duration of 1 h. The change in microstructure has been examined using X-ray diffraction (XRD) and transmission electron microscopy (TEM), which have revealed that the NC microstructure obtained by MA is retained after annealing for all three compositions. In addition, the elemental distribution across phases observed using the energy dispersive X-ray spectroscopy operated in scanning transmission electron microscopy mode (STEM-EDS) indicates that no second phase has formed in the annealed powders of both Zr and Y-added alloys. Furthermore, the drop in hardness of the B, Zr and Y-added alloys has been found to be much less than that observed in that having the base composition. These findings substantiate a significant improvement in the stability of the B, Zr and Y-added alloys. The experimental findings have been further supplemented using the established thermodynamic analysis framework, based on which it is inferred that during the isochronal annealing of MAed alloys, the grain boundary segregation plays a key role. On consolidation by spark plasma sintering (SPS), the primary phase constituents of the as-milled alloy are found to remain similar. To examine the in-service structural integrity of these alloys, the bulk compacts have been annealed at 1173 K for an extended duration of 10 h, and the corresponding change in microstructure and mechanical property (primarily hardness) has been evaluated systematically.

The isothermal annealing of the sintered base alloy shows a pronounced phase decomposition, with a significant (~40 %) rise in FCC phase fraction from 57 vol.% (after SPS) to 79 vol.% (after 10 h annealing). On the contrary, the solute micro-addition has significantly retarded the phase decomposition. The TEM analysis of 10 h annealed alloys have revealed that an average grain size of ~73 nm, ~68 nm and ~76 nm has retained for the B-alloyed, Zr-alloyed and Y-alloyed compositions. In addition, the Zr and Y additions have boosted the compressive strength of the sintered alloy by ~50% and ~30 % as compared to the base composition. After 10 h annealing, the alloys with 1 at. % additions of B, Zr and Y have been found to retain a hardness higher than that of the corresponding annealed base alloy by 9%, 14%, and 12%, respectively. Furthermore, the specific role of added solutes has been investigated using the atom probe tomography (APT). The three-dimensional atomic resolution composition analysis by APT has revealed that the B tends to segregate at the interfacial regions, whereas Zr and Y, other than segregation, also form Al-Zr-rich and Al-Y-rich clusters, and thereby trigger more than one mechanism contributing stability. Retention of the NC microstructure, corroborated with a higher fraction of BCC phase have resulted in retention of a higher hardness in newly developed alloys.

Keywords: *High-entropy alloys, Mechanical alloying, Spark plasma sintering, Nanocrystalline materials, Hardness, Transmission electron microscopy (TEM), Grain size, Strengthening mechanism, Thermal stability.*