Research Article

Processing and Properties of Nanocrystalline CoCrFeNiCuAlTiXVMo (X = Zn, Mn) High Entropy Alloys by Mechanical Alloying

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Fabrication of nanocrystalline equiatomic high entropy alloys is a crucial aspect for the product of many tools. The present study describes the synthesis of nanocrystalline equiatomic CoCrFeNiCuAlTiXVMo (X = Zn, Mn) high entropy alloys by mechanical alloying and their characterization by XRD and SEM. The CoCrFeNiCuAlTiXVMo (X = Zn, Mn) high entropy alloys have BCC solid solution with crystallite size less than 10 nm. These alloys are stable even after annealing at 600°C for 1 h. The hardness of the high entropy alloys is found to be 7.6 and 6.2 GPa, respectively.

1. Introduction

High entropy alloys are equiatomic or near-equiatomic multi-component alloys, wherein configurational entropy is maximized to obtain single-phase solid solution [1]. These new generation alloys are quite different from the traditional ones, which are based on one or two major elements. Solid solutions with multiprincipal elements have been generally found to be stable at elevated temperatures due to their large entropies of mixing, which lead to the sluggish diffusion of atoms [2–6], preventing the precipitation of intermetallic compounds.

The formation of solid solutions in high entropy alloys by melting is facilitated by small atomic size difference and small enthalpy of mixing between the constituent elements. It is expected that the same conditions facilitate the formation of solid state solution state when the alloy is formed by mechanical alloying as well. Mechanical alloying is a widely used solid state processing route for the synthesis of materials out of equilibrium with good homogeneity [7].

2. Experimental

The present study was taken up to prepare a new ten-element equiatomic multicomponent HEA alloy system with composition CoCrFeNiCuAlTiXVMo (X = Zn, Mn), starting from elemental powders.

Co, Cr, Fe, Ni, Cu, Al, Ti, Zn, V, Mo, and Mn powders with purity higher than 99.5% and particle size of $\leq 44 \mu\text{m}$ were used as starting materials. The elemental powders with a total mass of 5 g were milled in a planetary ball mill (Fritsch planetary ball mill) with tungsten carbide can and balls. The powder-to-ball weight ratio is 1:15, and 300 rpm speed was used. In order to confirm the alloy formation during milling, several mg samples were taken out after 5, 10, and 20 h.

After 20 h of milling the powder sample was removed from the vial for further characterization and consolidation. The powders were compacted using cold compaction at 800 MPa for 5 minutes followed by sintering at 600°C for 1 h.

The phase structure and stability of the as-milled and annealed (600°C for 1 h) samples were studied by Bruker

FIGURE 1: Schematic illustration of the sample processing and characterization methods.

D8 Advance X-ray diffractometer using Co K α radiation (Figure 1).

The hardness of the sintered samples was measured using Vickers hardness tester at 50 g load.

3. Results and Discussion

The formation of simple solid solutions instead of intermetallic compounds in the alloys is attributed to the effect of the high mixing entropy. Following Boltzmann's formula, S_{mix} of an n -element alloy is expressed as (1) and would reach the maximum when the alloy is of equiatomic ratio,

$$S_{\text{mix}} = -R \sum_{i=1}^n c_i \ln c_i, \quad (1)$$

where R is the gas constant, c_i the mole percent of the i th component, and $\sum_{i=1}^n c_i = 1$.

The atomic size difference is expressed in formula (2)

$$\delta = \sqrt{\sum_{i=1}^N c_i \left(1 - \frac{r_i}{\bar{r}}\right)^2}, \quad (2)$$

where N is the number of the components in alloy system, c_i is the atomic percentage of the i th component, and r is the atomic radius.

The δ of the CoCrFeNiCuAlTiXVMo ($X = \text{Zn, Mn}$) HEA were calculated using (1) as $\delta = 5.72$ and 5.88 , respectively. See Table 1.

The mixing enthalpy was calculated by the Miedema model [8]:

$$\Delta H^{\text{mix}} = \sum_{\substack{i=1 \\ i \neq j}}^n \Omega_{ij} c_i c_j, \quad (3)$$

where Ω_{ij} is the regular solution interaction parameter between i th and j th elements and is equal to 4 times the heat of mixing: $\Omega_{ij} = 4 \cdot \Delta H_{AB}^{\text{mix}}$ and c_i is the concentration of the i th elements.

The enthalpies of mixing of the CoCrFeNiCuAlTiXVMo ($X = \text{Zn, Mn}$) HEA were determined using (3) as $\Delta H^{\text{mix}} = -8.12$ and -8.6 kJ/mol, respectively.

Our ΔH^{mix} and δ values are within the limits given by [9] for the formation of solid solution: -18 kJ/mol $< \Delta H^{\text{mix}} < +5$ and $0 < \delta < 6$.

For our 10-component alloy, the $S_{\text{mix}} = R \cdot \ln 10 = 2.3R$, which is considerably larger than the change of entropy at melting ($\sim 1R$) and multiplying with $\Delta T \sim 1000$ K, the contribution to the free energy $S \cdot \Delta T = 2.3 \cdot 8.314 \cdot 1000 = 19.12$ kJ/mol is much larger than the contribution of the mixing enthalpy. The small values of ΔH^{mix} and δ and the large value of S_{mix} explain the tendency to form solid solution during mechanical alloying.

The evolution of the structure as a function of milling time can be followed in Figures 2(a) and 2(b). From the XRD results it is clear that the alloy formation is completed after 20 h milling with formation of BCC solid solution with some FCC phase impurity. The longer milling time needed for the solid solution formation in systems with larger number of elements could be attributed to slower diffusivity. In general in all the cases significant broadening of the XRD peaks and disappearance of all the peaks of the solid solution except the most intense one have been observed. To confirm the stability of the phases, the sample was annealed at 600°C for 1 h, and XRD analysis was carried out on the heat-treated sample. An XRD pattern of the milled powder after annealing at 600°C for 1 h in an argon atmosphere as shown in Figures 3(a) and 3(b) which reveals the majority of the alloy is still in a single-phase solid solution with BCC structure but the FCC phase is also present. The grains are nanosized even after sintering, which proves the high stability of the high entropy solid solution. The Vickers microhardness was measured on the sintered disk samples. The values of the sintered high entropy alloys are found to be $HV_{0.05} = 7.6$ and 6.2 GPa, respectively. The tensile strength, σ , can be estimated to be 2.53 and 2.06 GPa, respectively, by using the well-known relation, $HV = 3\sigma$. The high hardness can be attributed both to the solid solution strengthening and grain size strengthening in BCC and FCC phases.

An XRD pattern of the milled powder after annealing at 600°C for 1 h in an argon atmosphere as shown in Figures 3(a) and 3(b) evidenced the main BCC phase, along with small volume fraction of the FCC. In the as-milled sample, reflection of the FCC phases could not be indexed due to the unavailability of the successive peaks. After the heat-treated condition these peaks become visible clearly, which is useful to confirm the FCC peaks.

The scanning electron micrographs on the consolidated by cold compaction at 800 MPa for 5 minutes followed by annealing at 600°C for 1 h samples are shown in Figures 4(a)

TABLE 1: This table gives the size factor and enthalpy of mixing for the binary equiatomic alloys in the CoCrFeNiCuAlTiXVMo ($X = \text{Zn, Mn}$) system.

Alloys	Delta (δ)	ΔH^{mix} (kJ/mol)	HV (GPa)	σ (GPa)
CoCrFeNiCuAlTiZnVMo	5.72	-8.12	7.6	2.53
CoCrFeNiCuAlTiMnVMo	5.88	-8.6	6.2	2.06

FIGURE 2: XRD patterns of equiatomic CoCrFeNiCuAlTiXVMo ($X = \text{Zn}$ (a), Mn (b)) HEAs with varying milling time.

FIGURE 3: XRD patterns of equiatomic CoCrFeNiCuAlTiXVMo ($X = \text{Zn, Mn}$) HEA after 20 h of MA, heat-treated at 600°C for 1 h, and after HP.

FIGURE 4: SEM micrographs of nanocrystalline equiatomic CoCrFeNiCuAlTiXVMo (X = Zn, Mn) HEA after 20 h of MA.

and 4(b) which reveal the presence of the two phases and of some residual pores.

From the SEM images and the phases present in the XRD, it can be concluded that the grey phase with larger volume fraction is the major BCC phase, the white one with smaller volume fraction is FCC phase, and the black regions correspond to the pores.

4. Conclusion

Nanostructured equiatomic CoCrFeNiCuAlTiXVMo (X = Zn, Mn) high entropy alloys have been successfully synthesized by mechanical alloying and consolidated by cold compaction at 800 MPa for 5 minutes followed by sintering at 600°C for 1 h. The sintered CoCrFeNiCuAlTiXVMo (X = Zn, Mn) HEAs which have mainly a BCC phase and minor FCC phase were observed on HP. The very high hardness of $HV_{0.05} = 7.6$ and 6.2 GPa and the estimated tensile strength of 2.53 and 2.06 GPa, respectively, prove the promising future of these alloys.

Acknowledgments

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