**Table (ST1)** le-Bail profile fitting and estimated lattice parameter with c/a ratio of as-cast and annealed Ti-Zr-V-Cr-Ni-Fe Lave phase HEAs.

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Sample Name | a(Å) | c(Å) | c/a | GOF | Rp | wRp |
| Fe0.5 | 5.0357 | 8.2199 | 1.6323 | 1.06 | 4.46 | 5.82 |
| Fe1.0 | 4.9776 | 8.1153 | 1.6304 | 0.92 | 3.95 | 5.04 |
| Fe1.5 | 4.9535 | 8.0879 | 1.6327 | 0.96 | 3.49 | 4.55 |
| SC Fe0.5 | 5.0327 | 8.2120 | 1.6317 | 1.40 | 4.83 | 6.57 |
| SC Fe1.0 | 4.9763 | 8.1284 | 1.6334 | 0.91 | 3.79 | 4.85 |
| SC Fe1.5 | 4.9365 | 8.0499 | 1.6307 | 0.89 | 3.31 | 4.23 |
| RQ Fe0.5 | 4.9956 | 8.1430 | 1.6300 | 1.03 | 3.07 | 4.14 |
| RQ Fe1.0 | 4.9698 | 8.1270 | 1.6353 | 0.99 | 3.75 | 4.87 |
| RQ Fe1.5 | 4.9295 | 8.0465 | 1.6323 | 0.90 | 3.90 | 4.98 |

**Table (ST2)** The following thermodynamic values calculated from Meidema’s approach are used to determine the enthalpy of mixing of the high entropy alloy [A. Takeuchi at el., Mater. Trans. 12 (2005) 2817-2829]

|  |  |
| --- | --- |
|  | ΔHmix (kJ/mol) |
| Ti-Zr | 0 |
| Ti-V | -2 |
| Ti-Cr | -7 |
| Ti-Ni | -35 |
| Ti-Fe | -17 |
| Zr-V | -4 |
| Zr-Cr | -12 |
| Zr-Ni | -49 |
| Zr-Fe | -25 |
| V-Cr | -12 |
| V-Ni | -18 |
| V-Fe | -7 |
| Cr-Ni | -7 |
| Cr-Fe | -1 |
| Ni-Fe | -2 |

**Table (ST3)** The following data were used for calculation of thermodynamic parameters.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Element | Atomic radius (Å) | Allen electronegativity | VEC | Melting Temp. (°C) |
| Fe | 1.2412 | 1.80 | 8 | 1538 |
| Ni | 1.2459 | 1.88 | 10 | 1455 |
| Cr | 1.2491 | 1.65 | 6 | 1907 |
| V | 1.3160 | 1.53 | 5 | 1910 |
| Ti | 1.4615 | 1.38 | 4 | 1668 |
| Zr | 1.6025 | 1.32 | 4 | 1855 |

**(S1a)**

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**(S1b)**

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**(S1c)**

Fig. S1 le-Bail profile fitting of (a) as-cast (b) slow cooled and (c) rapidly quenched; (i) Fe 0.5, (ii) Fe1.0 and (iii) Fe1.5 HEAs.

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**Fig. (S2)** Magnified XRD patterns of simulated and experimentally observed Ti-Zr-V-Cr-Ni-Fe HEAs.