Supplemental Information

Extrinsic Hardening of Superhard Tungsten Tetraboride Alloys with Group 4 Transition Metals

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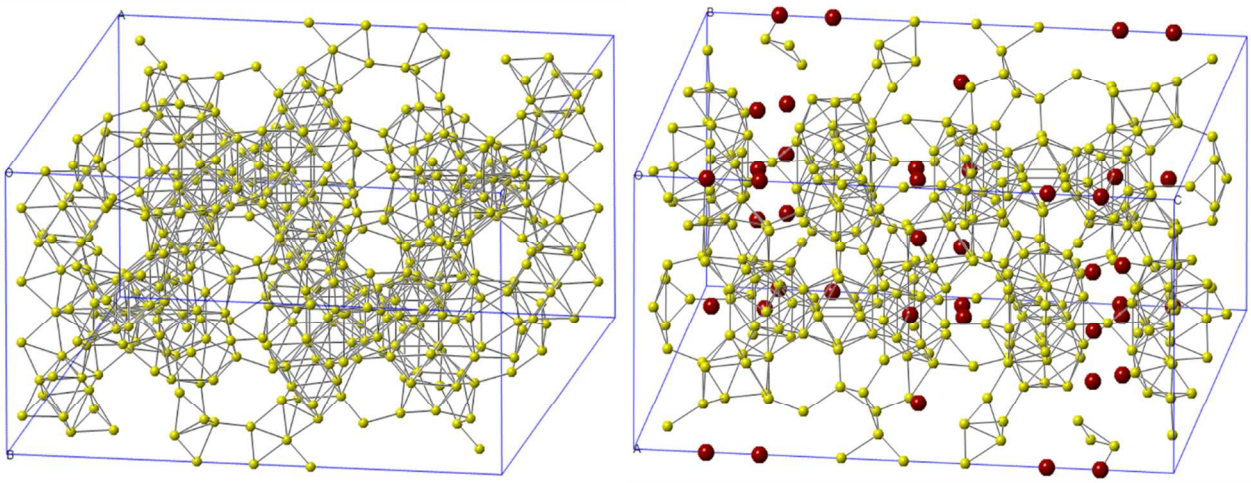
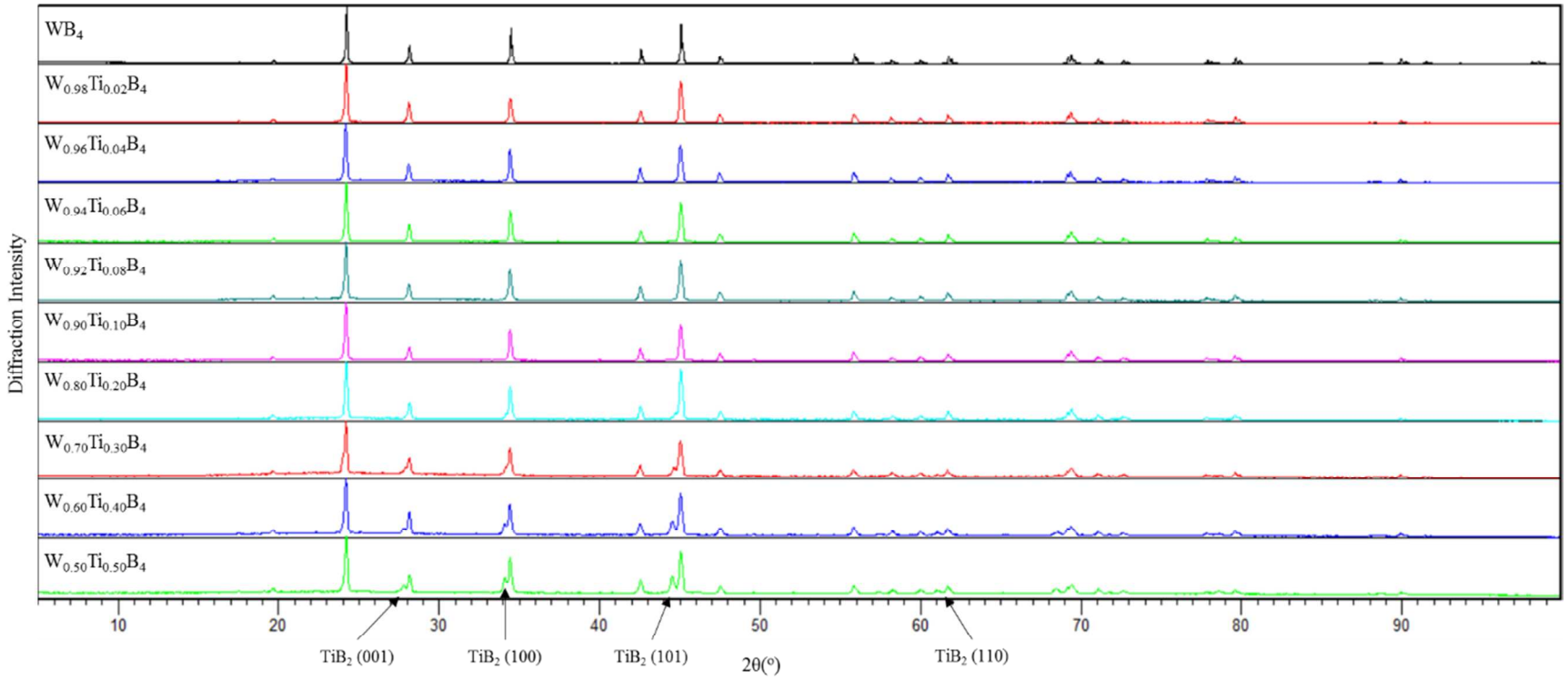
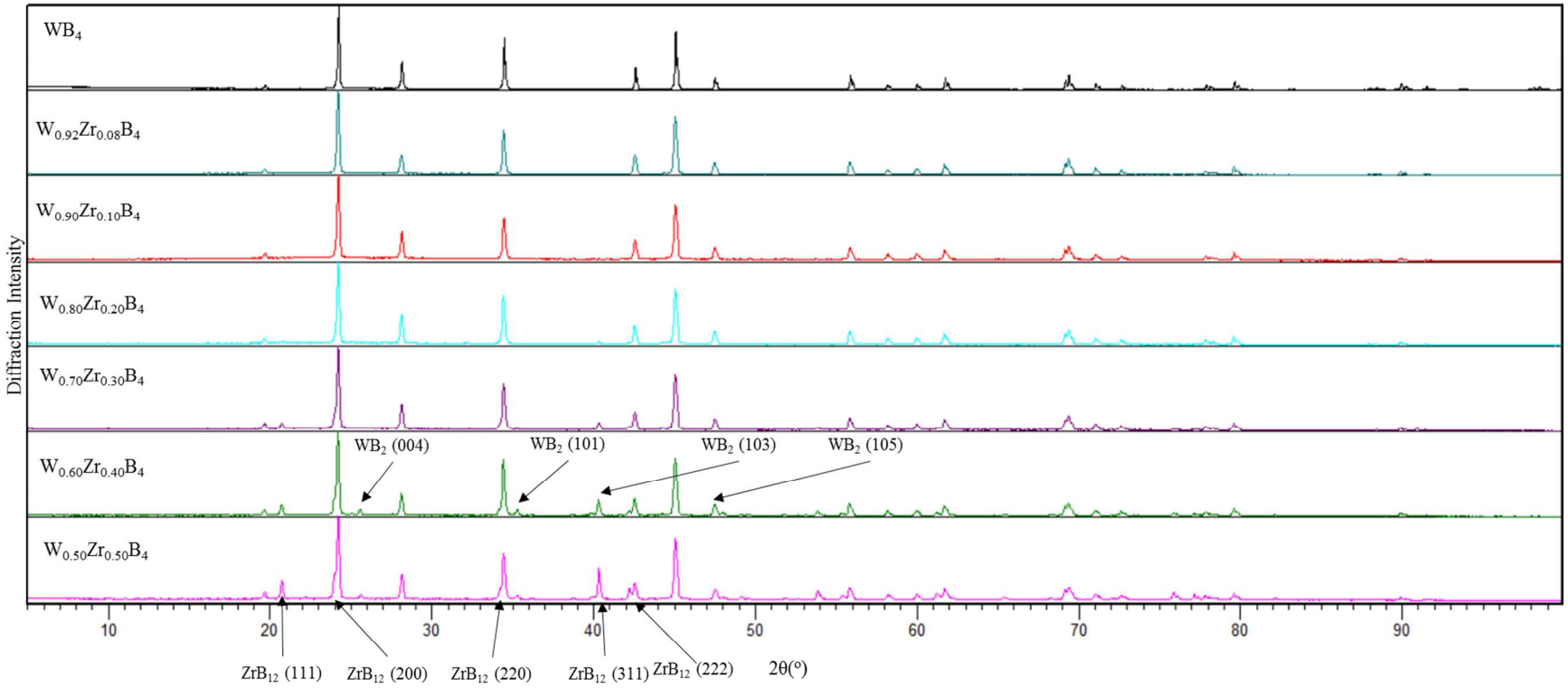


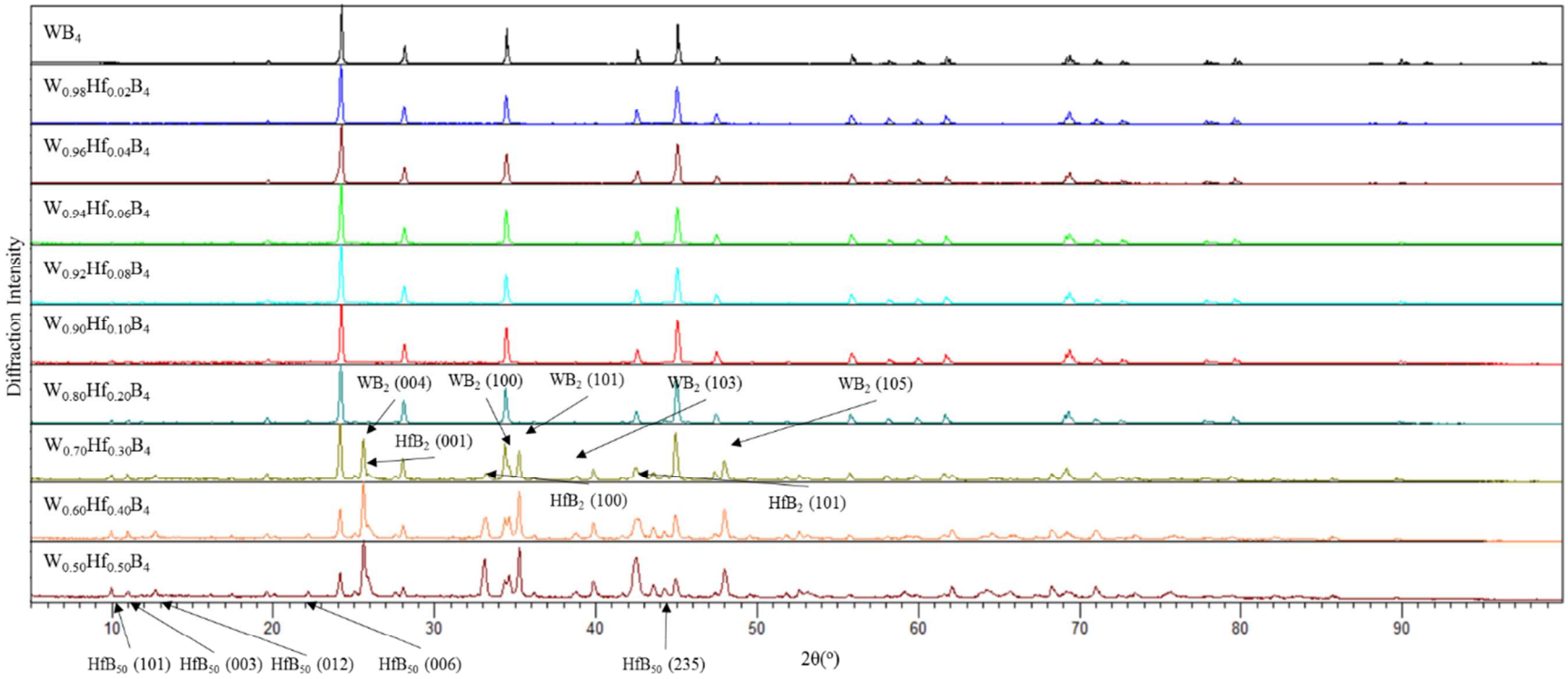
Figure S1. (Left) crystal structure of β-rhombohedral boron (ICSD 68104), showing characteristic boron icosahedra; (Right) crystal structure of a solid solution of hafnium in β-rhombohedral boron (known as the β-rhombohedral boron doping phase of hafnium – HfB_{50}) (ICSD 40396), showing Hf atoms in positions of some of the boron icosahedra. (Boron atoms are in yellow, hafnium atoms are in maroon).


WB4
W0.98Ti0.02B4
W0.96Ti0.04B4
W0.94Ti0.06B4
W0.92Ti0.08B4
W0.90Ti0.10B4
W0.80Ti0.20B4
W0.70Ti0.30B4
W0.60Ti0.40B4
W0.50Ti0.50B4
Diffraction Intensity
10
20
30
40
50
60
70
80
90
TiB2 (001)
TiB2 (100)
TiB2 (101)
2θ(°)
TiB2 (110)

(a)


WB4
W0.92Zr0.08B4
W0.90Zr0.10B4
W0.80Zr0.20B4
W0.70Zr0.30B4
W0.60Zr0.40B4
W0.50Zr0.50B4
Diffraction Intensity
WB2 (004)
WB2 (101)
WB2 (103)
WB2 (105)
10
20
30
40
50
60
70
80
90
ZrB12 (111)
ZrB12 (200)
ZrB12 (220)
ZrB12 (311)
ZrB12 (222)
2θ(°)

(b)



(c)

Figure S2. Powder XRD patterns of alloys of WB_4 with 2-50 at.% (a) Ti, (b) Zr and (c) Hf added on a metals basis. The top spectrum in each set is pure WB_4 (JCPDS 00-019-1373). The solubility limit is less than 20 at.% for Ti, 10 at.% for Zr and below 8 at.% for Hf. Above 20 at.% Ti, the secondary phases TiB_2 (JCPDS 01-075-0967), above 20 at.% Zr, ZrB_{12} (JCPDS 03-065-7806) and above 10 and 20 at.% Hf, HfB_{50} (known as the β-rhombohedral boron doping phase of hafnium) and HfB_2 (JCPDS 01-086-2400 and 01-089-3651) appear, respectively. In addition, peaks corresponding to WB_2 (JCPDS 01-073-1244) are observed at 40 at.% Zr and 30 at.% Hf.

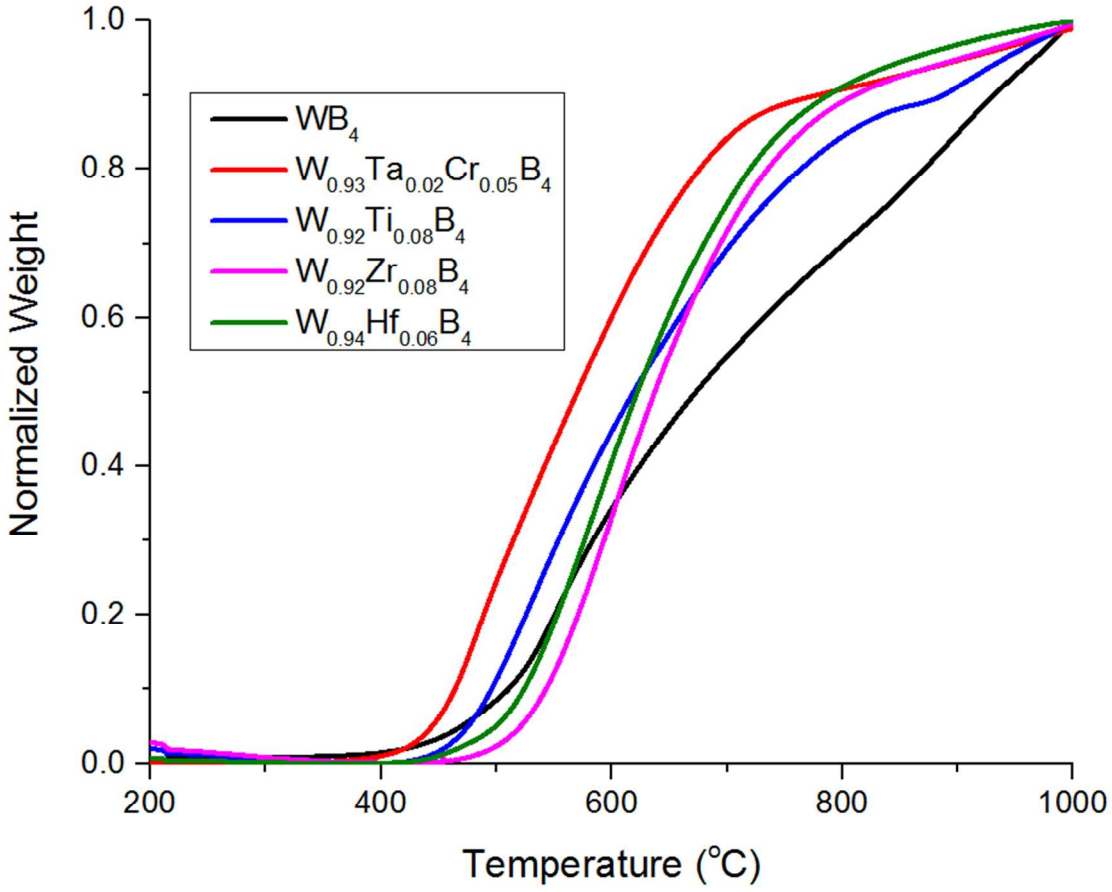


Figure S3. Thermal stability of the hardest tungsten tetraboride alloys with Ti, Zr and Hf as measured by thermal gravimetric analysis in air. The data for pure WB_4 and the hardest alloy $W_{0.93}Ta_{0.02}Cr_{0.05}B_4$ are given for comparison. These data show that $W_{0.92}Ti_{0.08}B_4$, $W_{0.92}Zr_{0.08}B_4$ and $W_{0.94}Hf_{0.06}B_4$ are stable up to ~460 ^oC, ~510 ^oC and ~490 ^oC, respectively (using the extrapolated oxidation onset), compared to ~400 ^oC for pure WB_4 and ~420 ^oC for the $W_{0.93}Ta_{0.02}Cr_{0.05}B_4$ alloy.