Effect of Re on the Microstructure and Mechanical Properties of NbTiZr and TaTiZr Equiatomic Alloys

Oleg N. Senkov 1,2,*, Stéphane Gorsse 3, Robert Wheeler 1,4, Eric J. Payton 1 and Daniel B. Miracle 1


Abstract: The microstructure, phase composition, and mechanical properties of NbTiZr, TaTiZr, Re0.3NbTiZr, and Re0.3TaTiZr are reported. The alloys were produced by vacuum arc melting and hot isostatically pressed (HIP'd) at 1400 °C for 3 h under 276 MPa hydrostatic pressure of high-purity argon prior to testing. NbTiZr had a single-phase BCC crystal structure, while TaTiZr had a Ti- and Zr-rich BCC matrix phase and Ta-rich nanometer-sized BCC precipitates, at volume fractions of 0.49 and 0.51, respectively. Re0.3NbTiZr consisted of a BCC matrix phase and Re-rich precipitates with a FCC crystal structure and the volume fraction of 0.14. The microstructure of Re0.3TaTiZr consisted of a Zr-rich BCC matrix phase and coarse, Re and Ta rich, BCC particles, which volume fraction was 0.47. NbTiZr and TaTiZr had a room temperature (RT) yield stress of 920 MPa and 1670 MPa, respectively. While, 10 at.% Re additions increased the RT yield stress to 1220 MPa in Re0.3NbTiZr and 1715 MPa in Re0.3TaTiZr. Re also considerably improved the RT ductility of TaTiZr, from about 2.5% to 10% of true strain. The positive strengthening effect from the Re additions was retained at high (800–1200 °C) temperatures.

Keywords: refractory alloy; microstructure; phase composition; CALPHAD; mechanical properties

1. Introduction

Many refractory alloys, including refractory complex concentrated alloys (RCCAs), have a BCC crystal structure and, as many BCC metals, exhibit a brittle-to-ductile transition (BDT) [1,2]. The transition occurs because of a strong temperature dependence of plastic (shear) stress and relatively weak temperature dependence of fracture (cleavage) stress. At low temperatures the shear stress can exceed the cleavage stress, and the BCC material becomes brittle. The shear stress decreases rapidly with increasing temperature, and when it becomes less than the cleavage stress, the material becomes ductile. The brittle-to-ductile transition temperature, T_{BDT}, depends strongly on the alloy composition and microstructure, and it is desirable for structural refractory alloys that the T_{BDT} is below room temperature.

One of the effective methods for improving ductility and decreasing the T_{BDT} of refractory alloys is alloying with Re [2,3]. By itself, Re has a hexagonal crystal structure. It has high ductility, high-temperature strength and creep resistance at levels superior to Mo, W, Nb, or Ta. Unfortunately, it is one of the most expensive refractory elements and, therefore, it is mostly used as an alloying addition to other refractory metals, especially Mo and W, to improve their processability. It is well-established that many refractory metals alloyed with Re show enhanced high-temperature strength, improved malleability, and decreased T_{BDT}.
Recently, the microstructure and mechanical properties of NbTiZr [4,5] and TaTiZr [6] were reported. These ternary alloys are the base for many currently available RCCAs [1]. Although Nb and Ta belong to the same subgroup VA of the periodic table and have similar chemical properties, alloying of these elements with Ti and Zr results in completely different phase compositions and mechanical properties. While NbTiZr has a single-phase BCC structure and is ductile at room temperature, TaTiZr consists of two BCC phases and is brittle at room temperature. In this work, we explore the effect of Re additions (10 at.% in both cases) on the microstructure and mechanical properties of NbTiZr and TaTiZr.

2. Materials and Methods

Four alloys, NbTiZr, TaTiZr, Re0.3NbTiZr, and Re0.3TaTiZr, were produced from high-purity metals (purity of 99.9% or higher) by vacuum arc melting. To close solidification porosity and homogenize the compositions, the alloys were hot isostatic pressed (HIP) at 1400 °C for 3 h under high-purity argon at a pressure of 276 MPa. The heating and cooling rates were 15 °C/min. To avoid contamination with residual oxygen, nitrogen and carbon, the samples were wrapped in Ta foil during HIP. The average alloy compositions were determined after HIP, using DC plasma atomic emission spectrometry for metal constituents, inert gas fusion for nitrogen and oxygen, and combustion infrared absorption for carbon. The alloy density was measured using a helium pycnometer. The measured values are given in Table 1. Vickers microhardness was measured using a diamond pyramid applied to a polished surface of an alloy sample at 1000 g load for 15 s. Phase analysis was conducted using X-ray diffraction under Cu Kα1 radiation in the 2θ range of 10 to 140°, as well as with the use of an electron backscatter diffraction (EBSD) technique. Microstructure and local chemical analysis were studied using scanning electron microscopy (SEM) equipped with backscatter electron (BSE) and energy dispersive spectroscopy (EDS) and EBSD detectors. Local crystal structure analysis was carried out by transmission electron microscopy (TEM), employing electron diffraction techniques on a sample that was extracted from the bulk using a conventional lift-out technique within a focused ion beam (FIB) microscope.

Table 1. Density (ρ) and composition of the produced alloys. The main elements are given in at.% and O, N, and C are given in weight parts per million.

<table>
<thead>
<tr>
<th></th>
<th>ρ g/cm³</th>
<th>Nb at.%</th>
<th>Re at.%</th>
<th>Ta at.%</th>
<th>Ti at.%</th>
<th>Zr at.%</th>
<th>O ppm</th>
<th>N ppm</th>
<th>C ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>NbTiZr</td>
<td>6.63</td>
<td>35.6</td>
<td>-</td>
<td>-</td>
<td>32.5</td>
<td>31.9</td>
<td>120</td>
<td>63</td>
<td>21</td>
</tr>
<tr>
<td>TaTiZr</td>
<td>9.06</td>
<td>-</td>
<td>-</td>
<td>32.3</td>
<td>33.8</td>
<td>33.9</td>
<td>70</td>
<td>20</td>
<td>21</td>
</tr>
<tr>
<td>Re0.3NbTiZr</td>
<td>7.85</td>
<td>28.8</td>
<td>10.6</td>
<td>-</td>
<td>31.4</td>
<td>29.0</td>
<td>90</td>
<td>20</td>
<td>16</td>
</tr>
<tr>
<td>Re0.3TaTiZr</td>
<td>9.90</td>
<td>-</td>
<td>9.3</td>
<td>30.2</td>
<td>29.5</td>
<td>31.0</td>
<td>110</td>
<td>20</td>
<td>17</td>
</tr>
</tbody>
</table>

Equilibrium phase diagrams for the studied alloys were calculated based on the CALPHAD method, using ThermoCalc software and the TCHEA4 thermodynamic database developed by ThermoCalc [7], and Pandat software and the PanNb2020 database developed by CompuTherm, LLC [5,8,9]. A Scheil–Gulliver non-equilibrium solidification model [10,11] was employed to predict the phase formation during solidification. The major assumptions of this model are local thermodynamic equilibrium at the liquid–solid interface, infinite diffusion in liquid, and no back-diffusion in solid.

Compression mechanical behavior was studied in the temperature range from 25 °C to 1200 °C and at a constant ram speed of 0.008 mm/s, which corresponded to an initial strain rate of 10⁻³ s⁻¹. Compression tests were chosen over tensile tests because they are less expensive (a smaller amount of material and cheaper testing setup are needed) and sufficient for screening purposes. Moreover, compression tests are more appropriate for simulating working processes, such as forging and rolling, while tensile tests are limited by strain localization. In fact, total elongation cannot be a criterion for the ductility/malleability of materials that are prone to necking, and their actual ductility during tensile testing is generally estimated through the local cross-section area reduction rather than elongation.
The compression specimens had a squared cross-section (5 mm × 5 mm) and a height of 8 mm. Room temperature tests were conducted in air, and high-temperature tests were conducted in vacuum of ~2 × 10^{-5} Pa. The temperature program for high-temperature compression testing consisted of heating at 50 °C/min to the test temperature, holding at the temperature for 15 min, deformation to a maximum of 50% height reduction (or until fracture), and cooling at an initial cooling rate of 100 °C/min or the rate of furnace cooling, whichever was slower; no forced cooling was applied.

3. Results
3.1. Mechanical Properties

The ternary alloy samples, NbTiZr and TaTiZr have a room temperature microhardness of 3.4 GPa and 4.4 GPa, respectively. Additions of Re increase the microhardness to 4.2 GPa in Re_{0.3}NbTiZr and 5.4 GPa in Re_{0.3}TaTiZr (Table 2). The room temperature yield stress also increases with Re additions (Figure 1, Table 3). Moreover, the deformation behavior also changes. For example, NbTiZr shows a small yield drop, after which the true stress increases at a nearly constant strengthening rate, from 890 MPa at the minimum of the yield drop (ε = 0.028), to 1315 MPa at ε = 0.6, when deformation stopped. At the same time, Re_{0.3}NbTiZr does not show the yield drop phenomenon. After yielding at 1220 MPa, its stress continuously increases until the peak stress of 1630 MPa is achieved at ε = 0.30. At larger strains, the true flow stress decreases with increasing true strain and reaches 1450 MPa when fracture occurs at ε = 0.53 (Figure 1a). Thus, although increasing the strength, Re additions decrease the ductility of NbTiZr. In the case of TaTiZr, Re additions increase both room temperature strength and ductility (Figure 1b). TaTiZr has a high yield stress of 1670 MPa but very limited compression ductility, and it fractures at a true strain of 0.025, after achieving a maximum true stress of 1700 MPa. Additions of 10% Re increase the yield stress to 1715 MPa, true maximum stress to 1950 MPa, and true fracture strain to 0.10 (Figure 1b, Table 3). Hence, Re additions have a beneficial effect on the strength, strain hardening, and ductility of TaTiZr.

Table 2. Vickers hardness of the studied alloys at room temperature.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>NbTiZr</th>
<th>Re_{0.3}NbTiZr</th>
<th>TaTiZr</th>
<th>Re_{0.3}TaTiZr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hv (GPa)</td>
<td>3.40 ± 0.02</td>
<td>4.14 ± 0.08</td>
<td>4.36 ± 0.07</td>
<td>5.40 ± 0.14</td>
</tr>
</tbody>
</table>

Figure 1. True stress versus true strain deformation curves for (a) NbTiZr and Re_{0.3}NbTiZr and (b) TaTiZr and Re_{0.3}TaTiZr acquired at room temperature.
Table 3. Yield stress (σ_y) and true fracture strain (ε_f) of the studied alloys at different temperatures.

<table>
<thead>
<tr>
<th>T, °C</th>
<th>Property</th>
<th>NbTiZr</th>
<th>TaTiZr</th>
<th>Re0.3NbTiZr</th>
<th>Re0.3TaTiZr</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>σ_y, MPa</td>
<td>920 ± 18</td>
<td>1670 ± 30</td>
<td>1220 ± 24</td>
<td>1715 ± 30</td>
</tr>
<tr>
<td>25</td>
<td>ε_f</td>
<td>&gt;0.6</td>
<td>0.025 ± 0.005</td>
<td>0.53 ± 0.07</td>
<td>0.10 ± 0.01</td>
</tr>
<tr>
<td>800</td>
<td>σ_y, MPa</td>
<td>465 ± 9</td>
<td>157 ± 6</td>
<td>805 ± 15</td>
<td>243 ± 7</td>
</tr>
<tr>
<td></td>
<td>ε_f*</td>
<td>&gt;0.69</td>
<td>&gt;0.69</td>
<td>&gt;0.69</td>
<td>&gt;0.69</td>
</tr>
<tr>
<td>1000</td>
<td>σ_y, MPa</td>
<td>146 ± 5</td>
<td>103 ± 5</td>
<td>323 ± 8</td>
<td>122 ± 5</td>
</tr>
<tr>
<td></td>
<td>ε_f*</td>
<td>&gt;0.69</td>
<td>&gt;0.69</td>
<td>&gt;0.69</td>
<td>&gt;0.69</td>
</tr>
<tr>
<td>1200</td>
<td>σ_y, MPa</td>
<td>61 ± 3</td>
<td>63 ± 3</td>
<td>89 ± 4</td>
<td>71 ± 3</td>
</tr>
<tr>
<td></td>
<td>ε_f*</td>
<td>&gt;0.69</td>
<td>&gt;0.69</td>
<td>&gt;0.69</td>
<td>&gt;0.69</td>
</tr>
</tbody>
</table>

* No fracture occurred during testing of all the studied alloys at 800–1200 °C.

The strengthening effects from Re additions to NbTiZr and TaTiZr are also observed at higher temperatures, at least up to 1200 °C (Table 3). The alloys are ductile and show no evidence of fracture during compression deformation at 800 °C, 1000 °C, and 1200 °C. With increasing temperature, the alloys lose strength rapidly. At 800 °C and 1000 °C, Re0.3NbTiZr is the strongest alloy, NbTiZr is the second strongest, and TaTiZr is the weakest alloy among those studied. At 1200 °C, all four alloys have yield stresses below 100 MPa. The yield stress values of NbTiZr and TaTiZr at this temperature are almost the same, 61 MPa and 63 MPa, while Re0.3NbTiZr and Re0.3TaTiZr have yield stress values of 89 MPa and 71 MPa, respectively (Table 3). As an example of the high-temperature behavior, Figure 2 shows the true stress versus true strain deformation curves for the studied alloys at 1000 °C. The alloys show a yield drop at the beginning of deformation, which is followed by slight strengthening (NbTiZr), softening (Re0.3NbTiZr and TaTiZr), or slight short strengthening followed by softening stages (Re0.3TaTiZr). The results indicate that in the temperature range of 800 °C to 1200 °C the Nb-containing alloys are stronger than the Ta-containing alloys, and additions of Re increase the high-temperature strength of NbTiZr more efficiently than that of TaTiZr.

![Figure 2](image_url) True stress versus true strain deformation curves for (a) NbTiZr and Re0.3NbTiZr and (b) TaTiZr and Re0.3TaTiZr acquired at 1000 °C.

3.2. X-ray Diffraction

X-ray diffraction patterns from the studied alloys in the 1400 °C HIP’d condition and 1000 °C deformed condition are given in Figure 3, and the identified phases and their lattice parameters are given in Table 4. For a better resolution of low-intensity peaks, a square root of the radiation intensities was used for the y-axis. NbTiZr has a single-phase BCC (A2) crystal structure, with the same lattice parameter a = 0.3404 nm in both conditions (Figure 3a). Addition of 10 at.% Re results in a two-phase crystal structure of Re0.3NbTiZr, with BCC as a major phase and a minor phase that is identified as a cubic FCC phase. This minor phase can also be identified as an hexagonal Laves phase (C14) or a sigma phase (Figure 3b); however, EBSD and TEM analyses reject the latter two phases (see Section 3.2).
In the HIP’d condition, the lattice parameter of the BCC phase is $a_{\text{BCC}} = 0.3346$ nm and that of the FCC is $a_{\text{FCC}} = 0.7560$ nm. After compression deformation of Re$_{0.3}$NbTiZr at 1000 °C, the diffraction peaks from the FCC phase become more intense, the lattice parameter of the BCC slightly increases to 0.3352 nm, and the FCC-phase lattice parameter increases to 0.7569 nm (Table 4).

TaTiZr has two BCC phases (Figure 3c). In the HIP’d condition, BCC1 has the lattice parameter $a_{\text{BCC1}} = 0.3421$ nm and BCC2 has $a_{\text{BCC2}} = 0.3320$ nm; thus, the difference in the lattice parameters of these BCC phases is 3.04%. After deformation at 1000 °C the lattice parameter of BCC1 slightly increases and that of BCC2 decreases (Table 4), resulting in an increase in the lattice parameter difference to 5.19%. Addition of 10 at.% Re to TaTiZr does not produce additional phases but widens the diffraction peaks from the BCC1 phase in the HIP’d condition (Figure 3d). The lattice parameters of the BCC1 and BCC2 phases in the HIP’d Re$_{0.3}$TaTiZr are $a_{\text{BCC1}} = 0.3423$ nm and $a_{\text{BCC2}} = 0.3255$ nm (Table 4). After

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**Table 4.** Lattice parameters of the observed phases in the studied alloys after HIP’ing at 1400 °C or compression deformation at 1000 °C.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>HIP’d at 1400 °C</th>
<th>Deformed at 1000 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>NbTiZr</td>
<td>BCC, $a = 0.3404$ nm</td>
<td>BCC, $a = 0.3404$ nm</td>
</tr>
<tr>
<td>Re$_{0.3}$NbTiZr</td>
<td>BCC, $a = 0.3346$ nm, FCC, $a = 0.7560$ nm</td>
<td>BCC, $a = 0.3352$ nm, FCC, $a = 0.7569$ nm</td>
</tr>
<tr>
<td>TaTiZr</td>
<td>BCC1, $a = 0.3421$ nm, BCC2, $a = 0.3320$ nm</td>
<td>BCC1, $a = 0.3488$ nm, BCC2, $a = 0.3316$ nm</td>
</tr>
<tr>
<td>Re$_{0.3}$TaTiZr</td>
<td>BCC1, $a = 0.3423$ nm, BCC2, $a = 0.3255$ nm</td>
<td>BCC1, $a = 0.3501$ nm, BCC2, $a = 0.3269$ nm</td>
</tr>
</tbody>
</table>
deformation at 1000 °C, the diffraction peaks from the BCC1 phase become sharper and the lattice parameter slightly increases (Table 4).

3.3. Microstructure
3.3.1. NbTiZr

After HIP’ing at 1400 °C and slow cooling, both secondary and backscattered electron images provide even contrasts from the polished surfaces of NbTiZr, and the individual grains are hardly recognized. Grains and grain boundaries in this alloy are therefore identified by etching and/or by taking EBSD inverse pole figure (IPF) maps (Figure 4). These methods reveal an equiaxed, coarse-grained structure, with an average grain diameter above 1 mm. Etching reveals the presence of well-distributed, fine features inside the grains (Figure 4a). The nature of these features is discussed in Section 4.1.1.

Compression deformation at 1000 °C makes grains elongated in the directions of plastic flow and results in the formation of a sub-grain structure inside grains and fine recrystallized grains along the former grain boundaries. This microstructure has been described in detail elsewhere [4,5].

![Figure 4. (a) Etched microstructure and (b) inverse pole figure map of grains of a HIP’d NbTiZr sample.](image)

3.3.2. TaTiZr

The microstructure of TaTiZr was studied in detail by Senkov et al. [6]. It consists of a coarse-grain structure of a Zr and Ti rich matrix phase, finer domains inside the grains, and Ta-rich, submicron-sized precipitates of a second phase (Figure 5a). The average grain and domain diameters are ~320 µm and 4 µm. The average precipitate size is ~0.25 µm, they are larger at the grain boundaries, and their volume fraction is ~0.51 (Figure 5b). The average compositions of the matrix phase and second-phase particles are given in Table 5. Both phases have BCC crystal structures. Correlating the compositions of the phases with the measured lattice parameters (Table 4) and taking into account that Zr has the largest atomic radius among the three elements, we conclude that the XRD-identified BCC1 (with a larger lattice parameter) is the Zr-rich phase and BCC2 is the Ta-rich phase. Previous studies indicated that the Ti- and Zr-rich matrix phase (BCC1) is likely metastable at room temperature, resulting in additional, much finer omega-phase precipitation, which can only be identified using high resolution TEM [6].
Previous studies indicated that the Ti- and Zr-rich matrix phase (BCC1) is likely metastable at room temperature, resulting in additional, much finer omega-phase precipitation, which can only be identified using high resolution TEM [6]. Additions of 10% Re to NbTiZr decrease the matrix grain size to ~150 \( \mu \)m and cause the precipitation of Re-rich particles (Figure 6). The particles are present both inside the matrix grains and at grain boundaries. Inside grains, the particles form a cellular structure, with the interior of the cells free of the particles (Figure 6a,b). EBSD analysis was conducted using the following assigned phases: BCC (space group 229), hexagonal Laves (194), FCC (225 and 227), and sigma (136). This analysis showed that the matrix has a BCC crystal structure, and the particles have an FCC crystal structure (Figure 6c). The hexagonal Laves phase shows poor correlation and the sigma phase shows no correlation with the collected EBSD patterns (EBSPs, see Supplementary Materials, Figure S1). The volume fraction of the particles is estimated to be \(~0.14\). EDS analysis shows that the matrix phase is slightly depleted in Re and Zr, and the particles are heavily enriched in Re (Table 6).

A detailed TEM analysis, with the use of selected area diffraction and convergent beam techniques, confirmed the BCC crystal structure of the matrix phase and the FCC crystal structure of the particles (Figures 7 and S2). The 3\( m\) symmetry in the [111] convergent beam pattern (Figure 7d) distinguishes the particle structure as cubic and not hexagonal, while the indexed diffraction patterns from the second-phase particle are consistent with a FCC rather than BCC structure. The TEM analysis also suggested orientation relationships between the particles and the matrix. In particular, the following orientation relationships can be identified from the combined, BCC and FCC, diffraction pattern (Figure 7b): (2\( \overline{2} \)0\( _{FCC} \) || (1\( \overline{1} \)0\( _{BCC} \) and [110]\( _{FCC} \) || [113]\( _{BCC} \).

### Table 5. Composition (in at.\%) of the matrix phase and second-phase particles in TaTiZr.

<table>
<thead>
<tr>
<th>Element</th>
<th>Ta</th>
<th>Ti</th>
<th>Zr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Matrix (BCC1)</td>
<td>15.8 ± 5.0</td>
<td>33.0 ± 4.1</td>
<td>51.2 ± 4.2</td>
</tr>
<tr>
<td>Particles (BCC2)</td>
<td>62.7 ± 3.1</td>
<td>27.1 ± 1.8</td>
<td>10.2 ± 2.2</td>
</tr>
</tbody>
</table>

3.3.3. Re\(_{0.3}\)NbTiZr

Additions of 10\% Re to NbTiZr decrease the matrix grain size to ~150 \( \mu \)m and cause the precipitation of Re-rich particles (Figure 6). The particles are present both inside the matrix grains and at grain boundaries. Inside grains, the particles form a cellular structure, with the interior of the cells free of the particles (Figure 6a,b). EBSD analysis was conducted using the following assigned phases: BCC (space group 229), hexagonal Laves (194), FCC (225 and 227), and sigma (136). This analysis showed that the matrix has a BCC crystal structure, and the particles have an FCC crystal structure (Figure 6c). The hexagonal Laves phase shows poor correlation and the sigma phase shows no correlation with the collected EBSD patterns (EBSPs, see Supplementary Materials, Figure S1). The volume fraction of the particles is estimated to be ~0.14. EDS analysis shows that the matrix phase is slightly depleted in Re and Zr, and the particles are heavily enriched in Re (Table 6).

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Figure 6. (a) Low-magnification and (b) higher-magnification BSE images of an Re$_{0.3}$NbTiZr alloy sample after HIP'ing at 1400 °C. (c) EBSD phase map (BCC is red and FCC is yellow) and (d) combined inverse pole figure (IPF) orientation map of the BCC matrix phase and FCC particles in the area shown in (b). The color-coding map of crystallographic orientations in BCC and FCC phases is shown on the right site of (d).

Table 6. Chemical composition (in at.%) and volume fraction ($V_f$) of the matrix phase and particles in Re$_{0.3}$NbTiZr after HIP'ing at 1400 °C and after additional compression deformation at 1000 °C.

<table>
<thead>
<tr>
<th>Condition</th>
<th>Constituent</th>
<th>$V_f$</th>
<th>Re</th>
<th>Nb</th>
<th>Ti</th>
<th>Zr</th>
</tr>
</thead>
<tbody>
<tr>
<td>HIP’d</td>
<td>Matrix phase</td>
<td>0.86</td>
<td>7.5 ± 0.9</td>
<td>33.4 ± 0.4</td>
<td>31.3 ± 1.0</td>
<td>27.8 ± 0.4</td>
</tr>
<tr>
<td></td>
<td>Particles</td>
<td>0.14</td>
<td>33.2 ± 2.3</td>
<td>15.5 ± 0.5</td>
<td>19.2 ± 0.8</td>
<td>32.0 ± 1.1</td>
</tr>
<tr>
<td>Deformed</td>
<td>Matrix phase</td>
<td>0.87</td>
<td>7.7 ± 1.1</td>
<td>31.9 ± 1.0</td>
<td>31.6 ± 0.6</td>
<td>28.9 ± 0.7</td>
</tr>
<tr>
<td></td>
<td>Particles</td>
<td>0.13</td>
<td>33.7 ± 0.5</td>
<td>14.4 ± 0.5</td>
<td>19.6 ± 0.5</td>
<td>32.3 ± 0.4</td>
</tr>
</tbody>
</table>

After compression deformation at 1000 °C, the grains and cells become elongated in the directions of plastic flow, and the cell boundaries enriched in the secondary particles form continuous channels (Figure 8a,b). EBSD analysis shows that the BCC matrix consists of fine equiaxed grains inside the channels and larger elongated grains inside the cells and the Re-rich precipitates retain their FCC crystal structure (Figure 9). It is likely that during deformation at 1000 °C dynamic recrystallization occurs in the regions enriched with second-phase particles. The volume fraction of the second-phase particles is estimated to be ~0.13 and the volume fraction of fine-grained matrix regions is ~0.3. The chemical compositions of the matrix phase and second phase particles in the deformed sample are given in Table 6, and they are similar to the compositions of the phases in the non-deformed alloy.
Figure 7. (a) TEM image of a thin area of Re$_{0.3}$NbTiZr foil containing a second phase particle. (b) Combined selected area diffraction pattern (SADP) from the particle ([110]$_{\text{FCC}}$ zone axis) and the matrix ([113]$_{\text{BCC}}$ zone axis, indexed reflections are underlined). (c) Selected area diffraction of [112]$_{\text{FCC}}$ from the particle. (d) A convergent-beam [111]$_{\text{FCC}}$ zone axis pattern from the second-phase particle indicating 3m symmetry in the transmitted disc.

Figure 8. (a,b) BSE images of the microstructure of a Re$_{0.3}$NbTiZr alloy sample after 55% compression deformation at 1000 °C.
3.3.4. Re_{0.3}TaTiZr

Additions of Re change the microstructure of TaTiZr dramatically. In particular, submicron-sized Ta-rich precipitates in TaTiZr (Figure 5) are replaced with much coarser, ~15 μm in diameter, Ta- and Re-rich particles in Re_{0.3}TaTiZr (Figure 10). These Ta- and Re-rich particles have a characteristic morphology consisting of a two-phase core and a single-phase shell. The compositions and volume fractions of the matrix phase and the bright areas of the particles determined by SEM-EDS are given in Table 7.

Figure 10. Cont.
Figure 10. (a) Low magnification and (b) higher magnification SEM images of the two-phase microstructure of the HIP’d Re$_{0.3}$TaTiZr alloy. (c–f) Element composition maps of (c) Re, (d) Ta, (e) Ti, and (f) Zr taken from the area shown in figure (b).

Table 7. Chemical composition (in at.%) and volume fraction ($V_f$) of the matrix phase and second-phase particles in the HIP’d and deformed Re$_{0.3}$TaTiZr alloy samples.

<table>
<thead>
<tr>
<th>Condition</th>
<th>Constituent</th>
<th>$V_f$</th>
<th>Re</th>
<th>Ta</th>
<th>Ti</th>
<th>Zr</th>
</tr>
</thead>
<tbody>
<tr>
<td>HIP’d</td>
<td>Matrix</td>
<td>0.53</td>
<td>1.1</td>
<td>9.4</td>
<td>35.1</td>
<td>54.4</td>
</tr>
<tr>
<td>HIP’d</td>
<td>Particles</td>
<td>0.47</td>
<td>15.1</td>
<td>53.3</td>
<td>24.8</td>
<td>6.8</td>
</tr>
<tr>
<td>Deformed</td>
<td>Matrix</td>
<td>0.52</td>
<td>1.2</td>
<td>8.7</td>
<td>35.6</td>
<td>54.5</td>
</tr>
<tr>
<td>Deformed</td>
<td>Particles</td>
<td>0.48</td>
<td>17.6</td>
<td>49.3</td>
<td>27.1</td>
<td>6.0</td>
</tr>
</tbody>
</table>

EBSD analysis of the HIP’d Re$_{0.3}$TaTiZr reveals that both the matrix and second-phase particles have BCC crystal structures (Figure 11a) and some of the particles have the same crystallographic orientation as the adjacent matrix phase (Figures 11b and S3). It also allows estimation of the average matrix grain diameter of ~38 µm.
After deformation at 1000 °C with a true compression strain of 0.69, grains become elongated and the second-phase particles become aligned along the directions of plastic flow (Figure 12). Many of the particles disintegrate into small pieces; however, without any evidence of crack formation. Fragments of the particle shells, dispersed particle core segments, and elongated particles can be found in the deformed alloy sample. The compositions and volume fractions of the matrix and the second phase remain almost the same as in the HIP’d, non-deformed alloy (Table 7).

EBSD analysis of a Re0.3TaTiZr alloy sample deformed at 1000 °C with true strain of 0.69 reveals that both the matrix and second-phase particles retain a BCC crystal structure (Figure 13a,b). The average grain diameter of the matrix phase decreases to ~8 μm after deformation, which indicates dynamic recrystallization occurs during deformation (Figure 13c,d). The poor image quality of some matrix grains may be a result of the high dislocation density inside the grains.

<table>
<thead>
<tr>
<th>Condition</th>
<th>Constituent</th>
<th>Vf (at.%) Matrix</th>
<th>Vf (at.%) Matrix</th>
<th>Vf (at.%) Matrix</th>
<th>Vf (at.%) Matrix</th>
</tr>
</thead>
<tbody>
<tr>
<td>Deformed Matrix</td>
<td>0.52</td>
<td>1.2 ± 0.1</td>
<td>8.7 ± 0.5</td>
<td>35.6 ± 0.4</td>
<td>54.5 ± 0.7</td>
</tr>
<tr>
<td>Deformed Matrix</td>
<td>0.48</td>
<td>15.1 ± 0.8</td>
<td>53.3 ± 0.9</td>
<td>24.8 ± 0.5</td>
<td>6.8 ± 0.3</td>
</tr>
</tbody>
</table>

Figure 10. (a) Low magnification and (b) higher magnification SEM images of Re0.3TaTiZr alloy sample after compression deformation at 1000 °C with a true strain of 0.69.

Figure 11. (a) EBSD map of BCC (red) phases and (b) combined inverse pole figure (IPF) orientation map of the BCC matric phase and particles. An IPF color-coding map is shown as an insert in (b). The maps were taken from the surface area of Re0.3TaTiZr shown in Figure 10b. Grain boundaries with misorientations >10° are shown as dark lines.

Figure 12. (a) Low magnification and (b) higher magnification BSE images of Re0.3TaTiZr alloy sample after compression deformation at 1000 °C with a true strain of 0.69.
segments, and elongated particles can be found in the deformed alloy sample. The compositions and volume fractions of the matrix and the second phase remain almost the same as in the HIP’d, non-deformed alloy (Table 7).

EBSD analysis of a Re0.3TaTiZr alloy sample deformed at 1000 °C with true strain of 0.69 reveals that both the matrix and second-phase particles retain a BCC crystal structure (Figure 13a,b). The average grain diameter of the matrix phase decreases to ~8 μm after deformation, which indicates dynamic recrystallization occurs during deformation (Figure 13c,d). The poor image quality of some matrix grains may be a result of the high dislocation density inside the grains.

Figure 12. (a) Low magnification and (b) higher magnification BSE images of Re0.3TaTiZr alloy sample after compression deformation at 1000 °C with a true strain of 0.69.

Figure 13. (a) A BSE image and (b–d) respective EBSD maps of the matrix and second-phase particles in Re0.3TaTiZr after compression deformation at 1000 °C with a true strain of 0.69. (b) Band contrast map, (c) phase map (BCC is red), and (d) IPF map in the compression direction of the BCC matrix phase and BCC particles. The IPF color-coding map is shown as an insert in (d). The compression direction is vertical.

4. Discussion

4.1. Effect of Re on the Microstructure and Phase Composition

In order to interpret the effect of Re additions on the microstructure evolution of the studied alloys, the experimental results were compared with the respective phase diagrams calculated using the CALPHAD approach. Results of first principal calculations for stable and metastable phases available at the Materials Project website [12], as well as already available phase diagrams [13,14], were also used in the analysis. Thermo-Calc software and the TCHEA4.1 database, as well as Pandat software and the PanNb2020 database, were used for CALPHAD calculations. The results are shown in Figures 14–16, and a detailed analysis is given below.

4.1.1. NbTiZr and TaTiZr

For NbTiZr, both TCHEA4.1 and PanNb2020 predicted similar phase diagrams, with a single-phase BCC1 range at temperatures above ~600 °C. At lower temperatures, BCC1 partially transforms to an Nb-rich BCC2 phase, and the parent BCC1 phase becomes enriched with Ti and Zr (Figure 14a,b). Only one BCC phase was identified in the XRD and SEM/EDS analyses, which may indicate that the BCC1 → BCC1 + BCC2 phase transformation requires more time at lower temperatures than was provided by the slow cooling from HIP’ing in the present work. In this case, the observed single-phase BCC1 microstructure in NbTiZr represents a kinetically metastable condition. On the other hand, etching reveals the presence of fine, well-distributed features (Figure 4a). CALPHAD predicts that the composition of the BCC1 phase at 600 °C is close to the alloy composition, while the BCC2 phase composition is 77.3% Nb, 13.5% Ti, and 9.2% Zr. Using this information and assuming the same compositions of these phases at room temperature, the lattice
parameters and average atomic numbers $Z$ of BCC1 and BCC2 phases are estimated using Equations (1) and (2) respectively:

$$a_{\text{BCC}} = \frac{4}{\sqrt{3}} \sum c_i r_i$$

(1)

$$Z = \sum c_i Z_i$$

(2)

Here, $c_i$ is the mole fraction of element $i$ in the phase, and $r_i$ and $Z_i$ are the atomic radius and atomic number of element $i$. Using known atomic radii and atomic numbers for Nb, Ti, and Zr, the following quantities are calculated: $a_{\text{BCC}1} = 0.3457 \text{ nm}$, $a_{\text{BCC}2} = 0.3349 \text{ nm}$, $Z_{\text{BCC}1} = 34.3$, and $Z_{\text{BCC}2} = 38.3$. A 3% difference in lattice constants should be resolved in XRD, and the high Z-contrast difference should provide good contrast in BSE images. The absence of evidence of a secondary BCC2 phase from XRD, BSE, and EDS may indicate that the particles have a very small size and low volume fraction. An alternative origin of the etched spots is dislocations. Indeed, the number densities of these etched spots do not exceed $10^{11} \text{ m}^{-2}$, which is comparable to the number density of dislocations in annealed metals [15]. Additional work, such as high resolution TEM, as well as a long annealing below 600 °C, are needed to determine conclusively if NbTiZr is a single-phase or multi-phase microstructure at room temperature.

A single-phase BCC1 region is also predicted for TaTiZr below the solidus (Figure 14c,d). Thermo-Calc calculations predict a BCC1 $\rightarrow$ BCC1 + BCC2 phase transformation below 1137 °C, while Pandat predicts the same below 1319 °C. In this alloy, after the transformation, BCC1 becomes enriched in Ti and Zr and the BCC2 phase is rich in Ta. At temperatures around 575 °C, all BCC1 transforms to a Ti- and Zr-rich HCP phase and a small amount of Ta-rich BCC2 phase. The calculated results support the experimental data, which showed that the microstructure consists of a Ti- and Zr-rich BCC1 matrix phase and Ta-rich BCC2 precipitates. The HCP phase was, however, not observed. Instead, a metastable omega phase was found inside the matrix phase [6], which is an indication of the metastability of BCC1 at room temperature.

![Figure 14. Equilibrium phase diagrams of (a,b) NbTiZr and (c,d) TaTiZr, calculated using the (a,c) TCHEA4.1 database and (b,d) PanNb2020 database.](image-url)
4.1.2. \( \text{Re}_{0.3}\text{NbTiZr} \)

The Thermo-Calc and Pandat calculated phase diagrams for \( \text{Re}_{0.3}\text{NbTiZr} \) are quite different (Figure 15a, b). Thermo-Calc predicts a wide, single-phase BCC1, temperature range below the solidus (1686 °C), followed by precipitation of a Zr- and Re-rich sigma phase (\( \text{ReZr}_2 \)) below 967 °C and additional precipitation of a Nb-rich BCC2 phase below 682 °C (Figures 16a and S4). After precipitation of the sigma phase, which, according to Thermo-Calc, consists of 33.3% Re and 66.7% Zr, the BCC1 phase becomes enriched with Nb and Ti, and after an additional precipitation of BCC2, the BCC1 becomes rich in Ti. On the other hand, Pandat predicts a very narrow single-phase BCC1 temperature range below the solidus (1703 °C), followed by precipitation of a Re- and Zr-rich hexagonal Laves phase (C14, an approximate composition is 22% Nb, 34% Zr, and 44% Re) below 1656 °C and additional precipitation of Nb-rich BCC2 phase below 698 °C (Figures 16b and S5). It can be seen that both databases agree with each other when predicting (a) the formation of a single BCC1 phase after solidification, (b) approximately the same solidus temperature, and (c) approximately the same solvus temperature for the BCC2 phase. The main disagreement between the TCHEA4.1 and PanNb2020 databases is in predicting different types of Re-rich phases. In particular, TCHEA4.1 predicts the presence of a \( \text{ReZr}_2 \) sigma phase below 967 °C, while PanNb2020 predicts a hexagonal C14 Laves phase below 1656 °C. Formation of the \( \text{ReZr}_2 \) sigma phase by a peritectic reaction at 1900 °C and the \( \text{ZrRe}_2 \) Laves phase by a peritectic reaction at 2450 °C in the binary Re-Zr system was previously reported by Savitski et al. [16,17]. First principle calculations show that the \( \text{ReZr}_2 \) sigma phase is metastable, while \( \text{ZrRe}_2 \) is thermodynamically stable in the binary Re-Zr system [18]. According to TCHEA4.1, Nb and Ti additions suppress the formation of the sigma phase to below 1000 °C and completely suppress formation of the Laves phase. On the other hand, according PanNb2020, Nb and Ti additions completely suppress formation of the sigma phase in favor of a ternary \( \text{Zr(Re, Nb)}_2 \) Laves phase.

Caution is needed in comparing CALPHAD predictions with the present experimental data, as the former represent equilibrium conditions and the latter represent a short annealing at a high temperature (1400 °C/3 h) during HIP, followed by a controlled cooling rate. Nevertheless, when the CALPHAD results are compared to the experimental data, it is found that neither database predicts a secondary phase with the FCC structure. It is likely that this phase forms in ternary or even quaternary systems and is absent in the TCHEA4.1 and PanNb2020 databases, which often emphasize binary data. As a result, ThermoCalc and Pandat instead minimize the energy among the other available phases; and Pandat gives a better agreement with the experiments. Indeed, the Re-rich second-phase particles have a composition and volume fraction similar to the calculated ternary Laves phase at ~1200–1250 °C. Moreover, the microstructure of deformed samples indicates that the second-phase particles are more likely to be present at 1000 °C, while according to TCHEA4.1, the alloy should be a single-phase BCC structure at this temperature. However, EBSD and TEM results indicate that the second phase has a FCC crystal structure, with a rather large lattice parameter \( a = 0.756 \text{ nm} \), while PanNb2020 predicts a hexagonal (C14) Laves phase. On the other hand, a first principle analysis of the Nb-Ti-Re system predicts the presence of a stable NbTiRe$_2$ Heusler phase, with the space group Fm$\overline{3}$m (225) and the lattice parameter \( a = 0.634 \text{ nm} \) [12]. The relative concentrations of Nb, Ti, and Re in the FCC particles (see Table 6) correspond to the composition of this Heusler phase. It is possible that this phase is also present in the quaternary, Nb-Ti-Re-Zr system, with Zr atoms distributed equally between Nb, Ti, and Re sub-lattices, and it is preferable over the hexagonal Laves phase. However, it is hard to explain an increase in the lattice parameter of this phase, from 0.634 nm to 0.756 nm, by the substitution of smaller Nb, Ti, and Re with larger Zr. Another possibility is that the presence of Nb transforms the hexagonal Laves (C14) phase, which is stable in the Re-Zr system, to a cubic Laves (C15) phase (space group 227, Fd$\overline{3}$m) in the Re$_{0.3}$NbTiZr alloy. The measured lattice parameter of the FCC particles is typical of a cubic Laves phase. However, C15 has never been mentioned in Re-Nb-Ti, Re-Ti-Zr and Nb-Ti-Zr systems [12–14], while data for Re-Nb-Ti-Zr are not available.
future work is recommended, including long anneals, to better approach equilibrium at a range of temperatures followed by quenching, as well as a more detailed analysis of the crystal structure of the second phase in the Re$_{0.3}$NbTiZr alloy.

Figure 15. Equilibrium phase diagrams of Re$_{0.3}$NbTiZr calculated using the (a) TCHEA4.1 database and (b) PanNb2020 database.

4.1.3. Re$_{0.3}$TaTiZr

The Thermo-Calc and Pandat calculated equilibrium phase diagrams for Re$_{0.3}$TaTiZr are also very different (Figure 16). Thermo-Calc predicts that solidification starts at 2390 °C by forming a hexagonal (C14) Laves phase from the liquid, and this reaction continues until the volume fraction of the Laves phase reaches a maximum value of 0.244. The high-temperature BCC1 phase starts to solidify at 1942 °C by consuming both liquid and Laves phases in the peritectic reaction, Liquid + Laves → BCC1, which is completed at 1712 °C when the liquid phase is exhausted and a small amount of the Laves phase is still present. The BCC1 phase has a composition close to that of the alloy, and the Laves (C14) phase is rich in Re and Ta and depleted in Ti and Zr (see Figure S6 in Supplementary Materials). The corresponding volume fractions are 0.92 and 0.08, respectively (Figure 16a). The two-phase BCC1 + Laves range persists to 1365 °C. A peritectoid reaction occurs below this temperature, when the Ta- and Re-rich BCC2 phase forms by consuming the BCC1 and Laves phases (Figure 16a). At 897 °C, the volume fractions of BCC1 and BCC2 are 0.61 and 0.39, respectively, and the Laves phase disappears. Below 897 °C, Thermo-Calc predicts partial transformation of BCC1 to a binary sigma phase (ReZr$_2$). The remaining BCC1 completely transforms to HCP and BCC2 phases by eutectoid transformation at 575–580 °C (Figure 16a).

Contrary to Thermo-Calc, Pandat does not predict the formation of a Laves phase during the equilibrium solidification of Re$_{0.3}$TaTiZr. According to Pandat, solidification
starts at 1926 °C and completes at 1559 °C with the formation of a single-phase BCC1 structure (Figure 16b). The high-temperature BCC1 phase separates into two BCC phases, Ti- and Zr-rich BCC1 and Re- and Ta-rich BCC2 below 1347 °C. A small amount (up to 0.017 by volume) of an hexagonal (C14) Laves phase is predicted in the temperature range of 1010 °C–1096 °C. A trigonal Re25Zr21 phase is predicted below 1010 °C, and an eutectoid transformation of the BCC1 into a Ti- and Zr-rich HCP and Ta-rich BCC2 phase is predicted at 552–557 °C. The only agreements of the TCHEA4.1 and PanNb2020 databases are (a) predictions of the separation of a high-temperature BCC1 phase to a Ti- and Zr-rich BCC1 and a Ta- and Re-rich BCC2 below ~1347–1365 °C; and (b) the eutectoid transformation of BCC1 to HCP and BCC2 below ~560–580 °C. While the Thermo-Calc database predicts a tetragonal sigma (ReZr2) phase, which, in the binary Re-Zr system, is metastable and decomposes to trigonal Re25Zr21 and HCP Zr [18], the Pandat database predicts the Re25Zr21 at T < 1000 °C.

The predicted low-temperature eutectoid transformation would likely require a rather long time for initiation and, therefore, the eutectoid transformation is likely to be kinetically restricted and did not occur in the studied Re0.3TaTiZr alloy under the applied processing conditions. Precipitation of Re-rich phases (ReZr2 or Re25Zr21) at temperatures below 1000 °C is also unlikely, as it is controlled by slow Re diffusion and requires a considerably longer time than the cooling time after the HIP process. Therefore, the experimental observation of two BCC phases in the HIP’d Re0.3TaTiZr alloy agrees with the Thermo-Calc and Pandat calculations under the assumption that this observed microstructure was quenched from temperatures above 1000 °C and, therefore, should be considered metastable.

The specific morphology of the BCC2 particles, each consisting of a single-phase BCC2 shell and a two phase BCC1 + BCC2 core, where the particles and the adjacent BCC1 matrix have the same crystallographic orientations, require additional explanation. Such a shell/core particle morphology often forms during incomplete peritectic or peritectoid reactions [19,20]. During these reactions, the low-temperature (LT) phase nucleates and grows at the interface boundaries of two high-temperature (HT) phases. If one of the HT phases is present in the form of particles, the LT phase produces continuous shells surrounding these HT particles, after which the rate of the peritectic/peritectoid reaction is controlled by the rate of diffusion of the reactants through the shell and can decrease considerably. As result, this reaction is generally sluggish and may not be completed during continuous cooling. Instead, metastable phases can be produced in the core of each particle from the remaining HT phase at lower temperatures [19,20].

The Pandat calculations do not show peritectic or peritectoid reactions in the Re0.3TaTiZr alloy (Figure 16b); however, the Thermo-Calc calculations (Figure 16a) show both peritectic and peritectoid reactions, as described above. Since the peritectic and peritectoid reactions each involve three phases in a quaternary system, they do not need to occur isothermally. Being in equilibrium with Laves and liquid phases, the BCC1 phase nucleates at the liquid-Laves interface and is initially heavily enriched in Ta and Re and depleted in Ti and Zr (Figure S6). At the end of equilibrium solidification, the concentrations of the alloying elements in the BCC1 phase become similar to the alloy concentration (Figure S6). During non-equilibrium solidification (via the Scheil model), a concentration gradient forms in the BCC1 phase; the regions adjacent to the Laves particles (i.e., those which solidify first) are heavily enriched in Ta and Re, and the regions far from the Laves particles (i.e., those which solidify last) are heavily enriched in Ti and Zr (Figure 17). In the case of solidification during arc melting, one can expect an intermediate situation; the concentration gradient is still present, but it is less pronounced than that in the Scheil’s model. Therefore, one can expect that, after solidification of the arc melted alloy, the BCC1 regions adjacent to the Laves particles are richer in Ta and Re than the regions located far from the Laves particles.
considerably. As a result, this reaction is generally sluggish and may not be completed surrounding these HT particles, after which the rate of the peritectic/peritectoid reaction phases is present in the form of particles, the LT phase produces continuous shells grows at the interface boundaries of two high-temperature (HT) phases. If one of the HT reactions [19,20]. During these reactions, the low-temperature (LT) phase nucleates and than the regions located far from the Laves particles.

Figure 17. Compositions of Laves (C14) and BCC1 phases (colored, labeled lines) as a function of the total mole fraction of solid phases during non-equilibrium solidification (Scheil model), predicted using Thermo-Calc and the TCHEA4.1 databases. After the primary solidification of Laves C14 phase, a composition gradient forms in the BCC1 phase as the solidification progresses. The temperature dependence of the total fraction of solid phases during solidification is also shown as a dashed line.

During the peritectoid reaction, the BCC2 phase quickly nucleates at the BCC1–Laves interface, which is already enriched with Ta and Re, and forms thick shells around the Laves particles. These continuous shells control the diffusion, decreasing the transformation rate in the core of the Laves particle, and result in a transformation of Laves to BCC1 and BCC2 inside the core. Non-equilibrium concentrations of the BCC1 and Laves phases after solidification likely trigger the BCC1 + Laves → BCC2 transformation at higher temperatures than predicted in the equilibrium condition. The peritectoid reaction also explains why the BCC2 particles have the same crystallographic orientations as parent BCC1 phase. Although the described scenarios realistically explain the morphology of the BCC2 particles, additional experiments are needed to verify the suggested phase transformation model.

4.2. Effect of Re on Mechanical Properties

Re significantly increases the RT yield strength of NbTiZr and decreases the rate of strength loss up to 800 °C, after which the strength drops more quickly than in the ternary. Nevertheless, Re addition to NbTiZr continues to provide significant strengthening up to 1200 °C. Specifically, Re raises the yield strength of NbTiZr by 300 MPa at RT and 340 MPa at 800 °C, and though the increment is only 27 MPa at 1200 °C, this still represents a 46% increase relative to the yield strength of the NbTiZr ternary. By contrast, Re had very little effect on the yield strength of TaTiZr over the full range of temperatures tested here. Re addition to TaTiZr elevates the yield strength by only 45 MPa at RT, 86 MPa at 800 °C, and 8 MPa at 1200 °C, a 13% increase relative to the TaTiZr ternary yield strength.

The mechanical properties of the alloys studied here may have been influenced by a wide range of compositional and microstructural effects, including the grain size; melting temperatures ($T_m$); solid solution hardening; and the size, shape, distribution, and type of second phases. The grain size effect can be estimated from the Hall–Petch relationship. The grain size decreases from 1000 μm in NbTiZr to 150 μm in Re$_{0.3}$NbTiZr, and using a typical Hall–Petch constant of $k_r = 400$ MPa μm$^{-0.5}$ [21], the Hall–Petch strengthening increases from ~12 MPa for NbTiZr to ~32 MPa for Re$_{0.3}$NbTiZr, a difference of ~20 MPa. Hall–Petch hardening does not appear to make a significant contribution to strengthening in Re$_{0.3}$NbTiZr. For Re addition to TaTiZr, the difference in grain sizes is 320 μm vs. 50 μm, so that the predicted Hall–Petch increment is about 34 MPa. This is roughly 75% of the strength increase at RT, so the Hall–Petch may account for much of the strengthening observed in this alloy.
The possible influence of $T_m$ on yield strength has recently been considered for RCCAs [22]. Melting temperature may influence the high temperature strength of a material, since thermally activated flow occurs above 0.56–0.70 $T_m$ (see Figure 7 in [22]). The $T_m$ values of the present alloys, taken here as the CALPHAD-predicted solidus temperatures, are rather low, ranging from about 1550 to 1725 °C. As a result, 800 °C represents 0.54–0.59 $T_m$. 1000 °C is 0.64–0.70 $T_m$, and 1200 °C is 0.74–0.81 $T_m$. The present results are broadly consistent with the earlier study, and all of the current alloys showed significant thermal softening at 800–1200 °C, with the exception of Re$_{0.3}$NbTiZr at 800 °C. The earlier study also explored a phenomenological correlation between RT yield strength and $T_m$ (see Figure 4a in [22]), and no clear trend was shown for multi-phase microstructures. In the present work, CALPHAD predictions of $T_m$ differed by less than 200 °C for all four alloys using the two different databases. This small difference in $T_m$ and the lack of a strong influence of $T_m$ on the strength in multi-phase RCCAs, suggests that this did not make a major contribution to the observed changes in the RT properties with Re additions.

The metallic atomic radius of Re ($r_{Re}$ = 137.5 pm) is smaller than all the other elements in the presently studied alloys ($r_{Nb}$ = 146.2 pm, $r_{Ta}$ = 134 pm, $r_{Zr}$ = 160.2 pm) [23,24]. Furthermore, the shear modulus of Re (G$_{Re}$ = 178 GPa) is much larger than the other elements (G$_{Nb}$ = 44 GPa, G$_{Zr}$ = 33 GPa, G$_{Ta}$ = 38 GPa, G$_{Ta}$ = 69 GPa) [25,26]. It might therefore be expected that Re could provide significant solid solution strengthening in the present alloys by local distortion of the host lattice and by localized shear modulus variations. A similar degree of strengthening might be anticipated from the lattice distortion contribution in both Re$_{0.3}$NbTiZr and Re$_{0.1}$TaTiZr, since $r_{Nb}$ = $r_{Ta}$, but a smaller effect might be speculated in TaTiZr from the shear modulus effect, since the difference between G$_{Re}$ and G$_{Ta}$ is smaller than for G$_{Re}$ and G$_{Nb}$. However, the continuous BCC phase in Re$_{0.3}$NbTiZr contains 7.5 ± 0.9% Re, while the continuous phase in Re$_{0.3}$TaTiZr has only 1.1 ± 0.1% Re. As a result, the lattice constant decreases from 0.3404 nm in NbTiZr to 0.3346 nm in Re$_{0.3}$NbTiZr, while the lattice constant of Re$_{0.3}$TaTiZr (0.3423 nm) is hardly changed and very slightly larger than that of Re$_{0.3}$TaTiZr (0.3421 nm). Re, thus, decreases the lattice constant of NbTiZr by 1.7% and increases the lattice constant of TaTiZr by less than 0.1%.

The Zr concentrations in the respective phases also contribute to these lattice constant values. Nevertheless, this simple analysis suggests that a significant degree of solid solution hardening may be provided by Re addition to NbTiZr and that only a minor change occurs when Re is added to TaTiZr. This is fully supported by the measured yield strengths. In addition to atom size and shear modulus effects, fluctuations in the stacking fault energy may also make significant contributions to solid solution hardening [27,28]. Detailed modeling is needed for more rigorous evaluation of the solid solution hardening effect and is suggested for future work.

The presence, type, size, shape, distribution, and volume fraction ($V_f$) of second phase particles is expected to provide an important contribution to mechanical properties. A detailed evaluation of these effects is beyond the scope of this work, but some simple observations can be made. As a summary, NbTiZr is nominally single phase BCC, with perhaps a small volume fraction of rather small precipitates that are difficult to detect with standard XRD, EBSD, and BSE methods (Figure 4). Addition of 10 at.% Re introduces an FCC second phase with $V_f$ = 0.14. The FCC particles are roughly equiaxed, with a size of ~5 µm, and are moderately well-distributed within grain interiors, but also show a preference for decorating grain boundaries (Figure 6). In contrast, TaTiZr is a two-phase microstructure with a continuous, Zr-rich BCC1 phase with $V_f$ = 0.49 and a well-distributed array of ~250 nm Ta-rich particles with $V_f$ = 0.51 (Figure 5). Addition of 10 at.% Re dramatically changes the size (to ~15 µm), morphology, and distribution of the second phase (Figure 10), but the volume fractions of the continuous BCC1 phase ($V_f$ = 0.53) and the second phase BCC2 particles ($V_f$ = 0.47) do not change by much from the ternary alloy. NbTiZr is the only alloy in the present study that showed a yield drop at RT. The presence of a well-distributed, small volume fraction of dispersoid-sized particles is consistent with this behavior, but more direct evidence is needed to conclude that such particles are
responsible for this observation. Previous work has shown that the strength of RCCAs at 1000 °C correlates with the \( V_f \) of a second phase at that temperature (see Figure 5a in [22]). The effect of Re additions to NbTiZr and TaTiZr are consistent with this trend. Specifically, both the second phase \( V_f \) and the strength increase with Re addition in NbTiZr, but in TaTiZr neither the strength nor the second phase \( V_f \) increase by much.

Re additions significantly changed the plastic response of the tested alloys only at RT (Figure 1). NbTiZr had a nearly constant work-hardening rate, and a total true compressive strain of 0.6 was achieved without fracture. However, Re\(_{0.3}\)NbTiZr exhibited a high initial work-hardening rate that decreased until a maximum stress was obtained at a true compressive strain of ~0.27, after which work-softening was observed. Failure occurred at a total true strain of 0.53. In contrast, TaTiZr failed soon after yield, at a total true compressive strain of ~0.025, but Re\(_{0.3}\)TaTiZr produced a relatively horizontal work-hardening response, and failure occurred at about 10% total true compressive strain. The discontinuous phases seem to be relatively non-deformable in Re\(_{0.3}\)NbTiZr (see Figure 8) and Re\(_{0.3}\)TaTiZr (see Figure 12), so that plasticity seems to be accommodated primarily by the continuous phases. The ductility decrease in Re\(_{0.3}\)NbTiZr is thus consistent with an increase in the volume fraction of the non-deformable second phase. The volume fractions of the continuous phases in TaTiZr and Re\(_{0.3}\)TaTiZr are not dramatically different, but the continuous phase in TaTiZr is very fine, certainly of sub-micron dimensions and perhaps as fine as 100 nm. This can lead to significant plastic constraint from the adjoining Ta-rich BCC2 phase. On the other hand, the size of the continuous phase in Re\(_{0.3}\)TaTiZr increases dramatically, to \( \geq 10 \) \( \mu \)m, and the resulting loss of constraint and a decrease in the volume fraction of interface areas may contribute to the increased ductility of this alloy. These subjective observations are consistent with the observed behaviors, but additional detailed work is needed to better understand the role of Re in the RT ductility of the studied alloys.

In summary, Re\(_{0.3}\)NbTiZr displays a relatively high Re concentration in the continuous, deformable phase (BCC1) and an increase in the volume fraction of a relatively non-deformable phase (FCC) relative to NbTiZr; both are consistent with an important contribution to strength and a decrease in ductility. The Re concentration of the continuous, deformable phase (BCC1) in Re\(_{0.3}\)TaTiZr is relatively low, and the volume fraction of the non-deformable phase is relatively unchanged; both supporting a small strengthening effect compared to TaTiZr. The decreased grain size in the Re-containing alloys provides only a small increment in strength; this was only a small fraction of the strengthening observed in Re\(_{0.3}\)NbTiZr, but it was a significant fraction of the strength increase in Re\(_{0.3}\)TaTiZr. The increased length scale and decreased plastic constraint of the continuous phase may contribute to the increased RT compressive ductility of Re\(_{0.3}\)TaTiZr relative to the ternary alloy.

5. Summary and Conclusions

The effect of 10 at.% Re additions on the microstructure, phase composition, and mechanical properties of NbTiZr and TaTiZr was reported and discussed in the context of CALPHAD predictions.

NbTiZr had a coarse, single-phase BCC grain structure, with an average grain size of over 1 mm. The RT yield stress was 920 MPa, and it decreased from 465 MPa to 61 MPa with increasing temperature from 800 °C to 1200 °C. Addition of 10 at.% Re caused precipitation of Re-rich particles with an FCC [likely cubic Laves (C15)] crystal structure and decreased the matrix grain size to ~150 \( \mu \)m in Re\(_{0.3}\)NbTiZr. The yield stress increased to 1200 MPa at 25 °C, 805 MPa at 800 °C, and 89 MPa at 1200 °C. Both NbTiZr and Re\(_{0.3}\)NbTiZr had good ductility at all studied temperatures.

The microstructure of TaTiZr consisted of a Zr-and Ti-rich matrix phase with an average grain size of 320 \( \mu \)m and nanometer-sized precipitates of the Ta-rich phase. Both phases have a BCC crystal structure. TaTiZr had a RT yield stress of 1670 MPa, with very low ductility. The stress considerably decreased, to 157 MPa, when increasing the temperature to 800 °C, and further to 63 MPa at 1200 °C, and the alloy became very ductile.
at 800–1200 °C. The microstructure of Re_{0.3}TaTiZr consisted of a Zr and Ti-rich BCC matrix with a grain size of ~50 µm and coarse, ~15 µm in diameter, Ta- and Re-rich second-phase (BCC) particles. The Re additions increased the yield stress to 1715 MPa at 25 °C, 243 MPa at 800 °C, and 71 MPa at 1200 °C and also considerably increased the alloy malleability at 25 °C.

Comparison of the observed and CALPHAD-calculated microstructures suggested that the limited time at lower temperatures during the controlled cooling after HIPping at 1400 °C was likely to be insufficient to achieve equilibrium. As a result, the microstructures of all four studied alloys were metastable at room temperature and represented microstructures frozen at 800–1200 °C, due to the slow diffusion of the alloying elements.

Significant strengthening in Re_{0.3}NbTiZr may be expected from solid solution hardening and from formation of an important volume fraction of a relatively non-deformable second phase. Neither of these effects are expected to make significant contributions to strengthening in Re_{0.3}TaTiZr. A small contribution from the Hall–Petch effect may account for much of the strengthening observed in this alloy. Improved RT ductility of Re_{0.3}TaTiZr relative to the ternary alloy may result from the loss of plastic constraint, due to coarsening of the continuous, deformable secondary phase.

**Supplementary Materials:** The following are available online at https://www.mdpi.com/article/10.3390/met11111819/s1, Figure S1: (a) An electron image, and (b–d) EBSD phase maps of BCC (I4/mmm, sky blue color), (b) FCC (Fm3m or Fd3m, blue), (c) sigma (P4_3/mmm, dark red, not identified), and (d) hexagonal Laves (P6_3/mmc, brown) phases. Black dots and areas correspond to zero solution. Figure S2: (a) TEM image of the second phase particle. (b) Combined selected area diffraction pattern (SADP) from the FCC particle (zone axis is [110]) and BCC matrix (zone axis [113], underlined reflections). The following orientation relationships can be identified: (220)_{FCC} || (110)_{BCC} and (Ti,Ta)_{FCC} || (211)_{BCC} and [110]_{FCC} || [113]_{BCC}. (c–e) Selected area diffraction patterns from the second-phase particle in zone axes (b) [112], (c) [323], and (d) [111]. (f) A convergent-beam [111] zone axis pattern from the second-phase particle indicating 3 m symmetry. Figure S3: Re_{0.3}TaTiZr in annealed condition. (a) Forward scatter electron image and (b–f) respective EBSD maps of (b) band contrast, (c) phase map (red is BCC) with outlined grain boundaries; (d) combined phase map and SEM image; (e) combined inverse pole figure (IPF) orientation map of the BCC phase and particles BCC (red) phases with outlined grain boundaries; and (f) the same as (e) combined with the respective SEM image. Figure S4: Phase fraction and phase composition as a function of temperature for equilibrium solidification of the Re_{0.3}NbTiZr alloy, predicted using Thermo-Calc and the TCHEA4.1 databases. Horizontal dashed lines draw boundaries between different phase regions. Phases in these regions are indicated in the figure. Figure S5: equilibrium phase diagrams of Re_{0.3}NbTiZr calculated using Pandat software and the PanNb2020 database: (a) temperature dependence of the volume fraction of the equilibrium phases. (b–d) Temperature dependence of the concentration of the alloying elements (in mole fractions) in (b) BCC1, (c) Laves (C14), and (d) BCC2 phases. Horizontal dashed lines draw boundaries between different phase regions. Phases in these regions are indicated in the figure. Figure S6: phase fraction and phase composition as a function of temperature for equilibrium solidification of the Re_{0.3}TaTiZr alloy, predicted using Thermo-Calc and the TCHEA4.1 database. Horizontal dashed lines draw boundaries between different phase regions. Phases in these regions are indicated in the figure.

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References


10. Scheil, E. Bemerkungen zur Schichtkristallbildung. Z. Met. 1942, 34, 70–72. [CrossRef]


28. Rao, S.I.; Akdim, B.; Antillon, E.; Woodward, C.; Parthasarathy, T.A.; Senkov, O.N. Modeling solution hardening in BCC refractory complex concentrated alloys: NbTiZr, Nb1.5TiZr0.5 and Nb0.5TiZr1.5. Acta Mater. 2019, 168, 222–236. [CrossRef]