Microstructure and phase stability of multi-phase alloys in refractory-metal base systems

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Introduction

The higher operation temperatures are pursued for gas turbines in order to obtain higher efficiency. Higher operation temperatures require high-temperature materials that can serve in the severe environment. The conventional Nickel-base superalloys are mostly widely used high-temperature structure materials because of the good combination of chemical resistance and mechanical properties. However, this class of materials will soon reach the limits of application and cannot meet the increasing demand of structural materials that can operate at higher temperatures due to the relatively low melting temperature. The refractory metals, especially Nb and Mo, which have relatively low density and high melting temperatures, are one of the candidates. However, these metals are susceptible to oxidation at high temperature. On the other hand, intermetallic compounds are also very attractive as high temperature structural materials because of their high melting temperature and superior high-temperature strength.

The AB2-type intermetallic Laves phases with topologically close-packed (TCP) structures have been considered for high-temperature structural materials, because of their high melting points and attractive mechanical properties at elevated temperature [1-3]. Although the concept of ductile phase toughening has been applied to improve their room temperature toughness of some alloys including Nb/NbCr2 and Cr/TaCr2 [4], the strength of the ductile phase, mostly the BCC structure for refractory-metal based materials, is not adequate at high temperatures [5]. The mechanical properties of two-phase alloys are strongly dependent on the morphology, volume fraction and the orientation relationship (OR) of the second phase. However, it is difficult to control the microstructure of two-phase alloys composed of Laves and ductile phases, especially in binary systems, because for almost all of the binary Laves systems, the dual phase is obtained by a eutectic reaction because many Laves phases are in equilibrium with the ductile BCC phase with a limited solid solubility, which is insufficient for the large volume fraction of Laves phase precipitation.

To overcome this trade-off relationship, a new BCC1/BCC2/Laves three-phase alloy is put forward. It is intended to introduce second BCC phase with a fine structure to bring the BCC1/BCC2 interfaces into the conventional single ductile phase. Similarly with Ni-based γ/γ’ alloys, high-temperature strength and creep resistance might be improved by the microstructure modification. In the meantime, AB2 Laves phase dispersed in the BCC1/BCC2 two-phase microstructure. Hence, in this aspect, the BCC1/BCC2/Laves three-phase alloys with a complicated structure is proposed. Besides, good high-temperature strength, as well as high microstructure stability, can also be expected.

To control the microstructure and avoid the aggregation of Laves phase, the Cr-Mo-Nb ternary system is selected to study the three-phase alloy. The existing two BCC phases provides higher strength than the singe BCC phase and a fine and stable structure can be obtained at high temperature by adjusting the lattice mismatch between the two BCC phases. The fine structure can restrain the growth of Laves phase and prohibit the crack propagation in Laves phase, thus improve the toughness of the alloy at low temperature. In this study, the isothermal sections of the ternary phase diagrams in Cr-Mo-Nb were investigated. The Lave phase precipitation behavior was studied in both Laves/BCC two-phase alloy and BCC1/BCC2/Laves three-phase alloy. The microstructure evolution of the three-phase alloy was observed and room temperature mechanical properties were evaluated. The effect of Si on the stability of Laves phase was also investigated.

Experimental procedures

1
All the alloys investigated in this study were prepared by NEV-AD03 arc melting furnace with a MRHP-300 (9-1) TIG welding power supply under an argon atmosphere. The purities of the raw materials (The Nilaco Corporation) were 99.9 wt% Nb, 99.99 wt% Cr, and 99.95 wt% Mo, respectively. 99.9 wt% Si was also employed to study the effect of Si on the stability of Laves phase. The nominal compositions of the tested alloys are shown in table 1.

<table>
<thead>
<tr>
<th>Alloy No.</th>
<th>Cr</th>
<th>Mo</th>
<th>Nb</th>
<th>Si</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>42.0</td>
<td>31.0</td>
<td>27.0</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>50.0</td>
<td>30.0</td>
<td>20.0</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>74.0</td>
<td>16.0</td>
<td>10.0</td>
<td>-</td>
</tr>
<tr>
<td>4</td>
<td>50.0</td>
<td>29.9</td>
<td>20.0</td>
<td>0.1</td>
</tr>
<tr>
<td>5</td>
<td>50.0</td>
<td>29.5</td>
<td>20.0</td>
<td>0.5</td>
</tr>
<tr>
<td>6</td>
<td>50.0</td>
<td>29.0</td>
<td>20.0</td>
<td>1.0</td>
</tr>
<tr>
<td>7</td>
<td>49.0</td>
<td>28.0</td>
<td>18.0</td>
<td>5.0</td>
</tr>
</tbody>
</table>

The arc-melted alloys were cut and sealed in quartz tubes using ULVAC VPC-051A vacuum pump with a vacuum degree under $2 \times 10^{-4}$ Pa and aged in different temperature conditions followed by water quenching or furnace cooling for phase equilibrium studies. In order to investigate the precipitation behavior of Laves phase in the supersaturated BCC matrix phase, solution treatment for alloys was performed in a high-frequency induction furnace (NEV-MO3C) at 1973 K, Then the solution treated samples were aged at 1473 K and other temperatures.

X-ray diffraction (XRD) (PANalytical X’Pert PRO, Cu Kα) with 20 scans from 30° to 80° were also performed on the as-cast and heat treated samples to identify the crystal structures of the constituent phases at a current of 40 mA and a voltage of 40 kV.

The microstructure was observed using field emission scanning electron microscope (FE-SEM, JEOL JXA-8530F) equipped with an electron probe micro-analyzer. Wavelength dispersive spectroscopy (WDS) was employed to determine the composition of constituent phases. An electron backscatter diffraction (EBSD) system attached in scanning electron microscope (SEM, JEOL JAMP-9500F) was used to investigate the orientation relationship between C15 Laves phase and the BCC matrix phase.

Transmission electron microscopy (TEM, JEOL JEM-2010) was employed to investigate the microstructure of the three-phase alloys heat treated at different conditions. The alloys were fabricated by (focused ion beam) FIB (JEOL JIB-4601F). Selected area diffraction (SAED) method was employed to determine the crystal structures of the constituent phases. Energy dispersive spectroscopy (EDS) in TEM was used to examine the composition of each phase.

The strength of the alloys heat-treated at different conditions is evaluated by micro hardness tester (type M, Shimadzu Seidakusho LTD.) under a load of 0.5kgf with a holding time of 30 s at room temperature. Nanoindentation test (Hysitron Ti 950) is also conducted on the sample polished by cross-section polisher (JEOL SM-09010) to assess the hardness of the constituent phases under the load of 4000 μN at room temperature. Parallelepiped compression samples with a dimension of $3 \times 3 \times 6$ mm were cut from the aged buttons by a wheel cutter and mirror-polished. Compression tests with an initial strain rate of $1 \times 10^{-4}$ s⁻¹ were conducted by Instron 5584 tester at room temperature.

**Results and discussion**

*Laves precipitation behavior*
Homogenous structures were obtained for three alloys (#1-3) at 1973 K, as shown in Fig. 1(a,c,g), which was determined to be single BCC phase. After subsequent annealing at 1473 K, each of the three alloys had different precipitation morphologies, as shown in Fig. 1(b,d,e,f,h). Gray precipitates appear at the GBs and cellular structures are formed in alloy #1, while precipitates appear not only at the GBs but also in the grain interior in alloy #3 in which the needle-like precipitates tend to grow in certain directions. The precipitates in both alloys were confirmed to be Laves phases. In alloy #2, BCC phase decomposes into two BCC phases (BCC$_1$ and BCC$_2$) during 12 h heat-treatment in a manner of a lamellar-like structure, then blocky gray Laves phase appears in sample heat-treated for 100 h ((e,f)). It is noteworthy that the Laves phase in alloy #2 seems to be surrounded by bright BCC$_2$ phase.

Fig. 1. Microstructure of alloy #3 (a,b), alloy #2 (c-f), and alloy #1 (g,h) heat-treated at different conditions. 
(a), (c) and (g): solution-treated at 1973 K for 1 h. 
(b), (d), (e), (f) and (h): heat-treated at 1473 K for various duration after the solution treatment.

The lattice misfit ($\delta$) between two planes of matrix (α) and precipitate (P) can be estimated with the planar disregistry proposed by Bramfitt [6] as:

$$\delta_{(hkl)\alpha}^{(hkl)P} = \sum_{i=1}^{3} \left\{ \frac{d_{[uvw]}[\alpha] \cos \theta - d_{[uvw]}[P]}{3d_{[uvw]}[P]} \right\} \times 100 \quad (1),$$

where (hkl)$_\alpha$ are the low-index planes of the BCC matrix and C15 precipitate, [uvw]$_\alpha$ are the low-index directions in (hkl)$_\alpha$, $d_{[uvw]}[\alpha]$ are the interatomic spacing along [uvw]$_\alpha$. $\theta$ is the angle between the [uvw]$_\alpha$ and [uvw]$_P$.

The atoms of the three matched BCC/C15 interfaces are illustrated in Fig. 2. the lattice misfit for the other alloys were determined, as presented in table 2. The orientation relationship (OR) of NbCr$_2$ in BCC matrix among BCC/Laves two-phase alloys and Cr-rich BCC$_1$/Mo-rich BCC$_2$/Laves three-phase alloy is different at 1473 K; OR 1: (011)BCC // (111)C15, [011]BCC // [110]C15 and OR 2: (411)BCC // (111)C15, [011]BCC // [110]C15 with low lattice mismatch are both
observed in Cr-rich alloys #3 and #2. OR 3: (011)BCC // (111)C15, [̅11̅1]BCC // [01̅1]C15 with a relatively larger lattice mismatch is only observed in alloy #2, which may be due to the presence of BCC1 and BCC2 interphases formed after BCC decomposition. Only discontinuous precipitation is observed at grain boundaries in alloy #1 without obvious OR.

![Fig. 2. Atomic matching at three BCC/C15 interfaces.](image)

**Table 2** Lattice misfit $\delta$, between C15 NbCr$_2$ and the BCC matrix.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>$\delta/%$</th>
<th>OR1</th>
<th>OR2</th>
<th>OR3</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>6.54</td>
<td>6.54</td>
<td>8.78</td>
<td></td>
</tr>
<tr>
<td>2-BCC$_1$</td>
<td>6.52</td>
<td>6.52</td>
<td>8.80</td>
<td></td>
</tr>
<tr>
<td>2-BCC$_2$</td>
<td>8.48</td>
<td>8.48</td>
<td>13.53</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>8.75</td>
<td>8.75</td>
<td>14.27</td>
<td></td>
</tr>
</tbody>
</table>

**Microstructure Evolution**

Figure 3(c)-(f) show TEM images of the alloy aged for 12 h, and SAED patterns for the original supersaturated BCC structure and the BCC$_1$/BCC$_2$ structure, which correspond to the original BCC area (A in 错误!未找到引用源。 (c)) and BCC$_1$/BCC$_2$ two-phase area (B in 错误!未找到引用源。 (c), and the magnified view in 错误!未找到引用源。 (d)), respectively. The supersaturated BCC single-phase solid solution alloy obtained by homogenization at 1973 K for 1 h underwent microstructural evolution during heat treatment at 1473 K. Intragranular nucleation of the Cr-rich BCC$_1$ phase occurred, which led to the formation of an alternating BCC$_1$/BCC$_2$ two-phase microstructure through a discontinuous precipitation process, followed by nucleation of the Laves phase at the BCC$_1$/BCC$_2$ interphase boundaries. The growth of the Laves phase in BCC$_1$/BCC$_2$ two-phase areas consumes the Cr-rich BCC$_1$ phase in the vicinity.

**Mechanical properties**

The mechanical properties of alloys heat treated at 1473 K for various periods after the solid solution treatment were also investigated. The highest fracture compressive strength of 1493 MPa and minimum hardness of 773±7 HV were obtained for the alloy aged for 24 h, where the BCC$_1$/BCC$_2$ two-phase microstructure dominates. The Vickers hardness of the alloy aged for 72 h with a fine structure including the Laves phase was 839±8 HV under a load of 0.5 kgf, as shown in Fig. 4 and no obvious microcracks were observed. As shown in Fig. 5, a minimum hardness and a highest fracture strength of 1493 MPa are obtained for the alloy aged at 1473 K for 24 h where the two BCC phases dominate the microstructure.
Fig. 3 TEM analyses of alloys aged at 1473 K for (a) 3 h, (b) 6 h, (c,d) 12 h, and (g,h) 100 h. SAED patterns for (e) region A in panel (c), (f) region B in panel (c), (i) region SA in panel (g), and (j) region SA in panel (h).

Fig. 4. (a) Vickers hardness for alloy #2 as function of aging time at 1473 K, and (b) hardness of each phase measured by nanoindentation.
**Effect of Si on the stability of Laves phase**

Silicon has been chosen to add to the Cr-Mo-Nb system to study the stability of NbCr$_2$ Laves phase. It is found that the amount of Laves phase in as-cast increases with the increase of the Si addition. In 1973 K heat-treated alloys with 0.5Si and 1Si, Laves phase still exists as shown in Fig. 6. It is also found that Si is enriched in NbCr$_2$ phase and Mo is also tend to be distributed into the Laves phase. It indicates that NbCr$_2$ is relatively stabilized with Si addition and the solvus line of BCC moves towards Mo-rich direction, as presented in Fig. 7.

**References**