INFLUENCE OF BORON ADDITIONS ON
PHYSICAL AND MECHANICAL PROPERTIES
OF ARC-MELTED TUNGSTEN AND
TUNGSTEN - 1 PERCENT TANTALUM ALLOY

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The effects of boron additions on the physical and mechanical properties of arc-melted tungsten and a tungsten-1 percent tantalum alloy were investigated. Boron additions significantly refined the as-melted grain size of tungsten. The 1-hour recrystallization temperature was initially increased by small boron additions (approx. 0.01 atomic percent boron), after which it decreased continuously with increasing boron content. High-temperature tensile tests showed that the boron additions produced an initial rapid rise in strength followed by a leveling off of the strength-composition curve. Boron in solid solution was postulated to be the cause of the rapid increase in strength.

INTRODUCTION

The technology of arc-melted tungsten and its alloys has been limited by the lack of forgeability of the as-melted ingots. This deficiency has been ascribed in part to the relatively large columnar grain size of the ingots. This coarse structure must be broken down by extrusion prior to conventional forging and rolling operations (ref. 1). In addition, grain growth in arc-melted tungsten occurs very rapidly at the contemplated use temperatures (ref. 2), which are generally above 3500°F. Finding a method to refine the as-melted grain size of tungsten and stabilize it against subsequent grain growth at elevated temperatures thus seems desirable.

The most successful method of achieving fine as-melted grain sizes in tungsten appears to be alloying. Attempts at this procedure have resulted in some grain refinement by most of the alloy additions studied previously (refs. 3 to 5). The most potent grain refiner for tungsten, however, appears to be boron. In addition, it has been demonstrated that as little as 0.005 atomic percent boron is sufficient to decrease the grain growth rate in tungsten by three orders of magnitude in the temperature range 3500°F to 4200°F (ref. 6).
approximately 4700° F and contains 23 atomic percent boron.

Few attempts, however, appear to have been made to characterize fully tungsten-boron alloys with respect to both their fabricability and their subsequent mechanical properties. The present investigation was directed toward a study of the influence of boron in the range 0.01 to 7.8 atomic percent on these properties. In addition, two ternary tungsten-tantalum-boron (W-Ta-B) alloys were melted to investigate the secondary influence of a typical solid-solution strengthen on the W-B binary. A portion of this work on both the W-B and the W-Ta-B alloys has appeared elsewhere (ref. 8).

EXPERIMENTAL PROCEDURE

The alloy compositions are given in table I. They were prepared by vacuum consumable arc melting of pressed and sintered electrodes compacted from elemental tungsten, boron, and tantalum powders. Details of these techniques are given in earlier reports (refs. 2, 6, and 8). The resulting ingots, measuring 2 or 2\textfrac{1}{2} inches in diameter were fabricated by extrusion, swaging, and rolling as shown in table I. The ingots were extruded either in a conventional hydraulic press or in the high-energy rate Dynapak. Extrusion temperatures varied from 2700° to 4180° F, and reduction ratios varied from 6 to 10 with a die angle of 120°. Some of the ingots were canned in 0.1-inch-thick molybdenum sheet.
### TABLE I. - CONSOLIDATION AND FABRICATION CONDITIONS

<table>
<thead>
<tr>
<th>Amount of boron</th>
<th>Interstitial analyses, ppm (a)</th>
<th>As-melted Vickers hardness (10-kg load)</th>
<th>As-melted grain size, cm</th>
<th>Extrusion temperature, °F</th>
<th>Reduction ratio</th>
<th>Swaging conditions</th>
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<td>(c)</td>
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<td>(c)</td>
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</table>

**Binary tungsten-boron alloys**

**Ternary tungsten - 1 atomic percent tantalum - boron alloys**

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(a) Analysis on extruded or swaged rod.
(b) Dynapak extruded.
(c) Not determined.
(d) Conventional hydraulic press extruded.
(e) Clad in 0.100-in. thick molybdenum sheet.
(f) Dendritic structure; grain size represents size of dendritic cells.

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All the alloys were satisfactorily extruded with the exception of tungsten - 7.8 percent boron, which disintegrated during an attempt at Dynapak extrusion. (All compositions are given in atomic percentages.)

Annealing treatments for recrystallization studies at temperatures up to 3200°F were conducted in a hydrogen-atmosphere induction-heated tube furnace. Annealing treatments above 3200°F were conducted in a vacuum furnace (5×10⁻⁵ mm Hg) with a tantalum or tungsten resistance heater. Temperatures up to 3200°F were measured with a tungsten - tungsten-26 percent rhenium (W - W-26Re) thermocouple placed on the specimens and are believed accurate to ±10°F. Temperatures above 3200°F were measured optically and are estimated to be accurate to ±25°F. The fraction recrystallized was measured by point counting and the average grain diameter by a line intercept method.

Tensile and creep tests were performed in vacuum, and temperature was measured with a W - W-26Re thermocouple tied to the center of the gage length. The gage diameter was 0.14 or 0.16 inch, and the gage length was 1 inch. The crosshead speed was 0.005 inch per minute to yield and 0.05 inch per minute from yield to fracture. More complete details of the testing procedures are documented in reference 2.
RESULTS AND DISCUSSION

**Ingot metallography.** Photomicrographs were taken of cross sections of slices from the tops of seven of the nine as-melted tungsten-boron alloy ingots (fig. 2). No precipitate was observed in the W - 0.01 percent B alloy (fig. 2(a)). In the alloy W - 0.03 percent B, a precipitate, presumably W₂B, was observed at the grain boundaries (fig. 2(b)). The specks within the grains in both alloys are etch pits and micropores. Increasing the boron content resulted in a general increase in the volume fraction of the boride phase (figs. 2(c) to (h)). The distribution of the phase, however, varied with boron content. In the W - 0.25 percent B alloy, the boride was present as a Widmanstätten precipitate within the grains (figs. 2(c) and (d)) in addition to the grain boundary film and round intragranular particles seen in the alloys containing 0.03 to 1.69 percent B. The microstructure of the W - 0.1 percent B alloy (not
shown) was similar to that of the W - 0.25 percent B alloy. Increasing the boron content to 0.47 and 0.67 percent (figs. 2(e) and (f)) increased the amount of intergranular boride film and spherical intragranular boride particles, but no Widmanstätten precipitate was observable. Similar changes in the character of the boride have been noted by other investigators (ref. 7). At higher boron contents (1.7 and 7.8 percent B), dendritic structures were observed as shown in figures 2(g) and (h). In addition, in the W - 7.8 percent B alloy (fig. 2(h)), a pronounced fine interdendritic eutectic was visible at high magnifications in the dark phase.

From the W-B phase diagram (ref. 7) as reproduced in figure 1 (p. 2), alloys with greater than approximately 0.2 percent B (the maximum solubility of boron in tungsten) should show a eutectic phase, while alloys with compositions below this amount should not. The black phase at the grain boundaries in figures 2(e) and (f) corresponds to the expected eutectic, since the grain boundaries in these alloys are rounded and thus imply liquid contact during solid-
ification. The round intragranular particles probably precipitated from the solid state because of a decreasing solubility of boron in tungsten at temperatures in the vicinity of the eutectic temperature and spheroidized after solidification of the eutectic.

With regard to the solid solubility limit, the present work shows that no precipitate was observed in the W - 0.01 percent B alloy at magnifications up to 1500, while a precipitate was observed at 0.03 percent B. The phase diagram in reference 7 gives the solubility at 1832° F as 0.1 percent. Although comparison of the present results with the phase diagram is not strictly valid since the cooling of the ingot occurs under nonequilibrium conditions, the present results do suggest that the microstructures are representative of a temperature lower than 1832° F or, more likely, that the solubility at temperatures in the vicinity of 1832° F is much lower than the 0.1 percent reported in reference 7.

The intragranular boride in the W - 0.25 percent B alloy evidently precipitated entirely from the solid state and its Widmanstätten character suggests a lower temperature precipitation than the precipitation of boride in the higher boron content alloys. The Widmanstätten phase was observed in the W - 0.1 percent B alloy also but not in the W - 0.03 percent B alloy. In addition, a Widmanstätten phase was also observed in the W - 1 percent Ta - 0.22 percent B alloy (not shown in the figures). This type of precipitation thus appears to be a characteristic of alloys containing between about 0.03 and 0.25 percent B, which is approximately the solid solubility limit as determined in reference 7. The nature of this phase, its habit plane, and the temperature ranges where it precipitates, however, are not derivable from the limited observations made in this study.

Grain refinement in as-melted ingots. - The average ingot grain diameter is plotted in figure 5 as a function of boron content. Boron appreciably refined the as-melted grain size of tungsten. For example, 0.67 percent B decreased the grain size of unalloyed tungsten from 0.175 to 0.037 centimeter. At 1.7 percent B, an array of polyhedral grains was no longer observed, and the measured grain diameter was determined as the dendritic cell size.

The decrease in grain size with increasing boron content suggests that grain refinement occurred by "constitutional supercooling." Constitutional supercooling is a direct consequence of the difference in solubility of a given solute in the liquid and in the solid (refs. 9 and 10). It is found in those systems in which the liquidus temperature decreases with increasing solute content. Thus, in order for the solid to freeze, solute must be rejected to the liquid, and as this process is slower than the rate of heat extraction by the mold walls, the rate of advancement of the solid-liquid interface is slow. This process eventually leads to a reduced as-cast grain size. Solutes which have a low value of the distribution coefficient, that is, the ratio of the solubility in the solid to that in the liquid, thus tend to be effective grain refiners (ref. 10).

The maximum distribution coefficient for the W-B system was calculated from the phase diagram as 9.1x10^-5. This value would result in a solute concentration in front of the solid-liquid interface of approximately 100 times
that of the bulk liquid and would be expected to produce a substantial decrease in the rate of the advance of the solid-liquid interface.

Further evidence for the mechanism of constitutional supercooling is the transition from a polyhedral to a dendritic mode of solidification at 1.7 percent B (fig. 2(g), p. 5). This transition has been found previously to be a feature of alloys which solidify by constitutional supercooling (ref. 11). During solidification, a large amount of solute occupies the region adjacent to the solid-liquid interface. At compositions where this buildup of solute is such that it becomes more and more difficult to diffuse this solute away from a planar solid-liquid interface, the interface breaks into the dendritic type and thus produces more surface area and, hence, a larger number of sites for the solute to reside.

Forgability studies. - Cylinders measuring 3/4 inch in diameter and 5/8 inch high were spark-machined from selected W-B alloys and an ingot of unalloyed tungsten. They were heated to 2400° to 2800° F in hydrogen and rapidly transferred to a drop hammer, where they were deformed approximately 50 percent in two to four blows, with intermediate heating between blows. Photographs of the forged cylinders are shown in figure 4. Forging by this technique could not be performed without the appearance of a large amount of edge cracking in the cylinders. The amount of cracking did not appear to be dependent upon temperature in the narrow range studied. The edge cracking was at a minimum for the W - 1.7 percent B alloy, which corresponded to the fine celled (0.007 cm) dendritic structure shown in figure 2(g)(p. 5). Metallographic examination of sections of the forged cylinders showed that the edge cracks were confined mainly to the surface. No forging experiments were performed on the W-Ta-B alloys.

If these results are combined with the extrusion data in table I(p. 3) can be seen that there was no systematic dependence of the fabricability on
Boron content (0.01 to 1.7 percent B) or grain size. The only instance where a lack of fabricability was noted was in the W - 7.8 percent B alloy, which disintegrated during an attempt to extrusion by the Dynapak method. This failure was probably due to the rapid input of energy in this process, which caused the temperature of the billet to exceed the eutectic temperature in the tungsten-boron system and consequently melt along the grain boundaries. This conclusion was borne out by the observation of a glassy coating on the surface of the pieces remaining from this extrusion.

Recrystallization and grain growth. Samples of the W-B and W-Ta-B alloys which had been swaged approximately 60 to 90 percent after extrusion were annealed for 1 hour in the temperature range 2400° to 4200° F. The samples were metallographically prepared, and hardness (10-kg load), grain size, and the fraction recrystallized were measured on each specimen. These data are given in table II.

The recrystallization temperature, defined as the temperature at which the structure was 50 percent recrystallized in 1 hour, is plotted in figure 5 as a function of boron content for both binary W-B and ternary W-Ta-B alloys. Boron additions produced an initial rapid increase of the recrystallization temperature from an average value of 2700° F for unalloyed arc-melted tungsten of a similar percentage reduction (ref. 2) to 3140° F for the W - 0.01 percent B alloy. Increasing the boron content then produced a continuous decrease in the recrystallization temperature to 2630° F for the W - 0.67 percent B alloy. The recrystallization temperature for the W-Ta-B alloys behaved in a fashion similar to that of the binary W-B alloys. The recrystallization temperature decreased from 3000° F for a non-boron-containing W - 1 percent Ta alloy (unpublished data) to 2800° F for the alloy containing 1.11 percent B. The recrystallization...
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<th>Annealing condition</th>
<th>Fraction recrystallized</th>
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The temperature of the W-Ta-B alloys was higher than that of similar binary W-B alloys, which reflected the effect of tantalum in solid solution.

Specimens of alloys of tungsten with 0.25, 0.59, and 0.67 percent boron were also annealed at 2700° F for times up to 4 hours. The fraction recrystallized and hardness are plotted in figure 6 as functions of time. In figure 6(a), the resistance to recrystallization decreases as the boron content is increased from 0.25 to 0.67 percent boron. In figure 6(b), maximum hardness is observed during the early stages of recrystallization. The maximum hardness is of the order of 4 to 10 percent greater than that for the as-swaged material. The initial increase in hardness on annealing at 2700° F (fig. 6(b)) may be a strain aging phenomenon, involving the precipitation of fine boride particles on dislocations and/or subgrain boundaries. Such hardness maxima have been observed previously in relatively impure tungsten wire (ref. 12) and in iron-manganese alloys (ref. 13).

The initial increase in recrystallization temperature at low boron contents is probably due to boron in solid solution. Boron in solid solution in tungsten reduces the grain boundary migration rate of unalloyed tungsten by three orders of magnitude (ref. 6). This decrease in the grain boundary migration rate by dissolved solutes is similar to that observed in other alloy systems (refs. 14 and 15). Explaining the decrease in recrystallization temperature observed upon adding additional boron, however, requires that the nucleation aspect of recrystallization be considered. Leslie, Peclety, and Michalak (ref. 14), for example, found that an air-melted low-carbon steel (0.06 weight percent) had a faster rate of recrystallization than higher purity vacuum or zone melted iron. They attributed this fact to a greater number of nucleation sites in the low-carbon steel, which could outweigh any decrease in the boundary migration rate caused by the higher solute content in the steel.
Figure 6. - Effect of annealing time at 2700°F on recrystallization and hardness of tungsten-boron alloys.
In the case of the tungsten-boron alloys, the observed borides had particle sizes ranging from 1 to 8 microns. During the deformation of these alloys, gross dislocation entanglements are believed to be formed in the vicinity of the boride particles in an effort to maintain strain continuity. Such dislocation entanglements near included particles have been observed in a variety of materials (refs. 16 and 17). This localized region of high strain energy may act as a preferred nucleation site for a recrystallized grain during subsequent annealing.

Metallographic studies conducted on the tungsten-boron alloys revealed the important feature shown in figure 7. Colonies of recrystallized grains clustered around two boride particles (see arrows) suggest that the grains were nucleated by the particle or in the region immediately adjacent to it. English and Backofen (ref. 18) also observed a similar type of particle-nucleated recrystallization in hot-worked silicon iron. The large boride particles thus appear to be responsible for the decrease in recrystallization temperature by acting as preferred nucleation sites.

Figure 8 shows the effect of temperature and boron content on the ultimate tensile strength of the binary W-B alloys. An initial rapid increase in strength as small amounts of boron were added was observed and was followed by a flattening of the strength-composition curves to an almost constant value at higher boron contents. The strength increase by the addition of 0.03 percent boron (the lowest boron content tested) was 50 percent at 2500°F, 47 percent at 3000°F, and 20 percent at 3500°F.

The addition of tantalum to selected W-B alloys produced additional strengthening (fig. 9). For example, the strength at 3500°F of a W - 0.22 percent B alloy (interpolated from the curve in fig. 6) was 13,000 psi. The addition of 1 percent tantalum increased the tensile strength to 18,600 psi. Increasing the boron content to 1.11 percent in the W - 1 percent Ta alloy did not appreciably alter the strength, in agreement with the trend observed in the binary alloys. In addition, the swaged W-Ta-B alloys which were tested at 3000°F had approximately the same strength as the annealed specimens. These alloys recrystallized during testing at 3000°F; the low resistance to recrystallization.
**Table III. High-Temperature Tensile Properties of Binary Tungsten-Boron Alloys**

<table>
<thead>
<tr>
<th>Annealing Condition</th>
<th>Test Temperature, °F</th>
<th>0.2 Percent Offset Yield Stress, psi</th>
<th>Ultimate Tensile Stress, psi</th>
<th>Elongation, percent</th>
<th>Reduction in Area, percent</th>
<th>Average Grain Diameter, cm</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Tungsten - 0.03 percent boron</strong></td>
<td>3600</td>
<td>1</td>
<td>2500</td>
<td>31 500</td>
<td>28</td>
<td>&gt;88</td>
</tr>
<tr>
<td></td>
<td>3000</td>
<td>12 520</td>
<td>20 650</td>
<td>48</td>
<td>&gt;88</td>
<td>.0097</td>
</tr>
<tr>
<td></td>
<td>3500</td>
<td>5 630</td>
<td>11 520</td>
<td>42</td>
<td>&gt;88</td>
<td>.0097</td>
</tr>
<tr>
<td><strong>Tungsten - 0.10 percent boron</strong></td>
<td>As extruded</td>
<td>2500</td>
<td>15 520</td>
<td>33 000</td>
<td>38</td>
<td>86</td>
</tr>
<tr>
<td></td>
<td>3000</td>
<td>8 170</td>
<td>21 820</td>
<td>76</td>
<td>&gt;88</td>
<td>------</td>
</tr>
<tr>
<td></td>
<td>3500</td>
<td>4 480</td>
<td>13 190</td>
<td>79</td>
<td>&gt;88</td>
<td>------</td>
</tr>
<tr>
<td></td>
<td>4000</td>
<td>3 170</td>
<td>7 730</td>
<td>88</td>
<td>&gt;88</td>
<td>------</td>
</tr>
<tr>
<td><strong>Tungsten - 0.25 percent boron</strong></td>
<td>3600</td>
<td>1</td>
<td>2500</td>
<td>18 000</td>
<td>34 430</td>
<td>33</td>
</tr>
<tr>
<td></td>
<td>3000</td>
<td>6 030</td>
<td>24 700</td>
<td>62</td>
<td>98</td>
<td>.006</td>
</tr>
<tr>
<td></td>
<td>3500</td>
<td>5 190</td>
<td>13 220</td>
<td>62</td>
<td>82</td>
<td>.006</td>
</tr>
<tr>
<td><strong>Tungsten - 0.47 percent boron</strong></td>
<td>As extruded</td>
<td>2500</td>
<td>17 000</td>
<td>36 900</td>
<td>36</td>
<td>73</td>
</tr>
<tr>
<td></td>
<td>3000</td>
<td>------</td>
<td>27 500</td>
<td>- -</td>
<td>- -</td>
<td>------</td>
</tr>
<tr>
<td></td>
<td>3500</td>
<td>6 520</td>
<td>15 300</td>
<td>61</td>
<td>96</td>
<td>------</td>
</tr>
<tr>
<td><strong>Tungsten - 0.59 percent boron</strong></td>
<td>3600</td>
<td>1</td>
<td>2500</td>
<td>13 090</td>
<td>32 100</td>
<td>31</td>
</tr>
<tr>
<td></td>
<td>3000</td>
<td>8 110</td>
<td>25 300</td>
<td>50</td>
<td>94</td>
<td>.0085</td>
</tr>
<tr>
<td></td>
<td>3500</td>
<td>6 500</td>
<td>13 100</td>
<td>88</td>
<td>98</td>
<td>.0085</td>
</tr>
<tr>
<td><strong>Tungsten - 0.67 percent boron</strong></td>
<td>3600</td>
<td>1</td>
<td>2500</td>
<td>8 670</td>
<td>34 200</td>
<td>56</td>
</tr>
<tr>
<td></td>
<td>3000</td>
<td>11 130</td>
<td>26 900</td>
<td>75</td>
<td>98</td>
<td>.0054</td>
</tr>
<tr>
<td></td>
<td>3500</td>
<td>6 570</td>
<td>14 360</td>
<td>84</td>
<td>98</td>
<td>.0054</td>
</tr>
</tbody>
</table>

aGrain diameter measured on undeformed button head of tensile specimens; value reported is an average of values for the three test temperatures.
TABLE IV. - HIGH-TEMPERATURE TENSILE PROPERTIES
OF TUNGSTEN-TANTALUM-BORON ALLOYS

<table>
<thead>
<tr>
<th>Annealing condition</th>
<th>Test temperature, °F</th>
<th>Yield stress, psi</th>
<th>Ultimate tensile strength, psi</th>
<th>Elongation, percent</th>
<th>Reduction in area, percent</th>
<th>Average grain diameter, cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tempering, °C, hr</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>As swaged</td>
<td>2500</td>
<td>43 600</td>
<td>84 300</td>
<td>13</td>
<td>69</td>
<td>Wrought</td>
</tr>
<tr>
<td></td>
<td>3000</td>
<td>14 100</td>
<td>56 900</td>
<td>57</td>
<td>56</td>
<td>0.0032</td>
</tr>
<tr>
<td></td>
<td>3500</td>
<td>8 680</td>
<td>18 600</td>
<td>87</td>
<td>98</td>
<td></td>
</tr>
<tr>
<td>Wrought</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tungsten - 1.0 percent tantalum - 0.22 percent boron</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>3200</td>
<td>24 400</td>
<td>55 600</td>
<td>31</td>
<td>79</td>
<td>0.0025</td>
</tr>
<tr>
<td></td>
<td>3000</td>
<td>14 420</td>
<td>37 900</td>
<td>60</td>
<td>53</td>
<td>0.0028</td>
</tr>
<tr>
<td>Tungsten - 1.0 percent tantalum - 1.11 percent boron</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>3600</td>
<td>20 600</td>
<td>50 000</td>
<td>50</td>
<td>76</td>
<td>0.0028</td>
</tr>
<tr>
<td></td>
<td>5000</td>
<td>16 000</td>
<td>36 500</td>
<td>79</td>
<td>87</td>
<td>0.0028</td>
</tr>
<tr>
<td></td>
<td>3500</td>
<td>9 320</td>
<td>18 300</td>
<td>87</td>
<td>94</td>
<td>0.0028</td>
</tr>
<tr>
<td></td>
<td>4000</td>
<td>5 610</td>
<td>9 420</td>
<td>147</td>
<td>97</td>
<td>0.0031</td>
</tr>
</tbody>
</table>

Recrystallization effects by large boron additions was thus substantiated. All the binary and ternary alloys exhibited high ductilities (see tables III and IV) at these temperatures, although there was no systematic variation with boron content.

Step load creep data were also obtained on four binary W-B alloys at 3500° F and at 2500°, 3000°, and 3500° F for the W - 1 percent Ta - 1.11 percent B alloy by use of the test methods described in reference 2. Figure 10 is a bar graph showing the interpolated stress at a linear creep rate of 10^-6 sec-ond^-1 at 3500° F, which corresponds to a rupture life of approximately 50 hours (ref. 2). There was a large degree of scatter in the data, and the only trends which were observed were an initial rapid increase in strength at the 0.03 percent boron level (as also noted in the tensile results) and an apparent maximum in the creep strength at low boron levels.

Figure 11 illustrates the influence of temperature on the creep strength of the W - 1 percent Ta - 1.11 percent B alloy. The stress at a rupture life of 50 hours at 2500° F was estimated from the transient creep data (ref. 2) as no steady-state creep was observed at this temperature. The creep strength for the W-Ta-B alloy was slightly higher than any of the binary W-B alloys tested (see fig. 10). The percentage increase in creep strength over that of unalloyed tungsten for this W-Ta-B alloy varied from 320 percent at 2500° F to
Figure 8. - Effect of temperature and boron content on ultimate tensile strength of arc-melted tungsten. All specimens tested in recrystallized condition; unalloyed tungsten data from reference 2.

Figure 9. - Effect of temperature on tensile strength of swaged and annealed tungsten-tantalum-boron alloys.
An attempt was made to rationalize the nature of the initial rapid strengthening by the boron additions observed in the tensile and creep tests. There are three possibilities: (1) solid-solution strengthening, (2) strengthening by a boride dispersion, or (3) strengthening by grain-size refinement. The latter effect has been noted in unalloyed tungsten (ref. 2) where the ultimate tensile strength varied by 40 percent for a grain-size change of twentyfold. The ultimate tensile strength of the W - 0.034 percent B alloy was thus compared with the strength of unalloyed tungsten of the same grain size from the plots in reference 2, and approximately 90 percent of the strengthening still remained unaccounted for. Recourse to possibility (1) or (2) must thus be made to explain the observations.

Since the solid solubility of boron in tungsten is greater than 0.1 atomic percent at temperatures greater than 2500°F (fig. 1, p. 2), the probability that boron in solid solution contributed to the observed strength is higher than that boride precipitates contributed. Strengthening by boron in solid solution will thus be considered first.

Fleischer and Hibbard (ref. 19) examined the rate of solid-solution strengthening in various alloy systems by a comparison of the shear-modulus-compensated rate of alloy
<table>
<thead>
<tr>
<th>Alloy</th>
<th>Temperature, °C</th>
<th>( \frac{1}{G} \frac{d\tau}{dc} ) (a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Substitutional alloying elements in aluminum, copper, iron, and columbium (ref. 19)</td>
<td>Room</td>
<td>0.05 - 0.10</td>
</tr>
<tr>
<td>Interstitial carbon in iron, (ref. 19)</td>
<td>Room</td>
<td>5</td>
</tr>
<tr>
<td>Interstitial nitrogen in columbium (ref. 19)</td>
<td>Room</td>
<td>2</td>
</tr>
<tr>
<td>Tungsten-boron alloys (present investigation)</td>
<td>2500, 3000, 3500</td>
<td>0.85, 0.58, 0.19</td>
</tr>
</tbody>
</table>

Values of G determined from approximate relation:
\[ G = \frac{E}{3} \] E is Young's modulus (Young's modulus from ref. 22). Shear stress \( \tau \) taken to be half the tensile stress.

and Hibbard (ref. 19) correlate the magnitude of \( \frac{1}{G} \frac{d\tau}{dc} \) with the type of lattice distortion present in the lattice due to the solute atom. High values of \( \frac{1}{G} \frac{d\tau}{dc} \) represent strengthening by tetragonal distortions induced by interstitials in solid solution, while low values suggest hemispherical distortions by substitutional atoms. The values of \( \frac{1}{G} \frac{d\tau}{dc} \) for W-B alloys are intermediate between the typical values given by reference 19 for interstitial and substitutional solid solutions (table V). There is some doubt in the literature as to whether boron occupies an interstitial or substitutional site in body-centered-cubic metals (refs. 8 and 20). It has been suggested that the boron atom may occupy both sites simultaneously. This possibility might explain the intermediate value of \( \frac{1}{G} \frac{d\tau}{dc} \) found in this investigation. Additional support for this proposition is found in reference 21 in which the data from this study are compared with data on binary tungsten-carbon alloys. Carbon has been definitely shown to be an interstitial in tungsten (ref. 8) and in contrast to the boron additions to produce an initial decrease in the strength of tungsten at 2500° to 4000° F. The initial rapid increase in strength with the boron additions thus is more suggestive of an interstitial-substitutional balance with the balance tending toward a substitutional solid solution.

In addition, there still remains the possibility that fine boride precipitates in the W - 0.03 percent B alloy may have contributed to the initial strengthening. Additions of boron of greater than about 0.25 percent, however, did not result in appreciable additional increases in strength. This lack of additional strengthening implies that the dispersion of boride existing in these alloys is not an effective strengthen and that the strength advantage of any of the tungsten-boron alloys over unalloyed tungsten is predominantly due to boron in solid solution.
CONCLUDING REMARKS

One of the main purposes for this work was to determine whether a distinct improvement in forgeability would result from grain refinement of arc-melted tungsten by boron additions. The limited studies performed showed that, although a significant amount of grain refinement of the ingot structure was effected by boron, an improvement in forgeability was not observed. It is possible that the presence of the brittle boride phase in these alloys negated the effect of the finer grain structure of the alloys and resulted in the insignificant improvements in forgeability.

CONCLUSIONS

In an investigation of the influence of boron additions on the physical and mechanical properties of arc-melted tungsten and tungsten - 1 percent tantalum alloy, the following conclusions were drawn:

1. Boron appreciably refines the as-melted grain size of arc-melted tungsten. This refinement has only a minor effect on ingot forgeability.

2. The grain refinement of tungsten by boron is due to "constitutional supercooling," which occurs because of the small distribution coefficient of boron in tungsten.

3. A boron addition of 0.01 atomic percent produced an initial rapid increase in the 1-hour recrystallization temperature. Additions of boron greater than this amount continuously decreased the recrystallization temperature because the boride particles acted as sites for nucleation of recrystallization.

4. Boron additions to arc-melted tungsten result in an initial rapid increase in the 2500° to 3500° F tensile strength followed by a leveling off of the strength-composition curve. The initial increase is presumably due to boron in solid solution. The distortion effect of boron in solid solution is intermediate between that of a substitutional and interstitial atom.

5. Tantalum additions to the binary tungsten-boron alloys raised the recrystallization temperature and increased the elevated temperature tensile and creep strength.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, October 8, 1965.
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