SUBSTRUCTURE FEATURES AND AXIS REORIENTATION OF W-RE SINGLE CRYSTALS UPON PLASMA-ARC MELTING

Kirillova V.M., Burkhanov G.S., Sdobyrev V.V.
Baikov Institute of Metallurgy and Material Science,
Russian Academy of Sciences,
Leninski pr.49 Moscow, 119991 Russia
Tel. +7(-499)+135-96-15
e-mail: genburkh@ultra.imet.ac.ru

Abstract
Plasma arc melting was used to grow large high purity W-Re single crystals in a wide concentration range (1-20wt%Re). Relationship between solidification parameters and growth structure of W-Re alloys was determined and shown as “C₀-G₀/R₁/₂” diagram. “Stripped” microstructure and crystallographic reorientation to the [100] preferable growth axis was found for (W-Re) single crystals upon growing. The narrow range of the dendritic structure and “abrupt transition” to the polycrystalline structure in the “C₀-G₀/R₁/₂” diagram for the W-Re single crystal explains the tendency to the formation of the polycrystalline structure. All these factors make the growing the perfect single crystals containing more than 1 wt% Re difficult. To produce the perfect W-Re single crystals, the following conditions should be provided: (1) using the high purity of the initial constituents and some re-melts; (2) intensive mixing the melt; (3) stable thermal conditions and regular feeding by starting alloy; (4) the growth rate must not exceed of 1, 5 mm/min at a temperature gradient of the liquid phase G of 50 deg/min.

Introduction
W-Re-alloys are characterized by maximum melting point (in comparison with other metallic alloys) and by combination of high strength and plasticity as well as creep strength at high temperatures; all these parameters allow one to use these alloys under extreme conditions [1].

High purity and single crystal structure of W-Re-alloys allows us to adequately determine chemical and physical interactions between the constituents, to detect new features of solidification. Moreover, the single-crystal structure of these alloys makes available to control their physical properties for the anisotropy. For the first time, the W-Re single crystals (in the range of substitution solid solution) have been grown by electron-beam zone melting [2, 3]; but, this method allows one to grow the single crystals of the alloys only to 10-15 mm in diameter. Commercial exploitation and more complete understanding of the structure and properties call for large single crystals.

The plasma-arc melting [3] allows one to grow large single crystals of refractory metallic alloys; they are characterized by high purity with respect to interstitial impurities( in particular, to carbon).

This paper summarizes the results demonstrating the relation between the structural features of large single crystals W-Re-alloys containing 1-20wt%Re and parameters of plasma-arc melting.

Experimental
The plasma-arc melting and setup used for growing of the large W-Re-single crystals were described in [1]. Electrical and technology parameters of the plasma-arc arc melting and composition of plasma-forming gas were varied with alloy composition; respectively, and the growth rates were 0, 5, 1, 5 and 1 mm/min. As plasma forming gas, we used argon, helium or mixture of these gases (Ar+1%He). The (W-1wt% Re), (W-5%Re), and (W-20wt% Re)-single crystals of 20mm in diameter and of 200-300mm in length had the [100]-, [110]-, and [111] orientation.
X-ray topography and light optical microscopy were used to investigate the single crystal structure of longitudinal and cross sections. For microstructure studies we used electro-polishing in 1%-NaOH water solution and chemical etching in NaOH + K3Fe(CN)6 water solution.

Results

Chemical analysis shows that the single crystals growing by the plasma-arc melting are substantially more pure (in particular, with respect to carbon) than single crystals produced by electron beam zone melting (see table).

<table>
<thead>
<tr>
<th>Melting Method</th>
<th>Impurity Content, ppm, wt</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plasma-arc</td>
<td>C 0, 2 – 0, 3 Si 5, 0</td>
</tr>
<tr>
<td>Electron beam zone</td>
<td>25, 0</td>
</tr>
</tbody>
</table>

The metallography and X-ray topography show that the structure of the W-Re- single crystal (produced by plasma-arc melting) characterized by grains elongated along the growth direction.

Small addition of Re (1 wt %) was found to increase the size of subgrains and to decrease the angle misorientation of them. With increasing Re content, the angle misorientation of subgrain and dislocation density increase. The W-5wt%Re – single crystals have subgrains of 1-5 cm in length (along the growth axis) and 1-5 mm in diameter and are characterized by 1-3° angle misorientation (Fig.1). The structural degradation of the single crystal containing more than 1 wt% Re is due to concentration super-cooling [5, 6]. Measuring the variation of the equilibrium and actual temperatures in the liquid phase with the distance from the solidification front, authors of [7] showed that the degree of concentration super-cooling in the W-Re-single crystals growing by plasma-arc melting increases with increasing Re content (more than 1wt%).

![Fig.1. Microstructure of the (W-5wt%Re) single crystal a) optical microscopy, x 500; b) X-ray topography.](image-url)
accurate following to technology parameters. Because of the concentration super-cooling, the optimum growth rate and Re-content (to obtain the perfect single crystal structure) were found to be no more than 1, 5 mm/min and 3, 5 wt%, respectively. The formation of the single crystal structure also is disrupted by twinning (typical of the W-Re-alloys) that disturbs the flat solidification front.

In addition to the data described above, there were found the following features of solidification of the large W-Re-single crystals (15-20 mm in diameter and 200 mm in length); these are the change in the direction of the growth axis or reorientation and the formation of the “stripped” structure. These features of the W-Re-single crystals should be taken into account in practice.

The reorientation consists in the progressive variation of the all growth directions to the [100] preferable growth axis. The dynamics of these changes is shown for the W-5 wt% Re-single crystals (Fig.3). For the single crystals growing from the seed with [100]-orientation, no reorientation of the growth direction was observed over the all length of the single crystal (up to 200mm) for all the growth rate used (0,5 – 4 mm/min); in this case, however, the mutual misorientation of subgrains increases to the end of the single crystal and, especially with increasing growth rate.

The W-Re-single crystals growing from the seed with the [110] and [111] orientations hold the preset orientation only within the certain distance from the seed, which is determined by the Re-content and the rate of withdrawing of the ingot, with decreasing Re-content to 1 wt%, the length of the single crystal with the seed orientation will increase by a factor of 2 in comparison with the length shown in Fig.3. The reorientation observed is due to the alloying of the single crystals. This fact is provided by the absence of the reorientation in no alloyed single crystals of tungsten (Fig.3).

The single crystals, in which the reorientation is observed upon growing, are characterized by the formation of three regions: the first region has the orientation corresponding to the seed orientation, the second region is the range of the progressively
varied orientation of the growth axis, and the third region is characterized by the [100] orientation. Substantial misorientation of subgrains in the second region leads to the formation of the polycrystalline structure. Due to competitive growth to the preferable growth of grains with the [100] orientation, the third region with the [100] orientation forms (that does not coincide with the seed orientation).

Fig.3 – Dynamics of reorientation to the [100] preferable growth axis for (W-5 wt% Re) single crystals produced at different growth rates (0.5 and 4 mm/min): 1 – no-alloyed W single crystal with any one of number of preset orientations; 2 – (W-Re) single crystal with the [100] orientation; 3 and 4 – (W-Re) single crystal with the [110] orientation; 5 and 6 – (W-Re) single crystal with the [111] orientation. (The second region is not shown).

Causes of the reorientation have been investigated in [5, 6]; these are primarily the concentration super-cooling, accumulation of impurities and alloying constituent before the solidification front. These features are especially typical of the single crystals produced by the plasma-arc melting. The concentration super-cooling also causes the formation of typical “stripped” structure observed in both longitudinal and cross sections of the W-Re-single crystals (Fig.4). This structure is alternating dark and bright strips (that are perpendicular to the growth axis) and is characterized by different density of dislocation and gas pores. The bright strips are characterized by a density of dislocations of $10^6$ sm$^{-2}$ and in these strips, the pores of 30-50µm in diameter were found; the dark strips content up to $(8-10)^5 \times 10^6$ sm$^{-2}$ dislocations.

Fig.4. “Stripped” structure of (W-5wt%Re) single crystals: a) – microstructure, x50; b) – microstructure showing pores in the bright strip, x 500.
Mechanism of the formation of the “stripped” structure have been investigated in [6] in more detail. It is known that impurities and alloying constituent accumulate at the boundaries of cells and dendrites that determine the formation of the alloy structure [5]. At these boundaries, concentration of different gas inclusions reaches maximum value and gas bubbles form. Gas bubbles were found to be a discharge for impurities accumulated before the solidification front. Thus, the super-saturation by the impurities fore the moving solidification front decreases. The solid phase entrains the gas bubbles and they remain after the interface; than, the accumulation of impurities and alloying constituent before the moving solidification front begins again. This interactive process repeats again and again during the single crystal growth and causes the formation of the alternating porous regions in the single crystal.

The average distance between the strips enriched by pores increases with increasing growth rate and mass of drop replenished the molten bath. The plasma-arc method is characterized by periodical variations of thermal conditions in the bath. Some cooling the melt upon heating and melting of the solid phase in the plasma arc leads to the increase in the momentary rate of solidification, and moving solidification front includes the gas-containing layers in the zone of the concentration super-cooling. Upon dropping liquid in the molten bath, the temperature of the molten bath increases; this leads to the decrease in the momentary rate of solidification.

It should be noted that the formation of the “stripped” structure correlates with the reorientation of the growth axis. New grains with the [100] preferable orientation generally nucleate in the layers with pores. The pores appears to provide the formation of more intricate relief of the solidification front, and thus, to facilitate the nucleation of new grains, including grains with the [100] preferable orientation.

Conclusions

The plasma-arc method allows one to produce large W-Re-single crystals (20 mm in diameter and 200 mm in length) and provides the high purity of them, in particular, with respect to interstitial impurities (carbon).

The narrow range of the dendritic structure and “abrupt transition” to the polycrystalline structure in the Co – G/R\(^{1/2}\) diagram for the W-Re single crystals explains the tendency to the formation of the polycrystalline structure. All these factors make the growing the perfect single crystals containing more than 1 wt% Re difficult.

The concentration super-cooling especially typical of the plasma-arc melting due to the structural features of the W-Re-single crystals; the reorientation of the growth axis to the [100] preferable direction and the formation of the “stripped” structure.

To produce the perfect W-Re-single crystals, the following conditions should be provided:

a) the high purity of the initial constituents and some re-melts;
b) intensive mixing the melt;
c) stable thermal conditions and regular feeding by starting alloy;
d) the growth rate must not exceed of 1.5 mm/min at a temperature gradient of the liquid phase G of 50 deg/min.
Literature References


