SPECIAL FEATURES OF STABILIZATION OF THE GROWTH PROCESS IN PLASMA-ARC GROWTH OF SINGLE CRYSTALS OF REFRACTORY COMPOUNDS FROM SHS PRODUCTS

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Problems of the stability of the growth process in growing single crystals of refractory compounds (carbides and borides of transition metals) by the method of plasma-arc remelting are considered. The main reasons behind the loss of stability of the spatial configuration of the melt (a shift of the anode lock-on of the arc from the center of the molten pool, disturbance of the symmetry of the plasma jet, superheating of the melt) are considered. The effect of cyclic perturbations in the crystallization system that appear upon replenishment on the fluctuation of the energy characteristics of the arc, the temperature of the melt, and the displacements of the crystallization surface is described. It is established that the crystallization rate and the process of coarsening of the crystallites in the formation of a columnar structure in the ingot depend on the frequency of feeding new portions and on their mass.

Among the methods of liquid-phase crystal growth, that of plasma-arc growth of single crystals provides the largest crystals of refractory compounds (carbides and borides of transition metals of groups IV – VI) [1]. The use of SHS products as a substance for remelting both in a compact form (rods) and in the form of a powder in plasma growth of single crystals makes it possible to combine the advantages of this growth technique with the advantages of a new method for preparing the initial material [2]. The growth of large single crystals in plasma-arc remelting is accompanied by considerable superheating of the molten substance and intense removal of impurities. Fabrication of initial preforms by the method of SHS is characterized by additional cleaning of the material of impurities during propagation of the deflagration wave [2 – 4]. These two factors are prerequisites for the growth of high-quality (foremost, high-purity) crystals [5, 6]. At the same time the plasma-arc method for growing single crystals is characterized by a high level of perturbation of the process parameters that affects its stability. The stability of crystal growth in plasma-arc remelting can be increased by reducing the thermal and hydrodynamic perturbations of the melt, which is achieved by using special systems for stabilizing the parameters of the process [2 – 4].

When single crystals are grown by the plasma-arc method without crucibles the stability of the growth of the crystals is strongly affected by the stability of the spatial position of the molten pool and the stability of its geometric parameters during the entire process [2 – 4]. The molten pool loses stability due to deviation of the axis of the pool from the axis of the system “plasma generator – ingot,” inclination of the pool relative to the horizontal level, and splashing of the molten pool.

Initially the molten pool deviates from the axis of “plasma generator – ingot” due to a shift of the anode lock-on of the arc from the center of the molten pool or due to disturbance of the symmetry of the plasma jet. A shift of the anode lock-on of the arc causes a stable inclination of the crystallization surface with respect to the horizontal position. The ingot grows in a direction that forms an angle with the initial axis of the ingot, which hampers formation of a single-crystal structure in the ingot and the process of its drawing.

When a rod is introduced into the plasma and during its contact with the melt in the stage of feeding, the crystallization plane is inclined relative to the horizontal level because of predominant cooling of the region of the melt closest to the feeding rod. After the rod is removed from the plasma the molten pool heats and its symmetry is restored. At $d_i/d_t \leq 2$ ($d_i$ is the ingot diameter, $d_t$ is the rod diameter) the slope of the crystallization plane can become critical (irreversible), is preserved in the pause between the feeding-in cycles, and increases with growth of the ingot. In this case the shape of the molten pool is distorted, and the vertical coordinate of the cooled edge of the ingot can exceed the level of the meniscus
Fig. 1. Diagram of the process of growth of a single crystal in plasma-arc remelting: 1) chamber; 2) crystal holder; 3) plasma generator; 4) plasma-forming gas; 5) plasma arc; 6) molten pool; 7) ingot; 8) rod obtained by SHS; 9) screen with photodiodes.

Fig. 2. Typical changes in the voltage of the arc U in cyclic feeding of a molten pool of titanium carbide \((d_i = 8\, \text{mm})\) from a rod \((d_r = 4.2\, \text{mm})\); (1 – 5) stages of the feeding cycle; \(I = 115\, \text{A}\).

As a consequence, the feeding is hampered, which disturbs the process of crystal growth. In early stages the symmetry of the temperature field in the molten pool and its initial shape can be restored by increasing the length of the pauses between feeding cycles or by rotation of the ingot.

In plasma-arc remelting the molten pool is formed in a capillary mode. The liquid refractory material is prevented from spreading only by the forces of surface tension. Under these conditions the molten pool can lose hydrostatic stability (spillage). The hydrostatic stability is disturbed when the height of the meniscus of the melt exceeds the maximum value due to superheating of the material or excessive perturbation of the melt in feeding.

The cyclic drop-by-drop feeding of the melt used in plasma remelting of the original rods affects the stability of the growth process and is accompanied by considerable fluctuation of the power characteristics of the electric arc, disturbance of the symmetry of the plasma jet, a change in the temperature of the melt, and rapid displacements of the crystallization surface. This effect of the feeding is clearly manifested at relatively low ratios \(d_i/d_r = 2 - 3\) (as a rule, \(d_i = 6 - 15\, \text{mm},\ d_r \approx 4\, \text{mm}\) \([1, 2]\). Figure 1 presents a diagram of the plasma-arc process of growth of a single crystal in remelting rods obtained by SHS. The process of feeding the remelted material into the melt can be broken into 5 successive stages, namely, (1) introduction of the rod into the plasma region accompanied by formation of a molten zone (a drop) on the end of the fed rod, (2) placement of the drop into the melt at the liquid-phase contact between the rod and the crystal, (3) subsequent breaking of this contact, (4) removal of the rod from the plasma, and (5) a pause accompanied by restoration of the symmetry of the plasma jet, the characteristics of the electric arc, the shape, and the temperature field in the molten pool.

Figure 2 illustrates the change in the voltage drop across the arc during a feeding cycle in the growth of a titanium carbide single crystal. The voltage across the arc fluctuates most when the rod makes contact with the central part of the molten pool (during separation of the drop). The variation of \(U\) with time is basically repeated for different regions of the contact between the rod and the melt and corresponds to the change in the arc length \(l_a\) during the feeding. The introduction of the rod into the plasma increases \(l_a\) and \(U\). When the rod touches the melt, the geometric shape of the molten pool changes markedly; simultaneously, the anode lock-on of the arc passes from the crystal to the rod; the considerable reduction of \(l_a\) appearing causes a substantial decrease in \(U\). When the contact between the rod and the melt is over and the rod is removed from the plasma, the voltage drop across the arc increases. During one feeding cycle a new layer of solid phase forms in the ingot, the thickness of which is determined by the mass of the portion of the material that has arrived in the melt. In fact the crystal grows during a feeding cycle in the stage when the rod is introduced into the plasma and makes contact with the melt, because in this very stage the heat flow passed from the electric arc to the melt decreases. In the stage when the rod is placed in the plasma the ingot undergoes crystallization at a mean rate \(v_1\) and the melt – crystal interface is inclined relative to the horizontal plane. In the stage of contact between the rod and the melt the ingot crystallizes at a mean rate \(v_2\). Visual observation of the displacements of the phase boundary visible on the surface of the ingot makes it possible to evaluate the order of magnitude of \(v_1\) and \(v_2\) (6 and 120 mm/min, respectively). The layer in the ingot formed as a result of one feeding cycle crystallizes at a rate 1 – 2 orders of magnitude higher than the mean rate of crystal growth \(v_g\) (\(v_g\) is the mean rate of the downward motion of the crystal holder with the ingot). In the general case the directions of crystallization of the layer in different stages do not coincide with each other or with the axis of the ingot.

When single crystals were grown from polycrystalline substrates a columnar structure grew as a result of the competitive growth of originally randomly oriented grains. When