Tantalum carbide coating via wet powder process: From slurry design to practical process tests

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ABSTRACT

TaC coatings were deposited on graphite substrates via wet powder forming and sintering to potentially achieve both a highly reliable and low-cost process. Non-aqueous solvent mixtures of TaC slurries were optimized through characterization of raw materials and a novel design guide based on Hansen solubility parameters. The optimized TaC slurries enabled the formation of high-quality TaC powder compact films with ultrahigh powder packing densities of ≥70% (ca. 85% at maximum), which contributed to prevent defect formation in the TaC coatings after sintering. The TaC-coated components were tested in practical high-temperature processes, such as AlN and SiC bulk single crystal growth processes, and a SiC device fabrication process, which confirmed sufficiently low-levels of impurity incorporation and surface contamination from the TaC layers. The novel TaC-coated graphite components will contribute to higher quality and lower cost for bulk crystal growth, device fabrication, and epitaxial film growth processes of group-III nitrides and SiC.

1. Introduction

Refractory metals and their compounds are useful for high-temperature applications such as reactor components (crucibles, susceptors, heaters, and thermal reflection shields) due to their excellent thermal stability and chemical inertness [1]. It has recently been reported that Ta and TaC components as crucibles and susceptors are suitable for SiC bulk crystal growth and chemical vapor deposition (CVD)-SiC epitaxial film growth processes [2–7], and W and TaC components are suitable for crucibles in AlN sublimation bulk growth processes [2,8–13]. However, the high prices of these components, including material and machining costs, have hampered their full-scale use in practical mass-production processes.

TaC is applicable to both SiC and nitride processes, where available production techniques and resultant components are surface-carbonized bulk Ta components [2,3], bulk TaC ceramics [14–16], and TaC-coated components (via CVD or plasma spray) [17–20]. The TaC coatings on foreign substrates, e.g. TaC-coated graphite, are particularly versatile, especially in terms of manufacturing complex-shaped components. However, whether existing TaC coating techniques and their products satisfy requirements,

i.e. both higher reliability and lower cost, has yet to be confirmed in real-world production processes and facilities.

To overcome these issues of TaC components, we have proposed highly-reliable ultrathick (ca. 100 μm) TaC coatings on graphite substrates via a potentially low-cost wet powder forming and sintering process, referred to as SinTaC [5,21]. However, the formation of dense films thicker than the critical thickness of ca. 50 μm by powder sintering have been considered to suffer from crack generation due to the stress accompanied with the sintering shrinkage of powder compact films and constraints from underlying substrates [22,23]. A thickness of ca. 100 μm was confirmed as necessary for SinTaC layers to endure highly-corrosive AlN sublimation growth conditions [21]; therefore, the critical thickness of ca. 50 μm must be surpassed to obtain highly-reliable coating without pinholes and cracks. To resolve the critical thickness issue, increased packing density (≥70%) and homogeneity of the TaC powder compact films than those of conventional powder processes are thus necessary [24].

Although the stabilization of colloidal ceramic slurries is important to enhance the packing density of resultant ceramic powder compacts [25], general rules to optimize slurry compositions are still unknown, and general techniques to apply ceramic slurries to complex-shaped substrates have yet to be confirmed.

Here we introduce Hansen solubility parameters (HSP) [26,27] as a guide to design optimized TaC slurries to achieve TaC powder compact films with ultrahigh packing densities. The opti-

mized slurries are applied to graphite substrates with various painting techniques and subsequently form ultrathick defect-free dense SinTaC layers on graphite substrates by sintering to realize complex-shaped large-sized SinTaC components on a practical level. Furthermore, SinTaC components are tested for AlN bulk single crystal growth [9–11,21,28], SiC bulk single crystal growth [5,29–31], and SiC post-implantation activation annealing [32,33] to evaluate the extent of impurities and surface contaminants from SinTaC layers and verify their applicability to practical processes.

2. Theory and experimental procedure

The SinTaC fabrication and characterization processes are categorized into the following steps (see Fig. S1, Supplementary data). (1) characterization of source materials and design of TaC slurry compositions, (2) preparation of TaC slurries and evaluation of TaC powder compact packing densities, (3) manufacturing through application of TaC slurries on graphite substrates by various techniques and sintering, and (4) characterization of SinTaC test pieces and testing SinTaC components in practical processes. Each step is explained in detail as follows.

2.1. Theoretical method on HSP characterization and design of slurry compositions

The HSP are a set of cohesive-energy densities tri-partitioned by the types of molecular interactions, i.e., characteristic thermodynamic values to explain material compatibility. The compatibility is expressed by a HSP distance R_a in a HSP space with Cartesian coordinates of three HSP values for dispersion (δD), polarity (δP), and hydrogen-bonding (δH) terms. When two HSPs of material #1 and material #2, are respectively [δD_1, δP_1, δH_1] and [δD_2, δP_2, δH_2], the R_a between the materials is defined by [26,27]:

$$R_a = \sqrt{4 \times \left(\delta D_1 - \delta D_2\right)^2 + \left(\delta P_1 - \delta P_2\right)^2 + \left(\delta H_1 - \delta H_2\right)^2}. \quad (1)$$

A smaller R_a results in better compatibility (solubility, dispersibility, and wettability). If the two materials are a polymer (or powder) and a solvent, then the HSP of the polymer (or powder) include an additional parameter of interaction radius, R_0. When R_a is smaller than R_0, the polymer (or powder) dissolve (or disperse) into the solvent. Conversely, when R_a is larger than R_0, the polymer (or powder) precipitates (or flocculates) in the solvent. Thus, R_0 defines the boundary value where the free energy of mixing for the two materials becomes zero.

To formulate ceramic slurry compositions, the HSP values of the component materials, i.e. ceramic powder (TaC powder hereafter) and binder resin, must be known to select appropriate solvent mixtures. Methods for the derivation of TaC powder and binder HSPs are as follows.

TaC powder dispersion in probe liquids and subsequent sedimentation experiments were conducted to determine the HSP of the TaC powder. The TaC powder (average particle diameter: 1–2 μm) was blended with each of 25 probe liquids (organic solvents) in vials with a solid content fraction of ca. 10 vol%. After dispersion, the vials were held still for 1–200 h and the sedimentation times when the height of the top clear liquid layer was 5 mm were measured. The sedimentation times were then calibrated according to the viscosities and densities of the probe liquids to give relative sedimentation times (RST) [26,27], whereby good/poor solvents could be determined in terms of TaC powder dispersibility. These good/poor results were fit by the SPHERE method [26,27] to calculate HSP center values [δD, δP, δH] and R_0 of the TaC powder HSP sphere.

Binder dissolution experiments were also performed to determine the HSP of the selected binder. The binder was blended with each of 72 probe liquids in vials with a solid content fraction of ca. 10 wt%. After stirring, the solubility was evaluated by visual inspection to sort the probe liquids into good/poor solvents for the binder. These results were also fit by the SPHERE method to obtain the binder HSP sphere.

The positional relationship between HSPs of the constituents in the binder, pigment/powder, and solvent mixture, as illustrated in Fig. 1(a) has been proposed as favorable to achieve thermodynamically stable dispersions. The HSP spheres of the binder and powder include each HSP center within each interaction radii, which indicates the combination of binder and powder has good compatibility. A design guide to select an appropriate solvent is for the solvent HSP to be as far as possible from the powder HSP sphere while close to the periphery of the binder HSP sphere [26,27,34]. These positional relationships assure that the powder is more compatible with the binder than the solvent, so that the binder polymer should adsorb to the powder surface and achieve steric stabilization [35].

The binder and powder do not always have good compatibility when raw materials are selected for specific aims or functions. For example, the main part of the binder polymer adopted in this study is not compatible with the TaC powder. The conventional three-constituent design guide is not applicable in this case; therefore, we propose a novel design guide for ceramic slurries in the case of poor compatibility between the binder and powder.

The introduction of a small amount of a functional group anchor to the polymer (to adsorb to the powder surface) could be a solution. Fig. 1(b) shows a combination of binder, TaC powder, and anchor (that is compatible with the TaC powder) as a model case for the novel design guide. The three-constituent design guide is extended to a four-constituent guide, in which the solvent HSP should simultaneously be (A) outside the TaC powder HSP sphere, (B) inside the binder HSP sphere, and (C) near the HSP shell of the anchor. With this design guide, the anchor parts in the binder polymer are expected to adsorb to the TaC powder surface with sufficient coverage, while the main part of the binder should extend into the solvent, i.e. steric stabilization.

35 organic solvent mixtures were prepared for TaC slurries containing 2–5 organic solvents, where their weighted-average HSP [26] was near the region predicted by the four-constituent design guide. The investigation was conducted with mixtures of multiple solvents [consisting of low boiling point (BP) solvents: BP < 100 °C, medium BP solvents: 100–200 °C, and high BP solvents: ≥ 200 °C] to control the stress exerted on the half-dry TaC powder compact during the final stage of the drying process. Precise control of the mixture of different BP solvents enables control of the TaC slurry drying rate during the early and final stages of the drying process, i.e., requirements for both a short process time at the early stage and reduced drying stress at the final stage can be satisfied.

2.2. Preparation of TaC slurry and packing density measurement

35 organic solvent mixtures were prepared and the binder (a nonionic polymer containing the anchor) was dissolved into these at a fraction of 0.5–0.6 wt% (with respect to the final TaC slurry). The TaC powder (70–73 wt%) and additives (<1 wt%) such as a sintering agent were added to the binder solutions, all of which in vials were then mixed by hand shaking and subsequently dispersed by sonication for 1 min in total (divided into twice 30 s sonication to prevent overheating) with an ultrasonic homogenizer.

Because potential application fields of SinTaC components are for bulk crystal growth, epitaxial film growth, and device fabrication of semiconductors, where contaminations originating from dispersants and residual carbon originating from polymer additives must be reduced as low-level as possible, no conventional dispersants such as salts, acids/bases, surfactants, and ionic polymers