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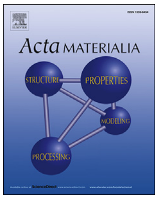

Full length article

Assessment of solid state and liquid phase sintering models by comparison of isothermal densification kinetics in W and W-Cu systems

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ABSTRACT

The role of liquid phase and grain growth during the intermediate stage of sintering is investigated by comparing the isothermal densification rate of the tungsten skeleton in two systems: solid-state sintered W and liquid-phase sintered W-10wt%Cu. Densification curves at 1380 °C, i.e. well after completion of capillary rearrangement in W-Cu, are confronted to the predictions of a model that considers a single representative grain size with quasi-equilibrium interfaces and a monotonic increase in grain size and coordination with density. In both systems, the densification mechanism is taken to be governed by W diffusion along grain boundaries. For system W-Cu, a phenomenological law is proposed to allow accounting for the decrease in liquid surface curvature during funicular filling of the pores by the liquid-phase. The kinetics of grain growth is described via current literature model. Good agreement is demonstrated between experimental measurements and model predictions when relying on material parameter values given in literature. In system W-Cu, the detrimental effect of the decrease in dihedral angle is, at the beginning of the funicular stage, compensated by the contribution to sintering stress brought about by the concave curvature of liquid/vapour interface. The sensitivity of computational results to model hypotheses and material parameters is assessed. The most influential parameters are diffusivities along W grain boundaries and along W/vapour and W/Cu interfaces.

1. Introduction

Microstructure-based models for the simulation of sintering kinetics embody the current understanding of basic phenomena underlying sintering. A step forward in microstructure-based modelling has been brought in a series of papers published in the nineties by the group of Riedel, Svoboda and co-workers [1–5]. Significant progresses along the same modelling approach have been contributed more recently by Wakai and co-workers [6–12]. Computational tools inspired by these models are available for practitioners of sintering technology [13]. Nevertheless, unlike the wealth of theoretical work, papers aiming at in-depth model assessment on the basis of experimental results are scarce [14].

Composites W-Cu arouse interest for potential application as materials for electrical contact or for thermal transfer management in fusion power plants [15–20]. Whereas pores contain only vapour in aggregates of pure W grains, they can contain both liquid and vapour in aggregates W-Cu. The kinetics of solid state sintering of W with and without addition of activator has been modelled by Johnson and German [21]. In the presence of a secondary phase such as Cu, densification evolves through three successive stages: (1) solid-state sintering before the melting of Cu; (2) W particle rearrangement driven by the formation of the liquid phase; (3) shrinkage of the W skeleton [5,16,17]. The objective of the present work is to confront experimental kinetics to computational predictions in view of assessing our understanding of the process of shrinkage of the solid skeleton during stage (3) with and without the presence of a liquid phase.

It is commonly agreed in literature that, in the temperature range usual for pressure-less sintering of crystalline materials, the

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rate-limiting mechanism for densification is diffusion along grain boundaries rather than diffusion through grain bulk. In the presence of open porosity, grain growth is controlled by pore-drag, i.e. by transport inside the pores, from surface to surface. Owing to the very low partial pressure of W in the gas phase and to the very low solubility of W in liquid Cu, it is also commonly assumed that the rate-limiting mechanism for grain growth is diffusion along pore surface rather than transport across pore volume via evaporation/condensation or dissolution precipitation. This assumption will be assessed in the Appendix at the end of this paper. If densification and grain growth are governed by these two mechanisms, the difference of densification kinetics between systems W and W-Cu is expected to arise from only two factors: the difference of sintering stress arising from the filling of the pores by either only vapour or both liquid and vapour, and the difference of grain growth rate arising from the different diffusivity along W/Cu and W/vapour interfaces.

Densification kinetics is currently modelled using periodic 3D arrangements of identical particles in which grain coordination is constrained to keep integer values [1–12,21]. In the present work, densification kinetics is computed using a model able to account for arbitrary values of coordination. This model allows the capture of the change of sintering stress and sintering viscosity due to the increase in grain coordination with relative density. The simultaneous grain growth kinetics will be computed using the model of Riedel and Svoboda [1].

Section 2 presents the experimental observations that underlie the present work [20]. Comparison is made of two aggregates presenting the same volume fraction of W in the initial packing: an aggregate of pure W powder and a composite aggregate of W with 19 vol% of Cu. The focus is on the difference in the evolution of densification rate during isothermal holding at 1380 °C. Section 3 presents the model for the simulation of the sintering rate of the W skeleton with and without a liquid phase. For system W-Cu, a phenomenological law is proposed for representing the monotonically decreasing contribution of Cu/vapour interface to sintering stress during funicular filling of the pores by the liquid. Computational results are presented in Section 4. Good agreement with experimental observations is obtained when relying on admissible values of material parameters. The analysis suggests that diffusion along W/vapour interface is three times faster than along W/Cu interface. The sensitivity of model predictions to the uncertainties on the underlying hypotheses and on the values of material parameters is evaluated in Section 5.

2. Experimental methods and observations

This paper relies on the experimental work of Raharijaona et al. [20] who have investigated the difference in sintering kinetics between a compact of pure W powder and a compact prepared using the same W powder with addition of 10.0 wt% (= 19.3 vol%) of pure Cu powder. These two samples will be shortly designated “W” and “W-Cu”. Full details about experimental methods can be found in the original paper.

Fig. 1a presents a SEM micrograph of the pure W powder used for preparing both samples. Chemical analysis indicated the presence of only 85 ppm of C, 15 ppm of Co, and 14 ppm of Fe. The BET surface area was 1.7 $m^2 g^{-1}$, which translates into an equivalent spherical grain diameter of 0.2 μm. For sample W-Cu, the powder mixture was obtained by milling the W powder with CuO powder of 1.8 μm equivalent BET diameter, followed by reduction at 623 K (350 °C) under He/H_2 flow. Cylinders of 8 mm diameter and 6 mm height were compacted uniaxially. The emphasis in the work of Raharijaona et al. [20] was to warrant the same skeleton density during the initial stage of the process. For this purpose, different compaction pressures were chosen for the two samples in such a way as to obtain the same initial fraction of 45 vol% of W in the compact. Accounting for the presence of Cu, this converts to a green density of 55% for sample W-Cu. The compacts were sintered under He/H_2 in a dilatometer allowing continuous monitoring of linear shrinkage. As shown on Fig. 2, the heat treatment involved successively.

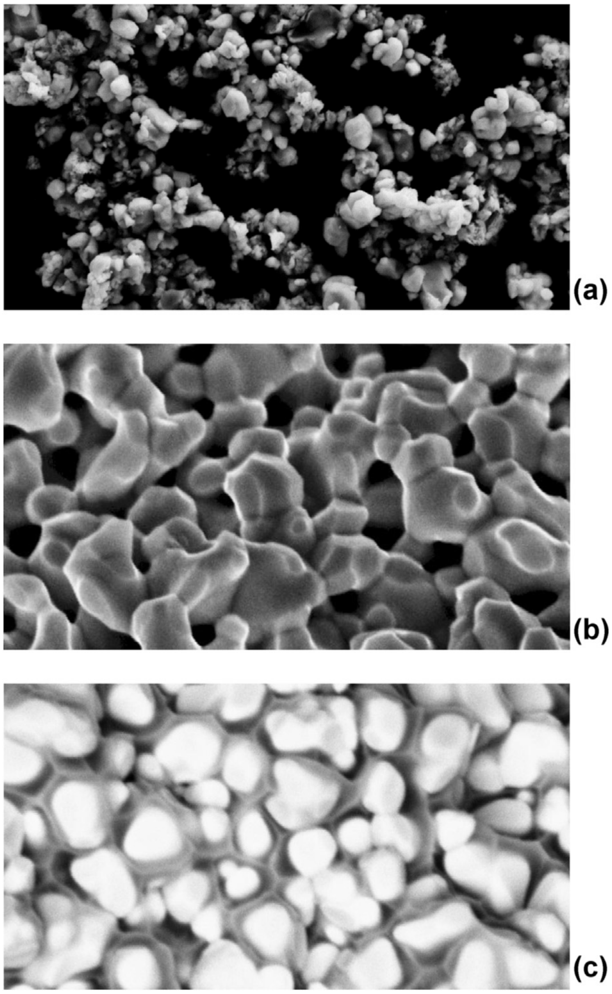

Fig. 1. SEM micrographs for comparison of W grain sizes (a) in the initial W powder, (b) in the pure W sample after sintering, and (c) in the W-19vol%Cu sample after sintering. b and c are reproduced from [20] by permission of Springer.

1. a heating ramp at 5 $K min^{-1}$ to 1050 °C,
2. a holding period of 1 h at 1050 °C to achieve full reduction of W,
3. a second ramp at 2.5 $K min^{-1}$ to 1380 °C,
4 a holding period of 120 min at 1380 °C
5. and a final cooling ramp at 20 $K min^{-1}$.

As illustrated on Fig. 1b and c, grain growth during the whole sintering process amounted to a similar factor in the two samples. According to measurements carried on SEM micrographs by computer-assisted image analysis, the mean linear intercept is 1.4 μm for W and 1.1 μm for W-Cu and the square root of the grain cross sectional area is 1.0 μm for W and 0.8 μm for W-Cu. These values should be taken with some caution as they are not obtained on true cross sections. Nevertheless, they indicate a lower grain growth in W-Cu, with a final size ratio $R_{GW\text{-}Cu}/R_{GW} \approx 0.8$ (we define R_G as the radius of a sphere of volume equal to the average grain