Tungsten/Copper Functionally Graded Materials : Possible Applications and Processing through the Powder Metallurgy Route

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Abstract

Processing of W-Cu graded materials from attritor-milled W-CuO mixtures is described. The powder reduction steps are investigated by TG and XRD analyses and by microstructural observations (SEM, TEM). Sintering of reduced powder with different compositions is analysed by dilatometry. Sintering behaviour of the graded component processed by co-compaction of a 10/20/30wt%Cu multi-layer material is briefly discussed. Liquid Cu migration is observed and smoothes the composition gradient. Perspectives to control this migration are discussed.

Keywords : functionally graded materials (FGM) ; oxide reduction ; sintering ; TG/DT analysis, Cu liquid migration

1. Introduction

W-Cu functionally graded materials offer the opportunity to combine a refractory W-rich phase having a low thermal expansion coefficient and a high strength with a Cu-rich phase having a high thermal and electrical conductivity. A possible application is first wall assembly samples for the future nuclear fusion experiment ITER [1]. In case of electrical contacts a graded structure between the contact area and the bulk materials could also be beneficial. Graded W-Cu structures are also used as heat sinks for packaging microelectronic devices, the composition in the W-rich part being adjusted to match the thermal expansion coefficient of the semi-conductor or ceramic material [2]. However, W-Cu powder mixtures usually exhibit a poor sinterability. Relatively high sintered densities could nevertheless be obtained with W-CuO powder mixtures, although the effect of the CuO reduction on sintering is still not clear [3].

2. Experimental and Results

W-CuO powder mixtures with compositions corresponding to 10, 20 and 30wt% Cu in the reduced mixture were prepared with CuO Aldrich 24174-1 and W Eurotunsgtene AW1106 powders. A first set of mixtures was processed through attritor milling for 3h in acetone media with tungsten carbide balls. Dried powders were uniaxially compacted into cylindrical samples under 400 MPa. The powder reduction steps were characterized by thermogravimetric analyses (TGA), dilatometry, XRD, SEM and TEM microstructural analyses. A second set of mixtures was processed to improve the sintering ability. The milling conditions were first optimized and powders were reduced at 350°C for 2h and granulated with 1wt% polyethylene glycol (PEG) before uniaxial compaction. Green compacts were sintered at temperatures up to 1300°C under He/H_2 reducing atmosphere (4vol% H_2). Graded samples were processed by co-compacting and co-sintering stack of powder layers with different compositions.

Analysis of W-CuO reduction steps. Reduction steps can be deduced from thermogravimetric plots (Fig. 1). The first weight loss between 50-150˚C is attributed to solvent or humidity elimination. The second weight loss between 150-350˚C, corresponds to the reduction of copper oxide. Indeed XRD analysis of a sample interrupted at 400°C in the heating cycle exhibits only W and Cu lines. The double peak on the DTG plot suggests a two-step reduction :

$$2\,CuO + H_2 \rightarrow Cu_2O + H_2O \qquad (1)$$
$$Cu_2O + H_2 \rightarrow 2\,Cu + H_2O \qquad (2)$$

Complete elimination of oxygen in copper oxide should give 2.5% weight loss in our mixture, but only 2% weight loss was measured. The missing 0,5% weight loss can be a result of reduction by a solid-state reaction between copper oxide and tungsten particles :

$$x\,CuO + W \rightarrow x\,Cu + WO_x \qquad (3)$$

A tungsten oxide phase was indeed observed by TEM between tungsten and reduced copper oxide particles. The last two weight losses observed above 400°C were attributed to reduction of tungsten oxides. The dilatometric results showed swelling associated to CuO reduction steps

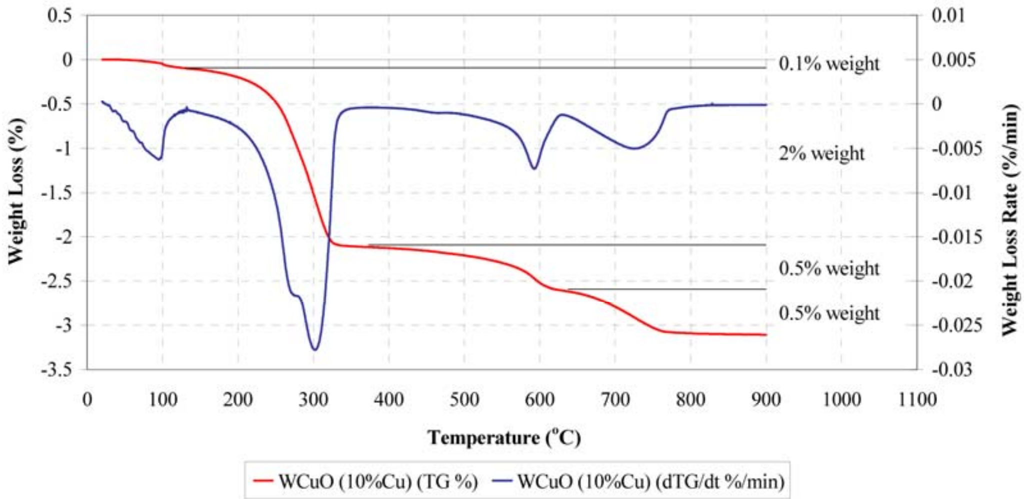

Fig. 1. Thermogravimetric behavior of W-CuO (10%Cu)

which was related to both the formation of porous Cu particles through reactions (1) and (2) and the formation of tungsten oxides through reaction (3). Swelling limits the final density and could cause delamination during processing of gradient material. A pre-reduction of powders was therefore performed before the compaction and sintering steps.

Processing of reduced W-CuO powder. Homogeneous W-Cu powder mixtures with high compaction and high sintering ability could be obtained by thermal reduction and granulation of W-CuO mixtures. Samples with fired density 92-95% of the theoretical density could be produced at 1300°C. Development of gradient material was investigated based on these results.

Processing of gradient material. The thermal cycle was optimized for graded W-Cu structure from the dilatometric plots of pure W-Cu mixtures. Relatively dense parts (≈ 95% theoretical density) could be obtained at 1300°C, with a good adhesion between the layers. However, micro-structural observations and EDS analyses indicated significant smoothing of the composition gradient, due to liquid phase migration between the layers, which caused macroscopic distortion of the structure.

3. Summary

W-Cu materials with varying compositions from 10wt% to 30wt% Cu were processed through powder metallurgy route, starting from attritor-milled W-CuO mixtures. The importance of swelling during reduction of copper oxide was emphasized, and could be explained by (i) a solid state reaction between CuO and W particles and (ii) the formation of porous Cu particles during reduction of CuO by hydrogen gas. Swelling limits the final density after sintering. A high compaction efficiency and a good sinterability could be obtained with pre-reduced powders. Multi-layer functionally graded materials were then processed. Samples with ≈ 95% of the theoretical density were obtained, with a good adhesion between layers. Liquid migration between layers was observed. It was responsible for distortion of the parts, and considerable smoothing of the composition gradient. It should be reduced in the future by optimizing the microstructure of individual layers as shown in recent models [4] or experiments performed on different materials [5, 6].

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