Image Anal Stereol 2002;21:133-138
Original Research Paper

QUANTITATIVE IMAGE ANALYSIS OF MICROSTRUCTURE EVOLUTION DURING SOLID STATE SINTERING OF W-Cu

ANA MARIA POPA AND JEAN-MARC CHAIX

Laboratoire de Thermodynamique et de Physico-Chimie Métallurgiques, UMR 5614 CNRS-INPG/UJF B.P.75, F-38402 Saint Martin d'Hères Cedex, France
e-mail: anaandy@yahoo.fr, JmChaix@ltpcm.inpg.fr
(Accepted May 21, 2002)

ABSTRACT

The microstructure evolution of W-Cu composites during solid state sintering at 1050°C is studied on samples quenched after different sintering times. The microstructure is formed by 3 phases: tungsten (W), copper (Cu) and pores. During the process, the initial mixture of W- and Cu-powder is transformed by migration of Cu and rearrangement of W particles. These microstructural changes are studied to identify the underlying phenomena and to control the material properties. Based on experiments performed with two different W powders, this paper deals with various aspects of the quantitative analysis of the observed evolution. A careful preparation of the images is necessary. The porous samples are impregnated with a resin under vacuum before being cut and carefully polished. Low voltage (<10 kV) is used during image acquisition on a scanning electron microscope. Area fraction measurements are used to check the quality of the images and the segmentation process. Classical measurements are used to study the spreading of Cu onto the surface of W particles: surface area of each phase, area of contact between phases, chord length distributions. New measurements based on classical methods are also developed to distinguish between two mechanisms of Cu migration in the microstructure : Cu spreading on W surface (wetting of the surface), and capillary penetration in the inter-W channels. An analysis of the location of Cu and pores in the space between W particles (inter-W space) is performed using a granulometry based on 2D openings. It evidences the mechanism of capillary penetration of Cu in the inter-W space in the case of small W-particles.

Keywords: image analysis, microstructure, solid state sintering, W-Cu composites.

INTRODUCTION

The densification of W-Cu micrometric powders has been studied by several authors and important aspects of microstructural evolution during solid state sintering have been reported (Skorokhod *et al*., 1984; Lee *et al*., 1985; Upadhyaya and German, 1998; Popa and Chaix, 2000). A small densification occurs during solid state sintering of these composites, but an important microstructural evolution is observed, especially at long sintering times. The microstructure is formed by 3 phases: W, Cu and pores. Typical microstructures and their evolution are illustrated by the micrographs in Fig. 1. At 1050°C (process temperature), the refractory W particles have almost no shape evolution and can only slightly move ("rearrangement"). On the contrary, the Cu phase, close to its melting point, undergoes obviously a significant migration within a matrix of W particles.

Image analysis has been used for a long time to support the mechanisms producing the microstructural evolution. For example, some candidate mechanisms have been described by Lee *et al*. (1985) based on image analysis measurements on selected parts of the microstructure, e.g., chord length distribution measurements showing an increase of the size of some W-Cu aggregates. In Lee *et al*. experiments, micrometric powders were simply dry mixed yielding, at the small scale, a non homogeneous repartition of Cu between the W grains (rich versus poor Cu zones). Lee *et al*. (1985) assumed that, in the rich Cu zones, Cu quickly spreads on the W particles i.e., forms a thin film of a few atomic layers at the surface of the W particles, leading to a rapid, but limited, rearrangement of the tungsten grains and to the formation of compact W-Cu aggregates. This rearrangement is associated to a local densification within the aggregates. Yet, the aggregates being separated by pores, no global densification is observed at the sample scale. According to Lee *et al*. (1985), the next step consists of a massive spreading of copper on the thin film, leading to an increase, with time, of the size of both W-Cu clusters and pores. Sample densification is observed if the clusters

become interconnected. After long sintering time (16 hrs) Lee *et al*. (1985) observed an homogenous distribution of copper between tungsten.

Other authors have studied the correlation between pore size evolution and densification (Skorokhod *et al*., 1984). When pores grow, the densification is small. A good densification is associated to a decrease in pore size at the beginning of the sintering and also to the ultimate disappearance of pores with time.

Although the studies discussed above have provided interesting results, they do not lead to a fully satisfying description of the mechanisms leading to the micro-structural evolution. Indeed, the measurements used by the authors to support their interpretation are limited, if not questionable in some cases (e.g., arbitrary selection of W-Cu zones). Furthermore, the spreading of a few atomic layers cannot be observed at the micrograph-scale. At last, neither the relation of the thin film of Cu to the rapid densification, nor the mechanisms originating the "massive spreading" are clearly understood. It is therefore necessary to perform systematic and quantitative microstructural measurements, and to support the mechanisms of the migration of Cu based on micro-structral features resolved at the micrograph-scale. In this paper, two possible routes for Cu migration are considered: a spreading on the W surface ("solid state wetting") and a capillary penetration into the structure, i.e., into the channels between the W grains.

EXPERIMENTS

This work relies on the comparison of the microstructural evolution of two W-Cu mixtures during solid state sintering at 1050°C. Herein, two tungsten powders are used: a fine one (*f*; laser sizer average diameter: 4 µm) and a "gross" one (*g*; 12 µm). The two powders are obtained by W oxide reduction processes and are made of agglomerated facetted W crystals. The fine copper powder (*f*; 5 µm) is obtained by a water atomization process, and is made of almost spherical particles. The two mixtures, referred to as *ff* (fine-fine) and *fg* (fine-gross), respectively, give rise to very different microstructures (Fig. 1): a fine grain microstructure for *ff*, and a coarser grain microstructure for *fg*. Mixtures with 20 vol.% Cu and 35 vol.% Cu have been used. The samples with 20 vol.% Cu leading to similar results, only the results for 35 vol.% Cu are presented (as recalled by the mark "35" in Figs. 2, 3 and 5).

The powders are dry mixed for 1 hour in a "Turbula" device. This simple mixing does not change the powder shape or size. Sintering is performed under hydrogen at a heating rate of 3°C/min to ensure the reduction of oxides on particle surfaces. After the isothermal solid state sintering of W-Cu, the samples are porous, the microstructure still contains the three phases: W, Cu and pores.

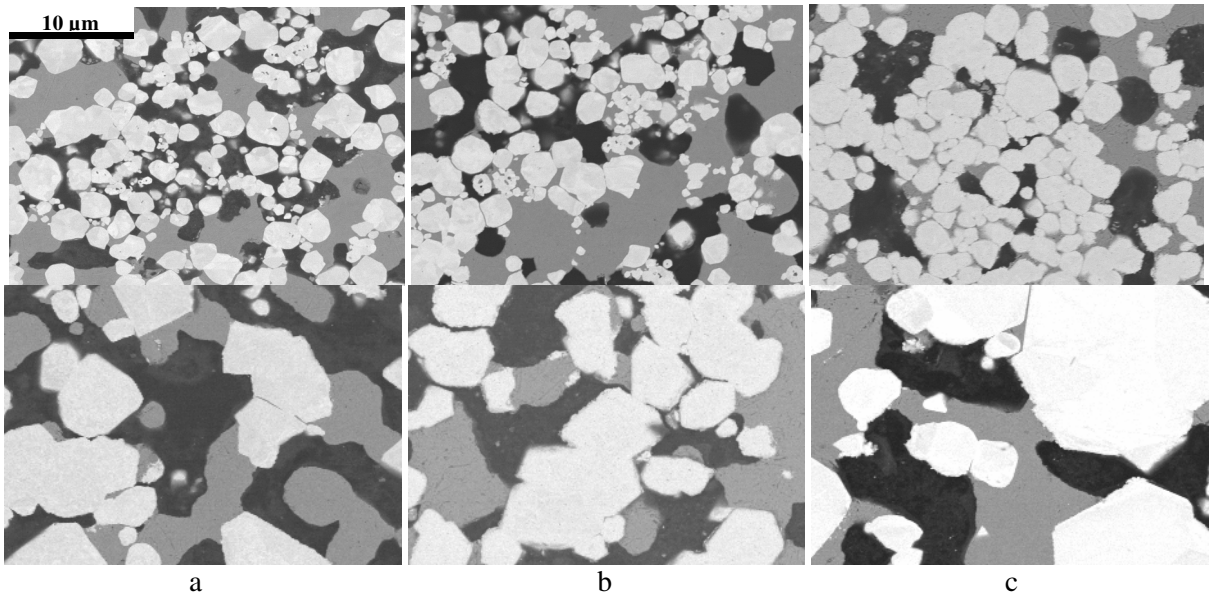

Fig. 1. *Evolution, during the isothermal (1050°C) solid state sintering, of the microstructure of two W-Cu mixtures: a fine one (ff, 1st line) and a gross one (fg, 2nd line). a) t = 0 min; b) t = 60 min; c) t = 400 min . The 3 phases are W (light grey), Cu (dark grey) and pores (black).*

To prevent the alteration of the microstructure during polishing, the samples are impregnated with a resin. Impregnation is made under vacuum, using a very fluid resin (Struers-Caldofix) polymerizing after 1 hour at 80°C. A soft automatical polishing is performed (low force and long time), starting with a "2400" SiC paper. Half an hour of final polishing on a ¼µm diamond then produces the high-grade sample surface, necessary to obtain high quality images. During image acquisition on a scanning electron microscope, a low voltage (<10 kV) is used to avoid artifacts (in particular due to the transparency of the resin). The image processing strategy used to segment the images is not presented herein. To check the quality of the images and the segmentation, area fraction measurements were compared to volume fractions of pores obtained by density measurement and to the Cu/W ratio expected from powder composition (not reported herein).

RESULTS AND DISCUSSION

After compaction, and before heating, the samples are very brittle. The (low) quality of the corresponding micrographs would not allow accurate measurements. Although a microstructural evolution is likely to happen while heating the samples up to 1050°C, the samples at the beginning of the isothermal stage ("0 min." at 1050°C) are therefore taken as reference in this paper.

The qualitative observation of the images in Fig. 1 shows some first tendencies. At the beginning of the isothermal 1050°C stage (Fig. 1a), the spatial dispersion of Cu in the W-structure is still largely explained by the distribution of the initial Cu spherical grains but is also determined by the deformation of the Cu particles and by Cu-Cu and W-Cu contacts that form when heating the samples up to 1050°C. The size of the Cu areas is larger in the case of the gross microstructure. The associated lower dispersion of Cu and statistically higher number of clusters of Cu-particles are here the consequence of the larger W particles at the mixing stage, and of contact formation and Cu sintering during heating. Another difference between the *ff* and *fg* structures is the amount of small pores. Much larger pores are observed in the *fg* case than in the *ff* case. During sintering (Figs. 1b, c), Cu migrates outwards its initial place, leaving porosity at its initial place. Two candidate mechanisms are here considered to explain the migration of Cu: Cu spreads on the W surface and wets it, and the small "channels" between W grains are filled by Cu. Our purpose is to support this interpretation based on quantitaive image analysis measurements.

Classical measurements are used to characterize the microstructural evolution during solid state sintering: specific surface area from intercept number ($S_V = 4N_L$) (Fig. 2a) and chord length distributions in the different phases (Fig. 3). The measurement of the specific surface area of copper and pores, S_{Cu} and S_p, respectively, show opposite behaviors (Fig. 2a). The evolution is strong for the fine structure *ff* and less pronounced for the gross one *fg*. After 400 min, the surface area of pores has almost the same value as the copper surface at the beginning of the sintering. This indicates that the copper spreads out from "blocks" and leaves big pores after sintering.

The contact surfaces (Fig. 2b) are derived from the specific surface measurements. The W-Cu surface ($S_{W\text{-}Cu}$) increases with time. For both mixtures, the rate is important during the first hour. After 1 hour, the evolution for *fg* is very small whereas *ff* still shows an important increase of the W-Cu surface till long sintering time (400 min).

The generalized contiguity index (Hersant *et al.*, 1976), the fraction of W surface in contact with Cu ($C_{WCu,W} = S_{W\text{-}Cu}/S_W$) (Fig. 2c), is another way to represent data displayed in Fig. 2b. It enables to compare the evolution of contact area with no influence of the W surface area value differing in the two *ff* and *fg* structures. At the beginning of sintering, the fraction of W in contact with Cu is almost the same for both mixtures (30% for *ff* and 27% for *fg*). During sintering, the fine structure *ff* shows a more important evolution (68%: the 2/3 of the W surface is juxtaposed against Cu), while the evolution for *fg* reaches only a value of 44%.

The chord length distribution (Fig. 3) confirms the small evolution of the gross microstructure *fg* during sintering, the size distributions in pores and Cu being similar. In the case of the fine structure *ff*, the evolution is strong. The pores and Cu size distributions are very different and seem to "exchange". Indeed, the chord distribution in pores after 400 min is almost identical to the chord distribution in Cu at 0 min, and inversely. This suggests a filling of small pores, *i.e.*, that copper infiltrates into the channels between tungsten grains.

To verify this hypothesis, we use in a new way the classical "2D openings based granulometry" method (Serra, 1982; Coster *et al.*, 1989) to obtain the distribution of pores and Cu as a function of the size of the inter-W space. Using an octagon as structuring element, the inter-W space smaller than an octagon of

diameter *D* is isolated by opening (Fig. 4b). Then, after intersection with the Cu and pores binary images, the copper and pores lying within the calibrated (size D) inter-W space are identified (Fig. 4c), and their surface is measured. *D* can be interpreted as a local "width" of the inter-W channels.

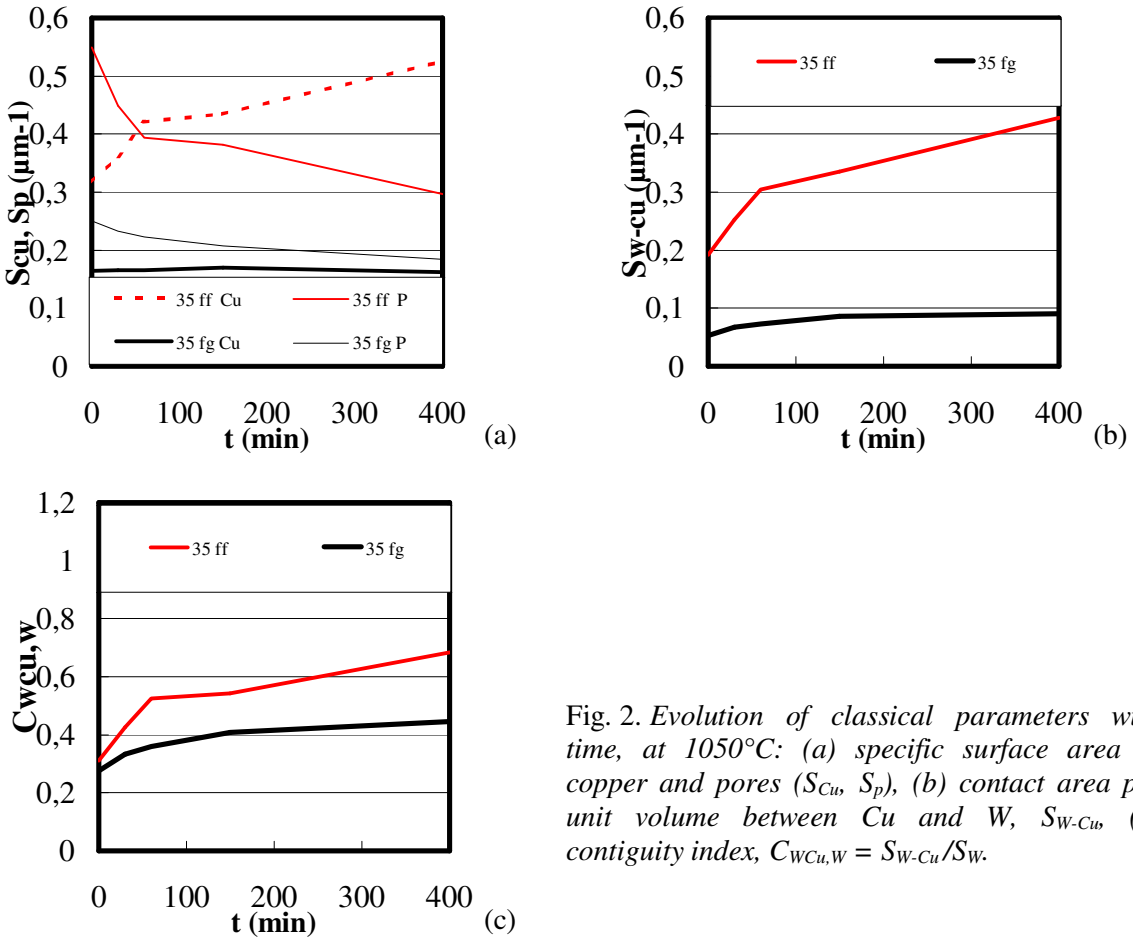

Fig. 2. *Evolution of classical parameters with time, at 1050°C: (a) specific surface area of copper and pores (S_{Cu}, S_p), (b) contact area per unit volume between Cu and W, $S_{W\text{-}Cu}$, (c) contiguity index, $C_{WCu,W} = S_{W\text{-}Cu}/S_W$.*

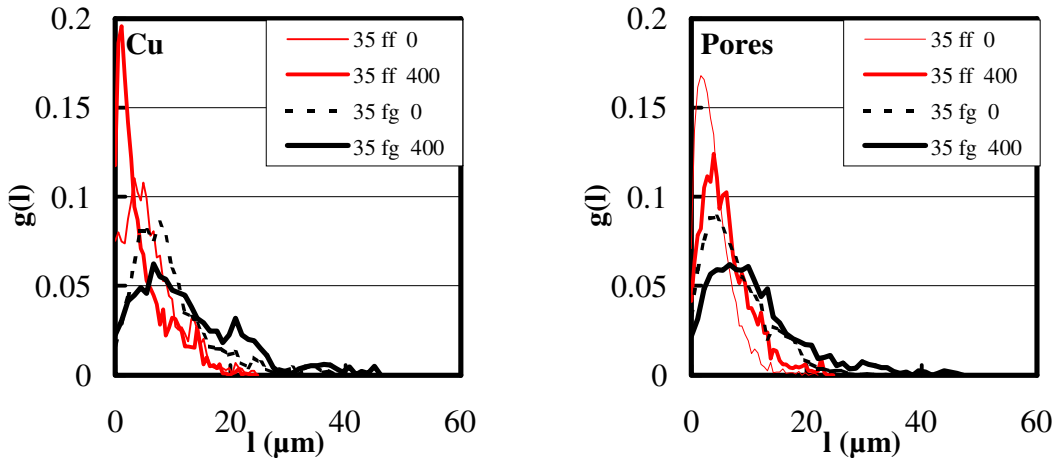

Fig. 3. *Evolution with time of the chord lengths distribution of copper and pores for the mixtures 'ff' and 'fg', 35 vol% Cu (g(l) denotes the length weighed chords distribution).*

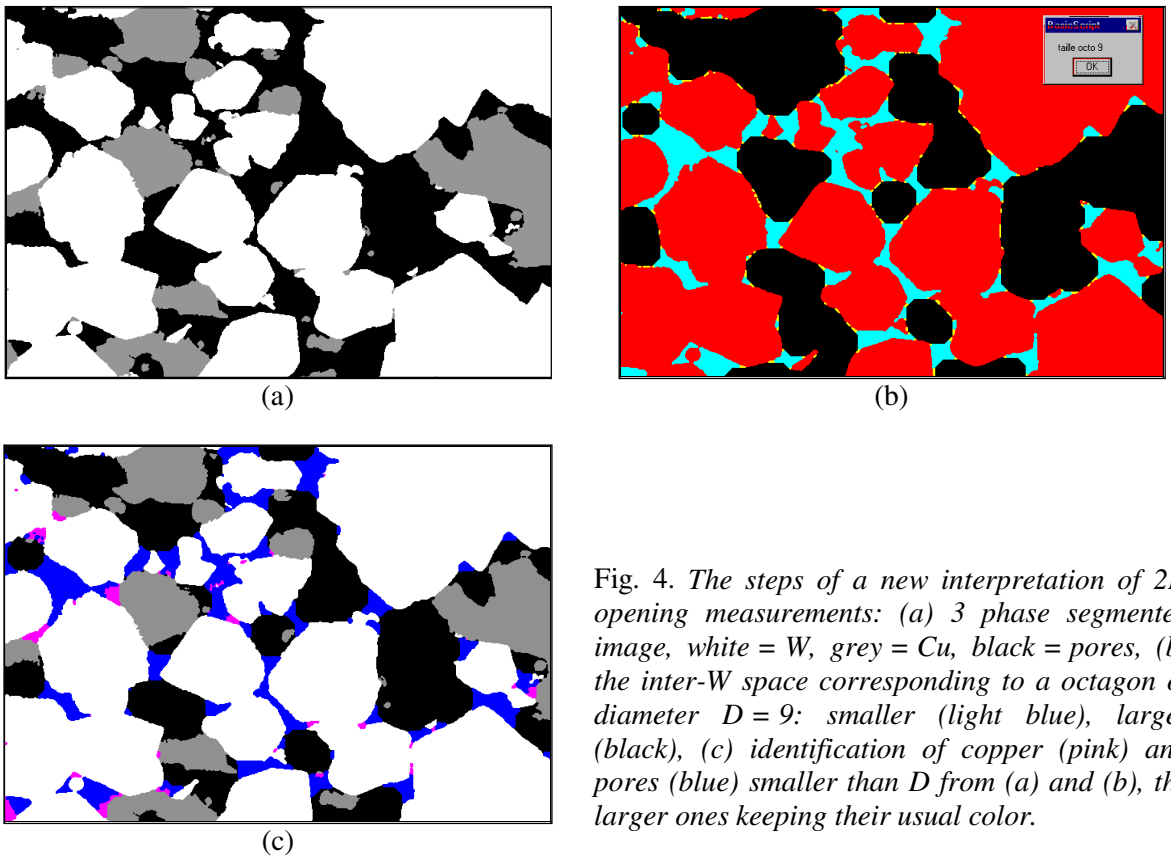

Fig. 4. *The steps of a new interpretation of 2D opening measurements: (a) 3 phase segmented image, white = W, grey = Cu, black = pores, (b) the inter-W space corresponding to a octagon of diameter D = 9: smaller (light blue), larger (black), (c) identification of copper (pink) and pores (blue) smaller than D from (a) and (b), the larger ones keeping their usual color.*

The curves in Fig. 5 show the distribution of copper and pores as a function of inter-W space size (D) obtained by 2D opening measurements. At the beginning, pores occupy most of the small places (width <5 µm) and Cu lies in large places, typically larger than the Cu particle size. During the isothermal stage, Cu fills the narrow channels, just as a wetting liquid fills a capillary. Cu finally occupies most of the small size W inter-space. The curves in Fig. 5 show that the 0 min pore peak at small sizes and the copper peak after 400 min are identical.

It must be noted that the sum of the values for pores and Cu represents the size distribution of width *D* of the inter-W space (classic granulometry using openings). Its evolution is very small in both mixtures. Only a small shift towards small sizes can be shown, indicating a very small rearrangement of W particles.

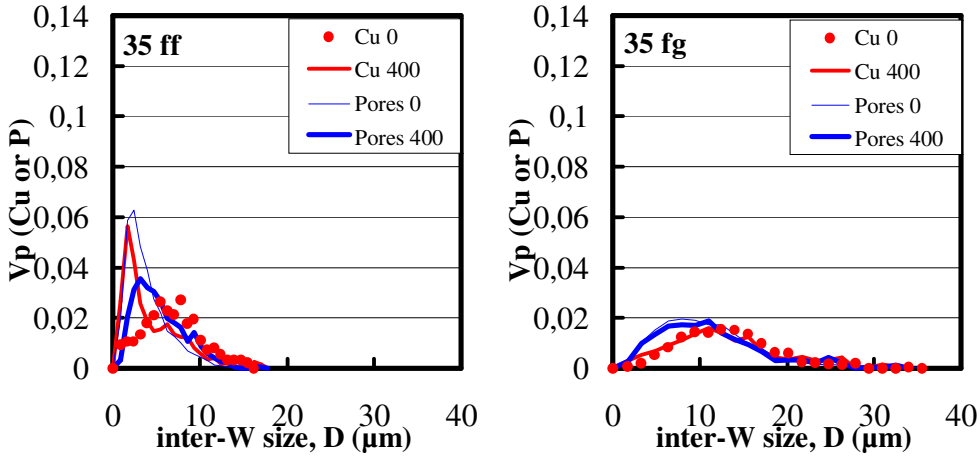

Fig. 5. *Distribution of Cu and pores as a function of inter-W size D obtained by 2D opening measurements for the two mixtures, ff and fg, 35% vol. Cu.*

CONCLUSION

In this work, the systematic use of quantitative image analysis to study the microstructure evolution has enabled to determine the characteristics of the main mechanisms involved in solid state sintering of W-Cu composites.

The tungsten size, determining the inter-W space size and the initial microstructure, has a crucial effect on sintering. The use of the proposed new 2D opening measurements clarifies the contribution of small pores to the microstructural evolution during sintering. In the case of fine mixture (*ff*), a large amount of small pores is present at the beginning of sintering. An infiltration mechanism can explain that a similar quantity of copper phase of the same size is found after 400 min at 1050°C. The significant microstructure evolution with time would be a consequence of this mechanism. Even if the rate of sintering is higher in the first hour at 1050°C, a long time is necessary to reach high values.

In the case of large tungsten mixture (*fg*), the absence of small pores leads to a limited contribution of infiltration: copper spreading would be here the main mechanism, with a lower efficiency.

REFERENCES

Coster, M Chermant, JL (1989). Précis d'analyse d'images. 2nd Edition. Paris: Les Presses du CNRS.

Hersant T, Jeulin D, Parnière P (1976). Notions de base de morphoplogie mathématique utilisée en métallurgie quantitative. CIT Revue de Métallurgie 6:1449-515.

Lee JS, Kaysser WA, Petzow G (1985). Microstructural changes in W-Cu and W-Cu-Ni compacts during heating up for liquid phase sintering. In: Aqua EN, Whitman SCI, eds. Modern Developments in Powder Metallurgy, 15:489-506.

Popa AM, Chaix JM (2000). Microstructural processes during solid state sintering of W-Cu composites. Science of Sintering special issue "sintering 2000":97-107.

Serra J (1982). Image analysis and mathematical morphology. New York: Academic Press.

Skorokhod WW, Solonin YM, Filippov NI (1984). Solid-phase sintering of ultrafine W(Mo)-Cu composite powder. Poroshk Metall 1(253):19-23.

Upadhyaya, A, German, RM (1998). Densification and Dilation of Sintered W-Cu Alloys. Int J Powder Metallurgy 34(2):43-54.