
A J Papworth, D K Agrawal, J Cheng

†Lehigh University, Dept. of Materials Science and Engineering, Bethlehem, PA 18015 USA.
#Pennsylvania State University, Materials Research Laboratory, University Park, PA 16802
*Dept. of Engineering, The University of Liverpool, Liverpool, L69 3GH, UK.

ABSTRACT: High-resolution analytical electron microscopy (AEM), a form of X-ray energy dispersive spectroscopy (EDS) X-ray maps, has been used to investigate microchemical and microstructural changes between WC/Co and Fe-Cu-C, which have been processed by either conventional or microwave sintering method. Differences in chemistry and microstructure were observed in all samples prepared by two methods. The microwave processed materials showed clean phases with no dissolution of phases.

1. INTRODUCTION

Recently, significant developments and advances have taken place in the field of microwave processing of ceramics and metals. Microwave processing of materials mostly has been confined, to ceramics, inorganic and polymeric materials. There is hardly any detailed report on microwave processing of metallic materials. The main reason for this little work in microwave heating/sintering of metals was due to the misconception that all metals reflect microwave and/or cause plasma formation, and hence cannot be heated. Only recently microwave sintering has been effectively and efficiently applied to powder metals [1]. Here, in this study we have conducted a microstructural investigation using Scanning Transmission Electron Microscopy (STEM) of powder metals and cemented carbides prepared by conventional and microwave sintering methods to examine the differences between two kinds of samples. Microwave heating of materials is fundamentally different from conventional conduction-convection heating. It is a sensitive function of the material being processed. Microwaves are electromagnetic radiation with wavelengths ranging from about 1 mm to 1 m in free space and frequencies between 300 GHz to 300 MHz, respectively. However, most research and industrial activities involve microwaves only at 2.45 GHz and 915 MHz frequencies. Microwave processing offers several advantages: rapid heating, shorter processing times, uniform heating and fine microstructures [2-5]. Tungsten Carbide - Cobalt (WC/Co) based hard metal composites due to their unique combination of hardness, toughness and strength, are universally used as cutting and polishing tools, and in drilling operations underground. The production of WC/Co components involves the mixing of WC powders with cobalt binder, and then compacting the mass into a pre-sintered green body followed by the sintering. Conventional methods for sintering of WC/Co green bodies involve high temperature and lengthy sintering cycles, consequently undesirable grain growth occurs in the presence of liquid Co phase. This has adverse effect on the mechanical properties of the tool.
Microwave sintering process offers an alternative method of sintering and providing finer microstructures with out using grain growth inhibitors. In 1991, J. P. Cheng in a Ph.D. thesis [6] first showed that WC/Co composites could be sintered in a microwave field. Gerdes and Willert-Porada [7,8] also reported the microwave sintering of WC objects with improved mechanical properties. In another independent work [9], Cheng et al. using a newly designed microwave apparatus were able to fully sinter WC commercial green bodies containing 12% and 6% Co. Metal powders are used in industry for many diverse products and applications. The conventional sintering of metallic powders is well established and well understood technique, which involves atomic motion via material diffusion. In many conventional powder consolidation processes, a major problem is that the time required for consolidation at high temperatures is quite long, and as a result undesirable coarse microstructures with grain boundary impurity phases are invariably formed. Some components require post sintering treatments (such as HIP) and machining, which add to the processing costs. Finer microstructures and near theoretical densities in metallic components are still elusive and challenging. Microwave sintering produces fine microstructures and better properties.

2. EXPERIMENTAL METHODS

WC/Co commercial green parts and test samples of 2.0 wt% Cu, 0.8 wt% C, and balance Fe (FC208) were successfully sintered using both a microwave system at 2.45 GHz (the details are given in reference [9]) and conventional sintering. The WC/Co microwave sintered parts took one tenth of the lengthy high temperature sintering cycles that are involved in the conventional method. Whereas the Fe alloy samples were sintered at 1250 °C for 20 minutes in both methods. All sintering experiments were performed inside an alumina tube containing flowing forming gas (5%H2-95%N2) atmosphere for FC208 and pure H2 for WC/Co material. Microwave samples were furnace cooled. TEM specimens of all the sintered materials were prepared by manual polishing of 3 mm discs to ~40 μm. The discs were then ion-beam thinned at an angle of 4°, using a Gatan precision ion polishing system. The microstructural and microchemical analyses were carried out using a VG HB603 FEGSTEM with a probe size of 1.4 nm (FWTM) and a beam current of 0.5 nA. The STEM uses a windowless Si(Li) XEDS with a large detector solid angle of 0.3 sr. X-ray acquisition was carried out on a Oxford (Link) exl system, where elemental windows were defined over the Kα lines of C, O, Al, Si, V, Cr, Mn, Fe, Co, Ni, Cu, Mo plus the Lα line of Mo, and the W Mα line. X-ray maps had an acquisition time of 100 ms/pixel with a 128×128 pixels resolution.

3. RESULTS AND DISCUSSION

A. WC/Co Sintered Samples: The WC/Co phase diagram shows that in a conventional heating molten Co will dissolve WC and during cooling it will precipitate out, leaving some amount of W in the Co phase. The X-ray maps in Figure 1 show that in microwave sintered material there has not been any dissolving of the WC by the liquid Co and that the Co has remained pure. This is in stark contrast with Figure 2, which shows X-ray maps of the conventionally sintered sample. Instead of the two very clean phases as shown in X-ray maps of microwave sintered material in Figure 1. The X-ray maps of the conventionally sintered WC/Co material show large amounts of dissolved W in the Co binder. The remaining WC particles in the conventionally sintered material no longer have clean edges, as those seen in Figure 1, which are very ragged. The question is why does the liquid Co dissolve WC in the conventional sintered material, but not in microwave sintering? Our explanation is that in conventional sintering the material is heated to the required temperature and then held for a prolonged period of time allowing Co and WC to intermix. In microwave sintering, which may not be enough to trigger the dissolution process. Further, microwaves preferentially heat materials, and it is the coupling rate between the microwaves and the material that determines the rate at which energy is transferred. The
WC phase being a ceramic has a poor rate of absorbing the microwave energy, unlike the powdered Co. The difference between the absorption of microwave energy between the two phases means that the WC phase remains relatively colder, while the Co powder is at melting point. The larger WC particle absorbs all the heat transferred to it by the liquid Co, therefore the WC particle never gets hot enough to be dissolved. In case of conventional heating there is no selective heating and therefore Co and WC are at the same temperature at all times, and so the dissolution process can easily occur.

Figure 1. W and Co X-ray maps from a microwave sintered sample. The sharp edge between the WC particle and the Co binder and the absence of W in the Co phase, shows that there has been no dissolving of the WC particles.

Figure 2. W and Co X-ray maps from a conventionally sintered material. The ragged edge between the WC particles and the multi-phases in the Co binder shows that there has been a considerable dissolution of the WC particles.

B. Fe-Cu-C System: In contrast to the WC/Co sample, microwave sintering of FC208 sample was performed under almost the sintering conditions as in the conventional method. Although there were some improvements in sintering times and mechanical properties between the two techniques, there were major differences in the microstructure. Figure 3 shows the Cu and Fe X-ray maps of the microwave sintered sample, these maps are typical of the whole structure found, although in some Fe grains the Cu precipitates were small than those shown in Figure 3. The conventionally sintered FC208 sample showed the same microstructure as that of microwave sample in the majority of the sample. However, there were areas where there was a completely different structure as seen in Figure 4. The regions shown in Figure 4 from the conventionally sintered Fe-Cu-C sample, were not in abundance, therefore it would account only for the slight differences in the mechanical properties observed between microwave and conventionally sintered sample. In general, more uniform distribution of Cu phase was observed in microwave sintered samples than in the conventional sample.
The X-ray maps of Figures 1 to 4 demonstrate the powerful technique of high spatial resolution X-ray mapping. Where slight differences in chemical composition can be detected as shown in the example of Fe-Cu-C material, as well as the large differences, which are apparent between the microwave and conventionally sintered WC/Co material.

![Figure 3. Cu and Fe X-ray maps from the microwave sintered Fe-Cu-C sample, the distribution of the Cu precipitates was found to be uniform throughout the sample.](image)

Figure 3. Cu and Fe X-ray maps from the microwave sintered Fe-Cu-C sample, the distribution of the Cu precipitates was found to be uniform throughout the sample.

![Figure 4. Cu and Fe X-ray maps from the conventionally sintered Fe-Cu-C sample, although there was a uniform distribution of Cu precipitates there were areas of undefined particles and phases as shown by the Fe and Cu maps.](image)

Figure 4. Cu and Fe X-ray maps from the conventionally sintered Fe-Cu-C sample, although there was a uniform distribution of Cu precipitates there were areas of undefined particles and phases as shown by the Fe and Cu maps.

4. CONCLUSIONS

High spatial resolution X-ray mapping is an excellent technique in determining phases and chemical changes within the microstructure of a material at nanometer level. It is clearly shown that Co does not dissolve the WC when microwave sintered, unlike in conventional sintering. In the case of Fe-Cu-C powders, microwave sintering again appears to show that mixing does not occur and more uniform distribution of Cu phase than in the conventional sample was observed.

REFERENCES


