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Local Grain Growth in Cemented Carbide Sintering

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Two possible origins for local grain growth during sintering of fine WC-Co grades have been investigated. The main origin for formation of big WC crystals in a fine WC-Co structure is the presence of big WC seed crystals or particles, already contained in WC powder, which at least partially survived WC + Co milling. Growing mechanism during sintering is Ostwald ripening. Another possible reason is the presence of heterogeneous impurities which locally form low melting alloys with the cobalt binder, thus enabling dissolution and crystallization of WC in that area much earlier than for bulk material. Contrary to many researchers' assumptions, no influence of carbon heterogeneities was found.

Key Words: Cemented carbide sintering, Local grain.

INTRODUCTION

A typical example of local or discontinuous grain growth in a fine grain WC-Co cemented carbide structure is shown in Fig. 1. In the literature there exists no exact knowledge about the origin of that phenomenon. Occasionally assumptions have been made and it was obvious that milling has a certain influence. During our investigations, we found two possible reasons which are responsible for local grain growth.

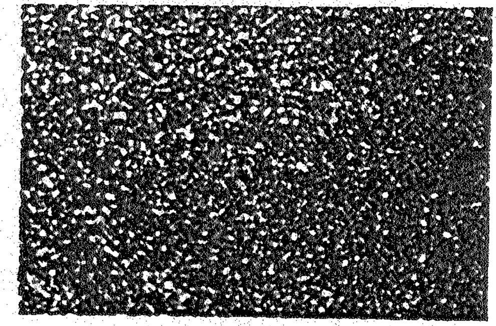


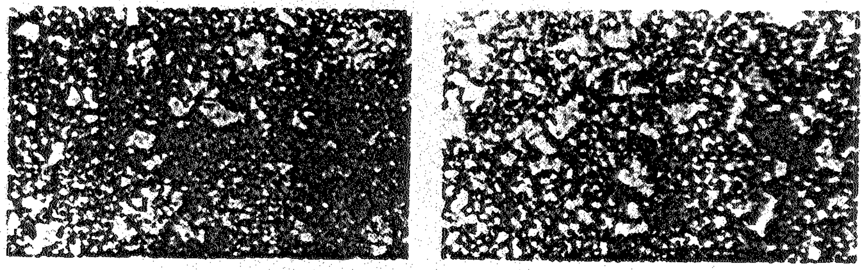
Fig. 1. Local grain growth of submicron WC during WC-10% Co-sintering; microstructure ×750

Influence of the presence of coarse particles in fine grain WC powder

The powder morphology of a submicron WC sample which showed excessive local grain growth (Fig. 2) within the bulk of fine WC grains, relatively often big particles (10–80/μm) of varying density could be observed (Fig. 3). For that sintered structure can be observed. Because of the fact that percentage of coarse WC addition was relatively small in all cases, one can assume that the probability for a coarse WC particle to be crushed is rather low.

It has been suggested that local grain growth would survive milling treatment to a certain extent and, even if they are crushed, mainly larger fractured parts will be formed having highly active faces. Therefore, the coarse WC particles and their fractured parts act as seeds or growing centres. Growing mechanism is the very well-known Ostwald ripening.

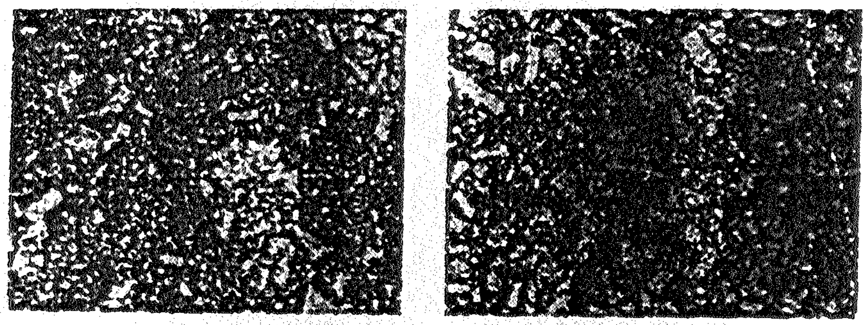
Influence of milling time can be derived from Fig. 5. Short milling shows more islands of coarse crystals, that means most of the polycrystalline large particles are attacked by the molten binder phase along grain boundaries but grain growth continues as long as particles are in close neighbourhood. Prolonged milling results in a structure with more distributed coarse crystals due to a disintegration of coarse polycrystalline WC particles.



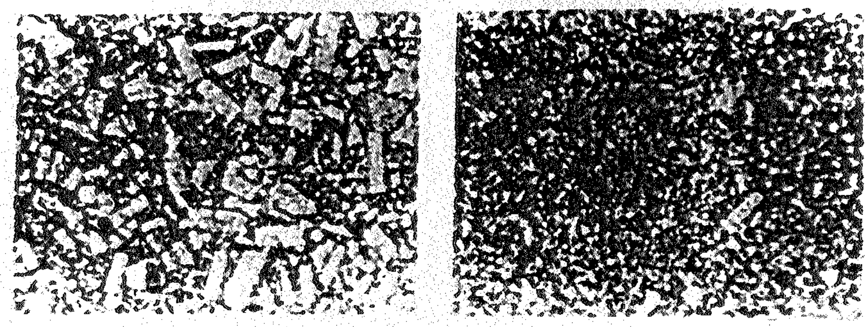
(a) 10 min milling time (b) 40 min milling time

Fig. 5. Structure of WC-10% Co (1 μm WC + addition of 4% 12 μm WC); dependence on milling time in a planetary ball mill ×380

Influence of temperature shows the normal trend. The higher the temperature the more grain growth occurs (Fig. 6).



(a) 1450°C (b) 1470°C



(c) 1500°C (d) 1500°C without coarse WC addition

Fig. 6. Structure of WC-10% Co (1 μm WC + addition of 4% 12 μm WC); temperature dependence ×380

So it can be stated that any coarse WC particle already contained in a fine starting WC powder will be the origin of an island of large crystals or of several distributed coarse WC crystals after sintering.

The origin for the presence of coarse particles in fine WC powder can be either a contamination by coarse WC during production or the survival of pseudomorphic APT shapes.

The influence of heterogeneously distributed phosphorus

During investigations in introducing traces of foreign elements *via* the cobalt powder into the cemented carbide it was found that phosphorus causes enhanced grain growth (Fig. 7). The reason is that phosphorus depresses the melting point of cobalt considerably. As it can be seen in Fig. 8, phosphorus containing sample shows much higher shrinkage than normal samples during 1 h presintering in hydrogen at 1000°C. Microstructure of that sample shows beginning of excessive grain growth. As a consequence, dissolution and crystallization process of WC starts in phosphorus containing cobalt binder earlier than in pure cobalt. If phosphorus distribution is heterogeneous, contaminated areas show local advanced grain growth.

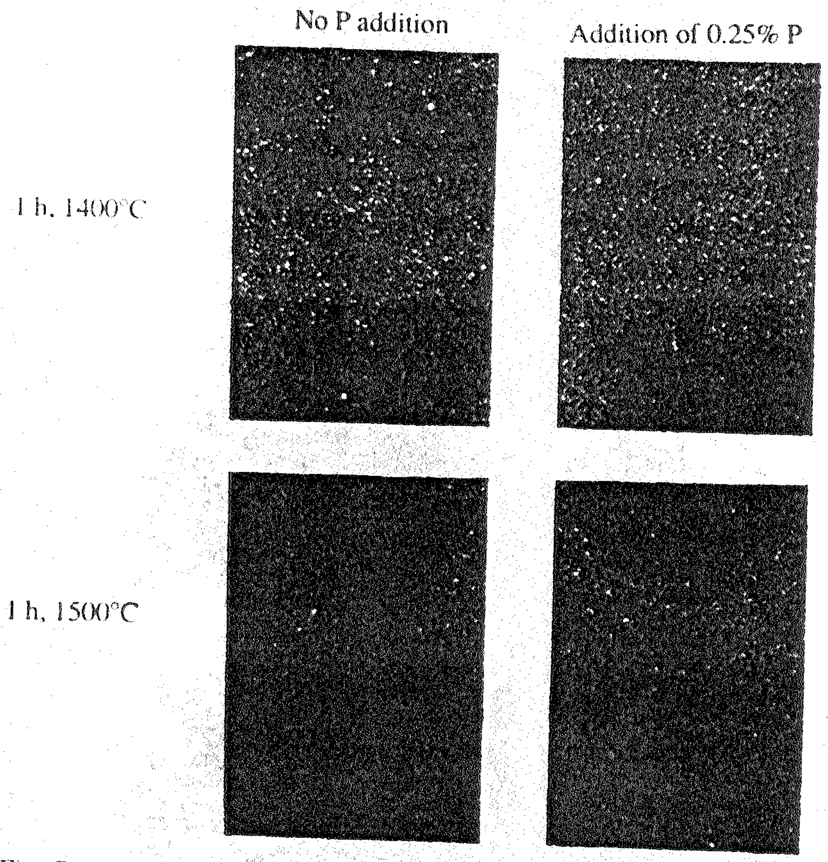
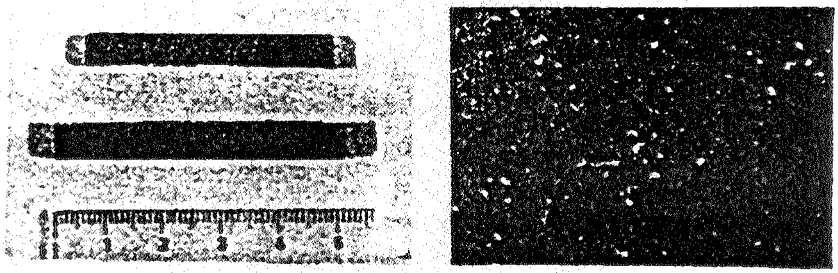


Fig. 7. Structure of 1 μm WC + 10% Co + 0.25% P; addition of$CO_3(PO_4)_2$ to Co powder; influence on grain growth in comparison with undoped sample; SEM ×250

Influence of carbon heterogeneity

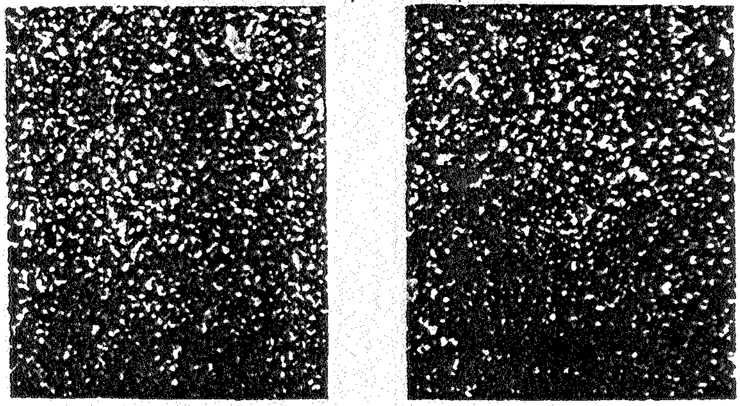
During several discussions at international meetings, it was assumed that the carbon heterogeneities may be responsible for local grain growth. Inhomogeneous carbon distribution can occur in processing of slightly understoichiometric WC. Layers closely connected to the graphite walls and the bottom of containers used in carburization process, due to carbon transfer *via* gaseous hydrocarbons from graphite to tungsten or tungsten carbide grains have always stoichiometric carbon content contrary to the bulk of the material. After deagglomeration and mixing, the stoichiometric WC particles are statistically distributed in the understoichiometric majority.



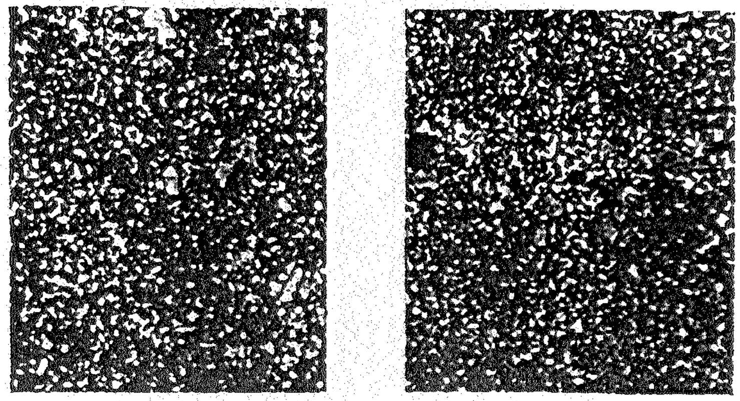
(a) Shrinkage (b) Microstructure ×100

Fig. 8. Shrinkage of undoped and P doped presintered WC-10% Co sample and microstructure

Fig. 9 shows the results of a test where understoichiometric WC (sample taken only from the centre of a container after carburization) was mixed with increasing percentage of stoichiometric WC of comparable grain size. As can be seen, local



(a) No addition (b) 0.5%



(c) 1.0% (b) 6.0%

Fig. 9. Structure of WC-10% (1.3 μm W (5.8% C) + addition of 1.3 μm WC (6.14%)) ×750

grain growth is comparable in all cases. Structure shown in Fig. 2a is derived from understoichiometric WC.

The structure after addition of lampblack to compensate the deficiency shows enhanced grain growth too. This enhanced grain growth is due to the higher carbon content of the molten binder phase which accelerates tungsten transfer.

From the above results, the conclusion can be drawn that carbon heterogeneities are not the origin of local grain growth.

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