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THERMODYNAMIC*AND SINTERING STUDIES IN THE Co-W-C SYSTEM

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ABSTRACT

Sintering studies of WC-11%Co samples have been performed in a dilatometer. The temperature dependence of the shrinkage and the shrinkage rate during heating and isothermal treatment has been determined using computer evaluation. The relative magnitude of the densification in the solid and liquid states, respectively, has been determined and correlated to the Co-W-C phase diagram. Furthermore, some structural changes occurring under decarburizing conditions have been explained. Mechanisms for solid and liquid state sintering are presented.

INTRODUCTION

WC-Co alloys are of great practical importance in cemented carbide applications. Manufacturing of cemented carbides includes a sintering process in the temperature range of 1350-1500°C, at which temperature the Co-rich binder phase is in the liquid state. Therefore, extensive investigations have been performed concerning the liquid phase sintering of the WC-Co system, (e.g. refs 1-4). Many of the investigations are only concerned with isothermal sintering at a temperature at which the binder is molten. The heating to the isothermal temperature is in these cases very rapid. However, in industrial sintering processes the heating is rather slow. This leads to a considerable amount of densification during the isothermal period.

In the present work it was intended to study the sintering behaviour also during both solid phase and liquid phase sintering.

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* Due to the limited space available for this paper, the thermodynamic studies will not be reported here.

EXPERIMENTAL

The two WC-Co alloys, No. 11 and No. 21, used in the sintering experiments both contained 11.0 wt-% cobalt but in alloy No. 21 a small amount carbon was added. In the two alloys, the carbon content was 5.46 and 5.52 wt-%, respectively.

The sintering experiments were performed with a THETA DILATRONIC II dilatometer. The temperature gradient was measured to be $\pm$ 1.5°C within 25 mm, which was equal to the original length of the samples. All the refractory parts in the measuring system were made of recrystallized alumina. The dilatometer was equipped with a "constant low load, long range" - measuring module, which had a linear range of 10 mm and a load of 0.25 N acting on the sample.

The temperature measurement was checked by heating a pure Fe rod and evaluating the α/γ and γ/α transition temperatures. These were found at 911 $\pm$ 1°C and at 1389 $\pm$ 2°C, respectively, which are in close agreement with the values 912°C and 1394°C, respectively, found in the literature (ref 5).

A sintering experiment was performed as follows: the dilatometer furnace was heated at 15°C/min to 1000°C with an atmosphere of pure helium (99.995%). Then the heating rate was decreased to 5°C/min and simultaneously the atmosphere was changed to a gas mixture of CO and CO_2 with a high carbon potential. The heating was stopped at four different temperatures, namely 1250, 1275, 1350 and 1425°C, for an isothermal heat treatment during three hours, consequently giving four series of sintered samples. The cooling rate was 5°C/min. The output signals from the dilatometer for each experiment were registered on a punched tape. This record was evaluated using a computer programme, which gave the dependence of the shrinkage and the shrinkage rate on the temperature and time. Correction was made for the thermal expansion of the measuring system.

RESULTS AND DISCUSSION

The computer evaluation of each sintering experiment gave corrected values of the temperature dependence and of the time dependence of the shrinkage during the heating stage and the isothermal stage, respectively. The programme also calculated the shrinkage rate, i.e. the time derivative of the shrinkage, by numerical differentiation of seven consecutive data points.

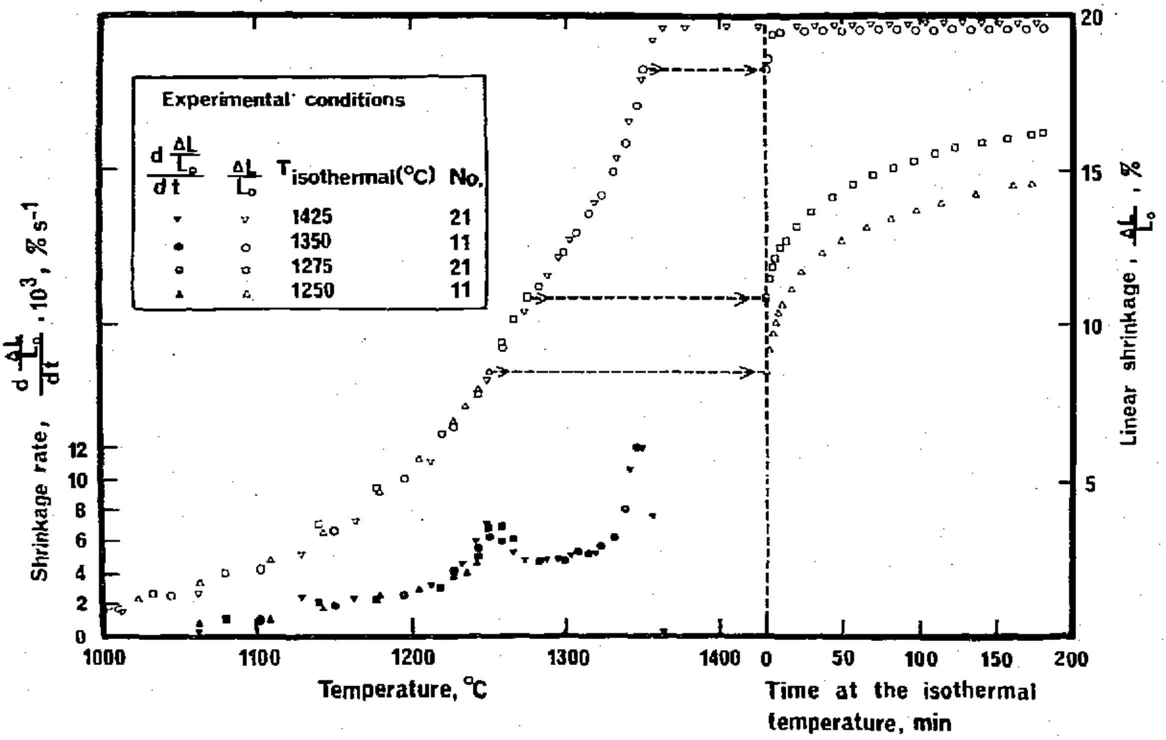

Fig 1. The shrinkage and shrinkage rate curves for four typical experiments, one at each isothermal temperature. (Carbon activity in the sintering atmosphere near unity in all experiments).

Fig 1. comprises information from one representative experiment at each isothermal temperature. The linear shrinkage of the samples is shown for both the heating stage and the isothermal stage. The shrinkage rate curve shows two distinct peaks, the first at about 1255°C and the second at about 1355°C and 1345°C, for alloys Nos. 11 and 21, respectively. The intermediate minimum is found at about 1305°C and 1295°C for alloys Nos. 11 and 21, respectively.

In a recent work (ref 6) it has been shown that the lowest temperature for co-existence of liquid, β (FCC-Co) and WC is 1275°C. At this equilibrium temperature graphite is present in the sample, i.e. $a_c = 1$. At lower carbon activities the temperature for the three-phase equilibrium is higher. A stoichiometric WC-Co alloy, such as alloy No. 11, reaches the three-phase equilibrium at about 1300°C and leaves it at about 1335°C. This means that the binder phase in this alloy starts to melt at 1300°C and is completely molten at 1335°C. For alloy No. 21, which is somewhat overstoichiometric with respect to carbon, the corresponding temperatures are about 1275°C and 1320°C, respectively.

From the temperature given above it is evident that the first peak must be related to reactions in the solid state and that the second peak can be correlated with the completed melting of the binder phase. In the same way it is relevant to compare the temperature of the minimum with the temperature for incipient melting. The discrepancies can be explained by a delay in the starting of the reactions due to the fact that these are diffusion-controlled. Furthermore, a time delay in the heating of the sample in relation to the heating of the thermocouple can probably account for a part of the discrepancy .

From the information given above it is evident that a large part of the densification of WC-Co samples takes place in the solid state, i.e. when the binder phase (β) still is solid. This solid state densification can now be estimated with the shrinkage at the minimum point of the shrinkage rate curve, according to the discussion above. Fig 1 then gives the solid state shrinkage as being about 13% and 12% for alloys Nos. 11 and 21, respectively. The lower value for alloy No. 21 is explained by the earlier formation of liquid phase in this alloy. Consequently the solid state shrinkage is about 0.60-0.65 of the total shrinkage.

This is a somewhat higher value than those reported earlier (refs 1, 2, 4). However, the amount of solid state shrinkage is strongly influenced by the heating rate and the cobalt content.

Another interesting correlation between the sintering results and the phase diagram Co-W-C has been found. Due to occasional decarburisation η phase, i.e. M_6C carbide, was formed in some of the samples during the isothermal treatment. However, the η phase was found in two completely different types of structure. In samples heat-treated at 1425°C, the η phase was mostly found as large "islands", even in the middle of the specimen, with a two-phase structure η + WC, cf. Fig 2. No such "islands" were found in the samples heat-treated at 1350°C and below. In these samples the η phase was found as fine-grained precipitates in the surface zone, cf. Fig 3. This can be correlated to the fact that the lowest temperature for co-existence between liquid phase and η phase, has recently (ref 6) been determined to be

1355°C. This explains the feature of the η phase structure: At 1425°C the η phase grows in contact with liquid phase which facilitates the growth of a coarse structure, but at 1350°C and below the growth must occur in the solid state at a low diffusion rate.

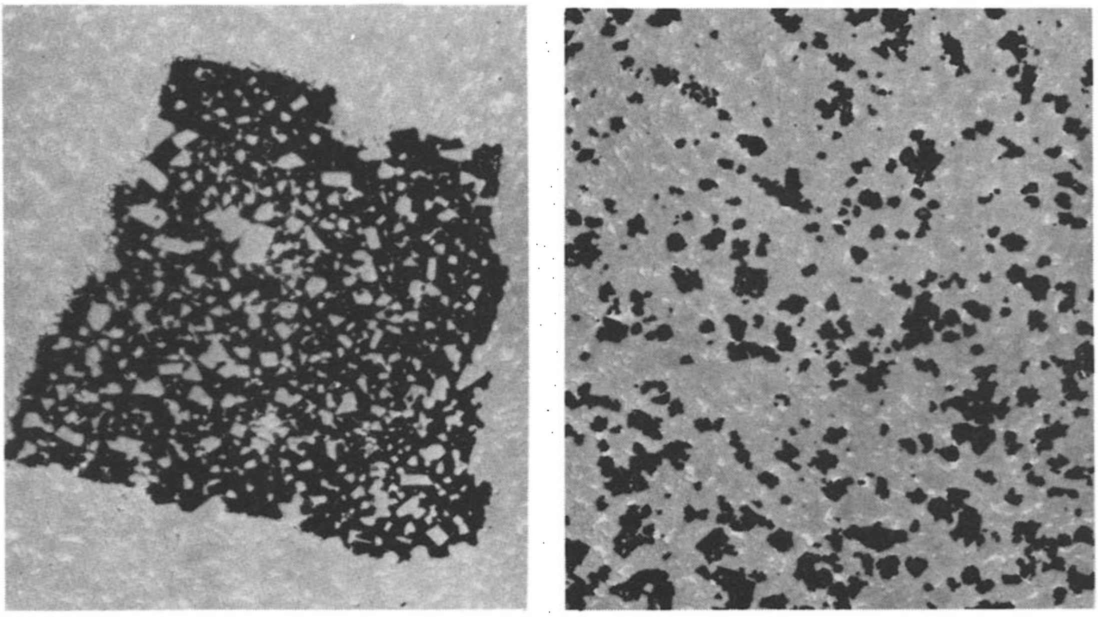

Fig 2. Sintered at 1425°C Fig 3. Sintered at 1350°C
Structures of two decarburized WC-11% Co alloys sintered at different temperatures. The η phase (M_6C) appears dark. Etched in Murakami's reagent. 800x.

Stages and mechanisms of sintering in WC-Co system

Sintering in the WC-Co system is usually regarded as a liquid phase sintering. However, in this work and in some earlier investigations (refs 1-2, 4), it has been revealed that a large part of the shrinkage takes place in the solid state. Therefore, the explanation of the sintering behaviour must involve a solid state sintering mechanism. There are some theories presented in the literature, and the one given by Meredith and Milner (ref 3) will mainly be used here. Characteristic for this theory is that after the slow initial shrinkage rate at low temperatures, a rapid solid state shrinkage occurs within a narrow temperature range, depending on a particle rearrangement process. This leads to a formation of relatively close-packed aggregates of WC-particles surrounded by large voids. The particle rearrangement is a result of the enhanced surface and interfacial diffusion of cobalt, which gives a viscous flow of the solid binder phase. In the present work this stage is indicated by the first peak in the shrinkage rate curve, cf. Fig 1.

Further densification requires a rearrangement of the large aggregates, a process that cannot start before the binder phase melts. Consequently, the shrinkage rate decreases, which is indicated by the minimum in the shrinkage rate curve. The amount of liquid phase increases slowly at first, giving a slow increase in the shrinkage rate. But, when the binder is completely molten a fast rearrangement, a collapse, of the aggregates occurs. This process is the origin of the second peak in the shrinkage rate curve. After this collapse a very slow tertiary shrinkage follows. During this stage an elimination of small pores occurs probably by the solution-precipitation mechanism proposed by Kingery (ref 7). Furthermore, a homogenization of the carbide distribution takes place during this stage, according to Meredith and Milner (ref 3).

CONCLUSIONS

It can be concluded that the sintering results obtained in the present work can easily be correlated to both the phase diagram Co-W-C and to existing theories of the sintering in the WC-Co system, and also give several new contributions to the understanding of this field.

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