

Phase Decomposition and Grain Growth in (W,Ti) C-Co-Alloys

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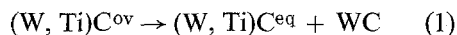
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The object of this study was to obtain information on the inhomogeneous structure of the WC-TiC solid-solution phase after sintering with cobalt or nickel acting as binder. For this purpose, the solubility of WC in TiC was determined at temperatures from 1500 to 2100°C. Furthermore, grain growth and phase decomposition behaviour were investigated in the temperature ranges 1450 to 1550°C and 1700 to 1850°C. Phase-decomposition of oversaturated mixed carbide solid solution which is not capable of further coarsening enabled the reaction constant at the solid-liquid interface to be determined.

1. Introduction

The properties of sintered hard metals containing mixed carbides are determined to a large extent by the structure of their individual components. In the last years several studies [1-4] have dealt with the qualitative and quantitative analysis of the composition of mixed carbide phases in (W, Ti, Ta)C-Co alloys and have discussed possible methods of forming inhomogeneous grains (borderzone, corezone) under different sintering conditions. The partially contradictory findings led us to examine the (W, Ti)C-Co system further, with the aim of explaining the origin of inhomogeneities in mixed carbides and of better understanding grain growth and phase decomposition of solid, multi-component particles in the presence of a liquid binder phase.

WC has a large, highly temperature-dependent solubility in face-centred cubic TiC. Therefore, if mixed carbides are produced at e.g. 2100°C and sintered in the presence of cobalt at e.g. 1500°C, phase decomposition will occur simultaneously with grain growth:



(eq = equilibrium phase, ov = oversaturated phase). The decomposed areas can be indicated metallographically, by X-rays or with the aid of a microprobe. In this way in the (W, Ti)C-Co system – in contrast to single-carbide alloys like WC-Co, TiC-Co, or TaC-Co – it is possible to determine the amount of carbide transformed during sintering. For these reasons, we made

efforts to investigate phase decomposition and grain growth separately.

For studying *phase decomposition*, the volume of the decomposed phase formed during the sintering of oversaturated, coarse-grained mixed carbides (not capable of further coarsening), was measured as a function of sintering time and oversaturation. To determine *grain growth*, we measured the mean grain size of (W-Ti)C-mixed crystals and determined the dependence of the grain size on original grain size, sintering temperature and sintering time.

2. Specimen Preparation

To produce oversaturated WC-TiC-mixed crystals, powder mixtures of 80% WC and 20% TiC, with 5 g of cobalt added per 100 g of mixture, were dry-ground for 24 h and heat-treated in a continuous furnace for 30 h at 2100°C in the presence of H₂. For the phase decomposition reaction a specimen size of about 10 × 10 × 10 mm³ was chosen. Homogeneity of the 50-100 μm mixed carbide grains could be confirmed by electron microprobe analysis. The highly porous specimens contained about 2% cobalt, which was present generally in 1-2 μm thick layers between the grains, but not on grain surfaces bordering on the pores (series Ia). To determine the influence of the binder on phase decomposition, its amount in the initial material was increased to 5% Co or 2% Co + 3% Ni by addition of these elements at 1510°C (series Ib and Ic).

The initial material for grain growth experiments was also a powder mixture of 80% WC and 20% TiC heat-treated for 30 h at 2100°C. After crushing, grinding and treatment with hydrochloric acid, cobalt was added to the powder and subsequently the mixture was pressed into green compacts (series II).

3. Testing Procedure and Results

3.1. Solubility of WC in TiC

Because there is a disagreement in the literature concerning the relationship between temperature and solubility of WC in TiC[2], the solubility of WC in TiC, namely in the temperature range of interest here, 1500 to 2000°C, was examined by direct phase analysis with an electron microprobe (fig. 1); differences between the published values and those measured by us are probably due to equilibrium conditions not having been fully established in the previous studies and also to inaccuracies in determining small amounts of free WC by X-rays.

3.2. Phase Decomposition

Specimens of series I were annealed for 5 h at 1800°C (heating up in 3 min; cooling to 1000°C in approx. 10 sec). By use of an electron microprobe, discontinuous changes in W and Ti concentration were found to exist in the grains (fig. 2) at the interface between phases β_{1}^{ov} and β_{1}^{eq} .

After heat-treating the specimens at different temperatures (1800°C/7 h and 1900°C/7 h) it was found metallographically that the growth

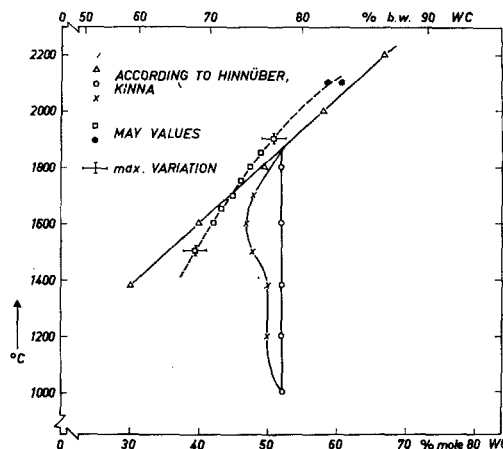


Figure 1 Solubility of WC in TiC (section through TiC-WC system).

direction of the phase β^{eq} was perpendicular to the binder layers, while the cobalt film migrates, ahead of the newly formed phase, into the dissolving mixed crystal. Below 1500°C, no measurable amount of phase β_{1}^{eq} was found even after annealing for 50 h. After removal of the binder from series Ia specimens by treatment with HCl and after subsequent annealing at 1800°C, only traces of the newly formed phase could be found in areas where residual cobalt was present.

The volume of the decomposed phase as a function of time and temperature was determined on the specimens of series Ia to Ic. The

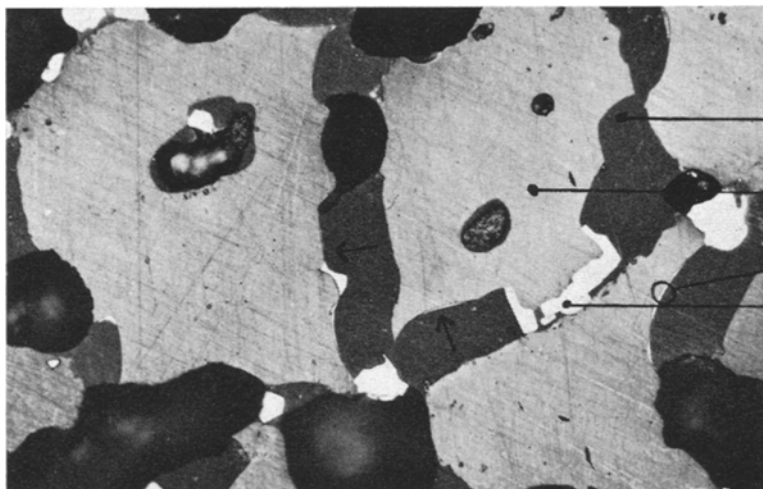


Figure 2 Structure of a heat-treated (W, Ti) C-mixed carbide (growth direction of β_{1}^{eq} :→).

specimens were annealed up to 5 h at temperatures of 1700, 1750, 1800, and 1850°C. The volume of the phase β_1^{eq} in relation to that of $\beta_1^{ov} + \beta_1^{eq}$ was determined by linear-analysis using a semiautomatic analyser according to Fischmeister [5]. All specimens showed a linear correlation between phase β_1^{eq} and sintering time (fig. 3).

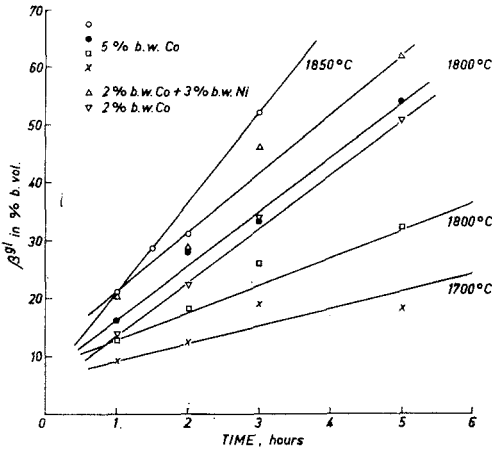


Figure 3 Phase decomposition rate for the mixed carbide phase β_1^{eq} ($\beta_1^{eq}(t = 0) = 0$).

In the various specimen series there is only a parallel shift toward higher values in the sequence Ia \rightarrow Ib \rightarrow Ic; in other words, type and proportion of the binder phase do not influence the slope ($\tan \alpha$) of the decomposition-rate straight-line plot.

For estimating the rate constants and their temperature dependence the following assumptions were made: The driving force for transferring the atoms from the oversaturated initial phase into the equilibrium phase is given by the difference between the free enthalpies of the phases. Thus the variation of the number of moles \dot{n} is set proportional to the difference in concentration Δc of WC in the oversaturated and the equilibrium phase as well as proportional to the effective interface area F' . With grains of nearly equal size, the effective fraction of the surface is determined by half the mean grain surface minus the adjacent surface of pores, which is estimated at 25%. From this follows:

$$\dot{n} = k_e \times F' \times \Delta c \quad (2)$$

The transformation constant k_e has the dimension of a velocity. Since in the temperature

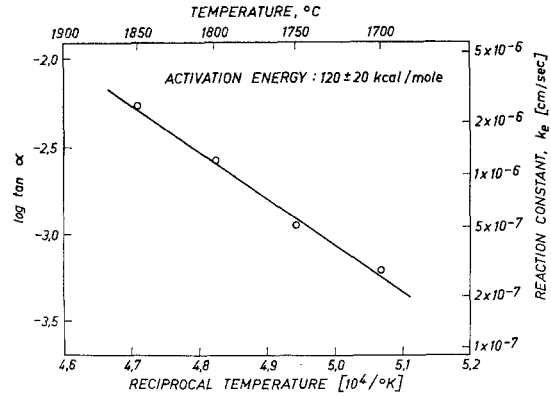


Figure 4 Arrhenius diagram for the phase decomposition.

interval studied Δc changes but little with temperature (fig. 1). We can assume

$$k_e = k_{e0} \times \exp(-Q_e/RT) \quad (3)$$

With an approximate constant interface area the activation energy Q_e can be determined from the Arrhenius diagram (fig. 4). Q_e is found to be 120 ± 15 kcal/mole.

From equation 2 and fig. 1 it follows that

$$k_e = 1.2 \times 10^{-6} \text{ cm/sec at } 1800^\circ\text{C} \\ (\Delta t = 5 \text{ h and } \Delta c = 0.0056 \text{ mole/cm}^3)$$

and from equation 3

$$k_{e0} = 5.5 \times 10^6 \text{ cm/sec.}$$

Since the characteristic values F' and Δc are not definitely known, further discussion will be based only on their order of magnitude.

3.3. Grain Growth

If the growth of the mixed carbide grains is determined by the solution-precipitation process, i.e. if coalescence of the grains, or digestion of smaller by larger particles is to be ignored, the structural change can be described quantitatively by the formulae developed by Wagner [6]. In reaction-controlled growth, the kinetics are determined by the transfer of the atoms at the solid-liquid interface.

The pre-sintered compacts in specimen series II were heat-treated for 30 min, 1, 2, and 4 h at 1450, 1500, and 1550°C in a Tammann Furnace in H_2 atmosphere. Heating and cooling times were comparable to those of series I. During heat-treatment about 50% of the Co contained in the specimens vaporised, the amount depending on temperature and duration of the treatment. The C-content of all specimens was sub-



Figure 5 Structure of a sintered (W, Ti) C-Co alloy, electron-micrograph (Mowital replica).

stoichiometric by about 0.3 to 0.4%, regardless of duration or temperature of the heat treatment. The average intersection length of the mixed carbide grains was determined from electron micrographs (fig. 5).

A significant difference can partially be discerned between the core (originally the coarse particles) and the border (originally the finest particles) at a mixed carbide. During solution and precipitation of the finest particles WC grains are precipitated to a degree depending on the WC solubility in TiC (cf. fig. 5). Coalescence (one grain with several cores) was not observed in case of (W, Ti)C-crystals. This, in agreement with the Stjernberg findings [7], satisfactorily demonstrates the dependence of grain growth rate on time, in fig. 6 the results are plotted as \bar{d}^2 vs. t .

Accordingly the growth law established by Wagner [6] can be expressed as follows:

$$\bar{d}^2 - d_0^2 = k' \times t \quad (4)$$

with

$$k' = 4 \times \frac{64}{81} \times \frac{\sigma k c_0 V_m^2}{RT}$$

where σ represents the interfacial tension, k the interface reaction constant, c_0 the equilibrium concentration on a plane surface (bulk solubility) and V_m the molar volume.

By using the equation

$$d = A(d) \exp(-Q_k/RT) \quad (5)$$

the relation between temperature and rate

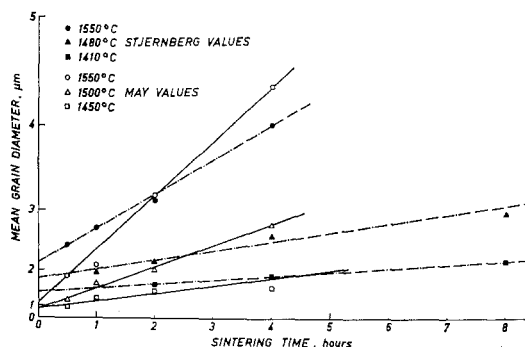


Figure 6 Grain growth at different annealing temperatures (plotted as \bar{d}^2 vs. t).

constants k' can be determined from the time necessary to reach a fixed value of mean grain size at various temperatures [7, 8]. Fig. 7 shows our data in comparison with those obtained by Stjernberg. Despite differing initial compositions, the values of activation energy agree within close limits of error: $Q_k = 120 \pm 15$ kcal/mole according to [7] and $Q_k = 130 \pm 15$ kcal/mole (this paper). This "apparent" activation energy is determined by the values of σ , c_0 , and k , all of which are influenced by temperature to different degrees. Since only a limited influence of the temperature on the interfacial energy σ [9] and solubility c_0 [10] must be assumed for the temperature interval of interest here, the reaction constant k remains the deciding factor in a discussion of the influence of temperature,

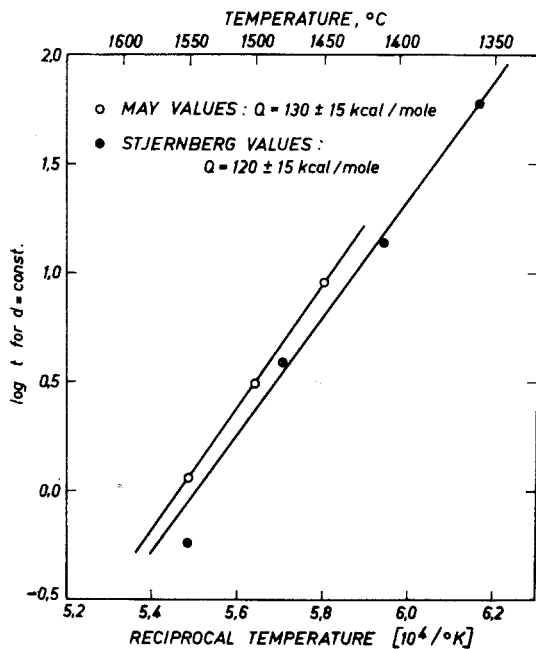


Figure 7 Arrhenius diagram for the grain growth of a (W, Ti) C-Co alloy.

i.e. the factor which determines the rate of grain growth. Assuming that $\sigma = 200$ erg/cm² [11], $c_0 = 0.05$ mole/cm³, and $V_m = 15.5$ cm³/mole, and using a grain diameter of 1.8 μ m (Heyn's grain size = 2.6 μ m) calculated from the measured values (cf. Exner [12]) it is found that for a heat-treatment at 1500°C for 4 h, $k = 4 \times 10^{-5}$ cm/sec. The solubility tests by Skolnick [13] showed a similarly high reaction-constant in the WC-Co system (25×10^{-5} cm/sec).

4. Discussion

The phase-decomposition and grain-growth experiments satisfactorily explain the presence of inhomogeneities which are formed in the mixed carbide phase during liquid-phase sintering. During grain growth a mixed carbide border zone may form which – in relation to the core – will be rich or poor in W, depending on the composition of the (W, Ti)C-mixed crystals used for sintering and on the amount of free WC added.

Furthermore, the values found for activation energies in phase decomposition and grain growth agree within close limits; on the other hand the rate-determining reaction constants of either process (for 1500°C: $k_e \approx 10^{-8}$ cm/sec –extrapolated– $k \approx 4 \times 10^{-5}$ cm/sec) differ by

several orders of magnitude. Since similarly high activation energies were found for the temperature function of the volume diffusion coefficients of W in TiC and of W in (W, Ti)C [14], it may be safely assumed that the kinetics of phase decomposition and grain growth are based on volume diffusion processes. It was possible to develop a model for the phase decomposition process according to which atomic transfer is determined by the diffusion flow in a boundary layer of the dissolving grain [15]. A similar model applicable to grain growth could not be established as yet, so that an explanation of the variation in reaction constants is still outstanding.

Acknowledgement

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