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X-ray diffraction analysis of diffusional alloying of HfC and TaC

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Diffusion in powder blends of HfC and TaC was studied by Rudman's X-ray diffraction method after 5, 20 and 200 h annealing at 1900° C. It was found that hafnium has a higher intrinsic diffusivity compared with tantalum and the homogenization rate is accelerated by grinding the powders together before annealing. The diffusion mechanism was observed to differ in the inner and in the surface parts of the pressed tablets. The degree of interdiffusion and the diffusion coefficients were also determined.

1. Introduction

X-ray diffraction analysis is a quantitative nondestructive method of determining concentration profiles. The method is based on concentration dependence of the interplanar distances and – according to Bragg's law – the corresponding concentration dependence of diffraction angles. The contemporary state of this method and examples of its diverse applications are given in [1]. One of the advantages of the method is its capability of investigating the concentration profiles in extremely small volumes, of the order of μm^3 or nm^3. This property is especially valuable in the investigation of diffusional homogenization of powder blends. Only an average state of interdiffusion in all particles is, of course, reflected in the results.

The purpose of this paper is to apply the method to the study of diffusional alloying of the powder blends of two carbides. Generally, carbides belong to the most prominent components in powder metallurgy and they usually form a basis for preparing hard and refractory materials. These materials are prepared by sintering, which is a procedure where the diffusion of matter plays a very important role. The paper presents the first quantitative results on interdiffusion in this type of material obtained by X-ray diffraction analysis. The HfC and TaC pair was chosen because both components have nearly the same scattering power for X-rays and thus corrections for different scattering factors of the composing atoms are relatively small. Both carbides have the same type of structure (NaCl), and they are completely soluble in solid state. This considerably simplifies the interpretation of results.

2. Experimental details

Commercially available powders supplied by H. C. Starck, Berlin, were used: HfC (average grain size $\sim 1\,\mu m$), TaC (average grain size $1.7\,\mu m$). The lattice parameters were determined by X-ray diffraction: $a_{HfC} = 4.633$ and $a_{TaC} = 4.456 \times 10^{-10}\,m$. The powders were mixed in the molar ratio of 1:1 by tumbling together in an agate mortar for about 75 h. The powder blends were cold-pressed at 15 MPa into the form of tablets. The diffusion annealing was performed in a graphite furnace in the vacuum of 10^{-3} Pa at the temperature of 1900° C for 5, 20, and 200 h. After the diffusion the surface layer ($\sim 200\,\mu m$) was removed by grinding.

The line profiles were measured in steps of

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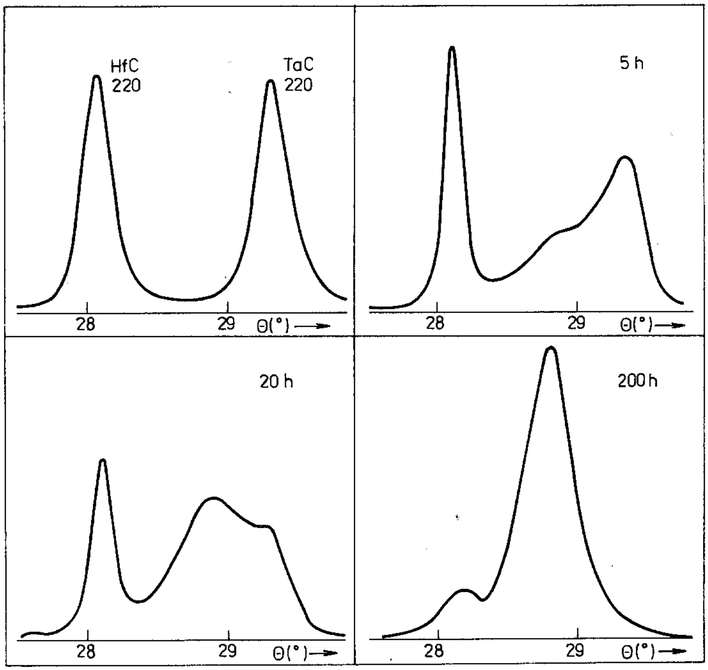

Figure 1 Diffraction profiles of the 2 2 0 reflection bands of HfC and TaC: top left, before annealing; top right, after 5 h annealing at 1900° C; bottom left, after 20 h annealing at 1900° C; bottom right, after 200 h annealing at 1900° C.

0.04° θ with a HZG-3 goniometer. The 2 2 0 reflection was measured with Cu$K\alpha$ radiation because of the good angular resolution and high intensity. The α_2 component was eliminated according to Keating [2] and Rudman [3] and the angular dependence of Lorentz-polarization factor was calculated for the compounds $Hf_{1-x}Ta_xC$, where x is the atomic fraction of tantalum in the metallic sublattice positions of the mixed carbide. The angular position of the 2 2 0 reflection for the given composition x was calculated from the lattice parameter determined by Vergard's law.

3. Results

The diffraction profiles obtained in different stages of the homogenization process are presented in Fig. 1. The profile obtained after 5 h annealing shows the lowering and asymmetrical broadening of the 2 2 0-TaC peak with the 2 2 0-HfC peak being narrower and with no displacement or deformation taking place. It follows from these features that TaC is contaminated much faster by hafnium atoms than HfC by tantalum atoms. This indicates a higher intrinsic diffusivity of hafnium compared with tantalum. The narrowing of the HfC peak after annealing is most probably caused by removing deformation due to the cold work. After 20 h annealing there may be seen a gradual increase of the intensity between the original peak positions which corresponds to the formation of solid solutions with a broad spectrum of composition. The lowered intensity of the HfC peak can be explained by a decrease of volume fraction of the pure HfC in the sample. The same tendency has also been observed in the profile from the samples annealed for 200 h: the pure TaC component completely disappears and the main maximum corresponds to a solid solution with the mean composition near $x = 0.55$. It may be seen that even after 200 h annealing there still survive some small fractions of nearly pure HfC. Back-reflection X-ray photographs of the samples after annealing indicate no appreciable increase of the grain size compared with the original materials.

The influence of the grinding of the powder blends on the diffusion homogenization process can be seen in Fig. 2 where we compare the diffraction profiles of the samples with and without grinding preceding the 200 h homogenization. The ground blend exhibits a considerably higher degree of interdiffusion after the same time of annealing compared with the unground blend. The role of grinding is known to chemists preparing mixed carbides by homogenization annealing but it is not yet well understood. It is believed that it can be connected with impurities, strains and lattice defects introduced

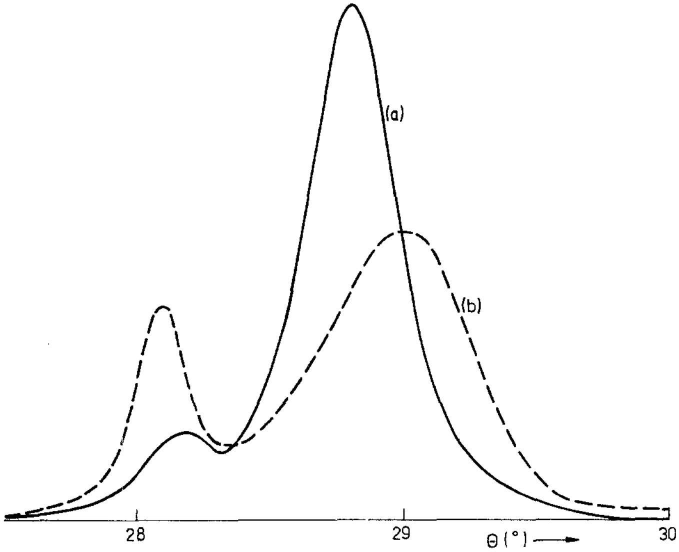

Figure 2 Grinding enhances the diffusion process. Both samples were homogenized for 200 h at 1900° C: (a) ground blend, (b) unground blend.

by grinding, which may enhance homogenization (at least at the initial stages of the process) but a more extensive systematic study is needed to explain this effect. The influence of grain size reduction and mutual rubbing can be also regarded as possible explanations. The connection with possible pre-alloying will be discussed below.

Fig. 3 shows results obtained after a 200 h anneal of two portions of the sample: the first taken from the inner part of the tablet and the second prepared from filings removed from the surface after annealing. The results obtained from the surface portions of the sample indicate the less developed state of interdiffusion compared with the interdiffusion in the bulk and also the activation of a different mechanism of diffusion: the overall picture can be described as the prevailing diffusion on the grain surfaces which leaves considerable inner parts of the grains undisturbed. This can be inferred from the remaining narrow peaks in the positions of

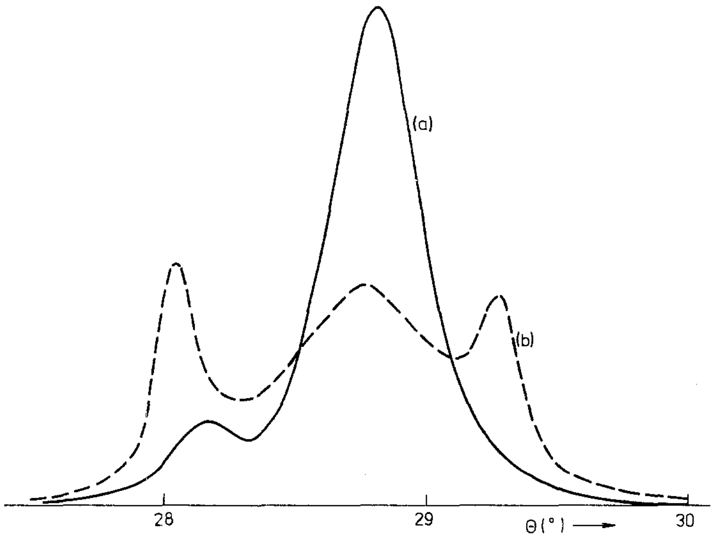

Figure 3 Comparison of the diffraction profiles from the inner (a) and the surface (b) parts of the sample homogenized for 200 h at 1900° C.

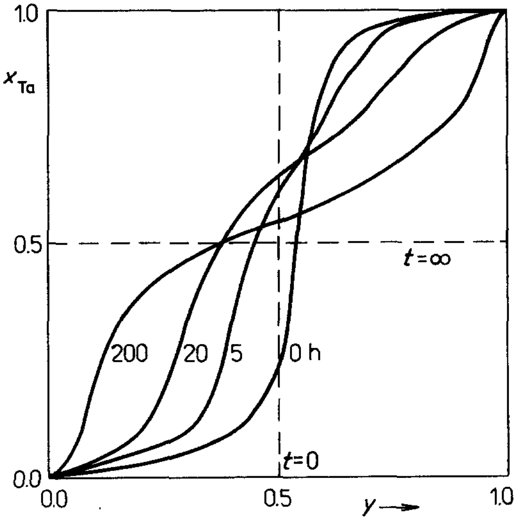

Figure 4 Concentration–effective penetration curves of HfC and TaC powder blends at 1900° C for various times of annealing.

the pure HfC and TaC reflections. This grain-surface diffusion can be expected equally well to contribute in the bulk of the specimen at the start of homogenization. Actually, certain similar features can be found in the diffraction band profiles of the surface-portion sample after 200 h anneal (Fig. 3b) and of the inner-portion sample after a 20 h anneal (Fig. 1). But the remaining distinctions and the quite different annealing times need to be explained. A possible reason for these differences may be the existence of a texture developed during compression in the surface layers of the tablets [4].

The quantitative analysis followed Rudman [3] and Delhez *et al.* [4]. The analysed samples were all from the inner parts of the tablets pressed from the ground blends. The integration of the corrected diffraction profiles yielded the concentration–effective penetration curves which are shown in Fig. 4. Here x is the atomic fraction of the tantalum atoms in the metallic sites in a mixed carbide and the effective penetration y is defined as

$$y = \int_0^x N(x)\partial x \qquad (1)$$

where

$$N(x)\partial x = C\frac{(-\partial d(x)/\partial x)V(x)^2}{d(x)^2}f(\theta)\partial x \qquad (2)$$

represent the volume fraction of compositions between x and $x + \partial x$; $V(x)$ is the volume of the unit cell at a concentration x, $f(\theta)$ is the pure α_1 diffraction profile corrected for the Lorentz-polarization and structure factor, $d(x)$ is the interplanar distance and C is a constant. The effective penetration depth is usually normalized so that $y = 1$ for $x = 1$ (see e.g. [3] and [4]). The lines $t = 0$ and $t = \infty$ in Fig. 4 correspond to the theoretical curves for the limiting cases of time of interdiffusion for the given ratio of components.

TABLE I Summary of results (F is the degree of interdiffusion and D the diffusion coefficient)

	0	5	20	200
F	0.16	0.26	0.39	0.66
Dt (μm^2)	–	0.010	0.024	0.073
D ($10^{-8}\,\mu$m^2 sec^{-1})	–	56	33	10

The complicated form of the concentration–effective penetration curves for the samples obtained by annealing for 5 and 20 h reflects the observed coexistence of solid solutions differing in composition with the rest of pure HfC. From the concentration–effective penetration curves the following degrees of interdiffusion were determined:

$$F = \frac{\int_{x=0}^{x(y=y_M)} (y_M - y)\,\mathrm{d}x}{\bar{x}y_M}, \qquad (3)$$

where y_M represents the Mantano interface and $\bar{x}$ is the average composition of the sample. The values of the degree of interdiffusion are presented in Table I. A non-zero value of F for $t = 0$ is mainly caused by the presence of size/strain broadening which is appreciable at $t = 0$ and this value is thus incomparable with the other F-values derived for $t > 0$. The effect cannot be ascribed to pre-alloying because the broadening of the HfC peak is removed after 5 h anneal (see Fig. 1). The remaining instrumental and spectral broadening affects the other F-values negligibly (see e.g. [6]). It can also be seen from Fig. 1 that the homogenization process is still incomplete even after a 200 h anneal.

Using a model of concentric spheres [3] we have calculated theoretical dependencies of the degree of interdiffusion F on the product of the diffusion coefficient D and the time t. Fig. 5 presents the F-values obtained from the model with the inner sphere of HfC surrounded by the TaC shell. (For the equimolar ratio and nearly the same melting points of components the

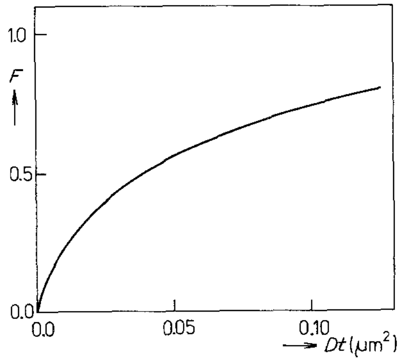

Figure 5 Degree of interdiffusion F as a function of Dt calculated according to the model of concentric spheres (D is diffusion coefficient and t is time) with the inner HfC sphere (radius of 1.3 μm) and the outer TaC shell (outermost radius equal to 1.6 μm).

choice of a configuration is rather arbitrary – see for example [6]; the surviving peak of the pure HfC leads us to the suggestion of a model of HfC grains enveloped by TaC.) The diffusion coefficients D, also presented in Table I, have been determined from the observed degrees of interdiffusion and the chosen times of annealing. The decrease of the diffusion coefficient with the increasing time at temperature unchanged is probably caused by the effects of non-ideal mixing and non-uniform particle sizes [7]. It should be noted, however, that the diffusion coefficient values arrived at by this method are only relative.

4. Discussion and conclusions

Usually extremely small particles are needed to obtain single phase homogenized solid solutions of the HfC and TaC below 2500° C. In [5] a temperature of 2600° C was applied for the diffusion of the components with ~0.2 μm grain sizes and grain sizes nearly a hundred times larger were achieved after 1 h annealing. The diffusion at 1900° C, which was the temperature of annealing used in our experiment, is naturally much slower, but no appreciable increase of grain size was observed even at the degree of interdiffusion approximating 70%. The slow process of interdiffusion may be an advantage in cases where a fine-grained structure is aimed at – as is usually the case of sintering in powder metallurgy.

The present investigation of the interdiffusion in carbides revealed the applicability of the X-ray diffraction method for this important class of materials. Further studies are needed to evaluate the influence of sample preparation and grain size on the process of interdiffusion.

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