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THE USE OF TERNARY PHASE DIAGRAM SECTIONS IN SOLID-STATE REACTIONS INVOLVING TiC FORMATION

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Solid-state diffusion couples are used as simulation experiments to study the diffusional interaction between iron-carbon or cobalt-carbon substrates and titanium carbide coatings deposited by chemical vapour deposition. The plotting of diffusion paths on the ternary phase diagram cross sections Fe-Ti-C and Co-Ti-C reveals information concerning the solid-state diffusion process during this deposition.

A diffusion path illustrates only phenomenological features; for kinetic information composition profiles as a function of distance may be used.

1. INTRODUCTION

Titanium carbide (TiC) is used as a protective coating on tool parts for abrasive applications, with the main aim of improving their wear resistance. It can be deposited by means of chemical vapour deposition (CVD), a technique using the reactive gases TiCl_4 and (mostly) CH_4 as carbon source. Hydrogen is being employed as a carrier gas; all deposition experiments of TiC were performed at a temperature of 1273K. In CVD practice of TiC mostly steel or cemented carbide (Co-WC two-phase material) substrates are used, which also contribute carbon atoms to form the TiC coating. These kind of substrates have the clear advantage that the bonding between surface layer and substrate is greatly enhanced because of the diffusional interaction. However, for the abrasive application of TiC coatings, this diffusional interaction could also turn into a disadvantage: in many cases the carbon containing substrate is strongly decarburized, which results in a decrease of hardness and mechanical strength¹.

In this paper we will describe the phenomenology of the underlying diffusion process by plotting diffusion paths on ternary phase

diagram cross sections. In our investigations we started with binary substrates only, viz. $\text{Fe}_{100-y}\text{C}_y$ and $\text{Co}_{100-y}\text{C}_y$. This simplifying approach has the advantage that a ternary system has developed after the deposition of TiC on those substrates, so that the appropriate ternary phase diagrams Fe-Ti-C and Co-Ti-C can be used (in situations assuming thermodynamical equilibrium). Future research efforts are aimed at an extension towards the quaternary systems Fe-Cr-Ti-C and Co-W-Ti-C, linking up with the CVD practice of coating steel or cobalt-based cemented carbide substrates with TiC.

This work is part of a research program with the aim of studying the kinetics of TiC formation by CVD (using $\text{TiCl}_4/\text{CH}_4/\text{H}_2$) in relation to the diffusion processes involved^{2,3}.

2. DETERMINATION OF PHASE DIAGRAM CROSS SECTIONS

The determination of the phase diagram cross sections in the systems Fe-Ti-C and Co-Ti-C at 1273K has been described elsewhere^{4,5}. The most important analysis technique we used in those investigations was electron probe microanalysis (EPMA). At this moment we will only present the Fe-Ti-C and Co-Ti-C cross sections at 1273K, see figs. 1,2:

FIGURE 1.
Isothermal section of the phase diagram Fe-Ti-C at 1273K.

FIGURE 2.
Isothermal section of the phase diagram Co-Ti-C at 1273K.

3. OBSERVED DIFFUSION PATHS; THE DIFFUSION COUPLE ANALOGY

To describe diffusional interactions between phases in ternary systems so-called diffusion paths can be plotted on the isothermal cross sections. A diffusion path represents the average concentration profile of the various elements in the diffusion zone. In single-phase materials this path coincides with the concentration profile: it is determined by measuring concentrations using point measurements (in our case obtained by EPMA). For multiphase materials, however, point measurements of concentrations are not sufficient to establish the course of a diffusion path. In that case concentrations have to be averaged in a lateral direction (perpendicular to the diffusion direction) to account for the presence of different phases. For the construction of diffusion paths we followed the rules proposed by Kirkaldy⁶ and conventionalized by Clark⁷.

For instance, a solid line crossing a single phase field denotes an existing layer of that phase in the diffusion couple. A dashed line crossing a two-phase field parallel to the tie lines represents an interface between the two phases with interfacial compositions designated by the ends of the tie line. Such a dashed line represents no spatial extent.

Constructed in this way diffusion paths give information about the phenomenology, that is to say the morphology and composition of a solid-state reaction zone. They do not, however, contain direct information of a kinetic nature.

Especially in case of multiphase ternary diffusion the diffusion path approach is very effective in describing the phenomenology of the reaction zone⁸. By plotting observed diffusion paths on isothermal cross sections of different ternary systems the course of these paths can be compared. This eventually could lead to a better understanding of the

factors determining which of the (theoretically) possible diffusion pathways is chosen by nature. To illustrate this we may note that Rapp et al.⁹ predicted in a similar way the morphology, and composition of diffusion reaction layers.

To construct diffusion paths in the systems Fe-Ti-C and Co-Ti-C solid state diffusion couples (heat-treated at 1273K) have been used as model experiments for CVD-treated samples. The excellent suitability of diffusion couples for simulation purposes has already been demonstrated for the Fe-Ti-C system⁵.

Diffusion couples Ti-Fe_{100-y}C_y and Ti-Co_{100-y}C_y, heat-treated at 1273K, can develop a reaction layer consisting of TiC, when the iron-rich (or cobalt-rich) side of the couple is containing a sufficient amount of carbon. For Ti-Fe_{100-y}C_y resp. Ti-Co_{100-y}C_y couples values of $y > 6.5$ at% carbon resp. $y > 2.0$ at.% carbon were found^{4,5}. For carbon contents lower than these values no closed TiC reaction layer is found, but interdiffusion of titanium and iron (or cobalt) takes place, the TiC being present as precipitates in one or more of the inter-metallic phases.

The diffusion paths describing TiC formation for Ti-Fe_{100-y}C_y diffusion couples are given in figs. 3 and 4.

Figure 5 shows an enlargement of a section of figs. 3 and 4. In this section the diffusion path is reflecting the decarburisation of the iron starting material which is responsible for TiC formation. For Ti-Co_{100-y}C_y couples the same course of diffusion paths is followed as described in figs. 3 and 4⁴. To compare the decarburisation in this case with that observed in Ti-Fe_{100-y}C_y diffusion couples a cobalt-rich section is shown in figure 6.

FIGURE 3.
Observed diffusion path for couples Ti-Fe_{100-y}C_y,
0.2 < y < 6.5.

FIGURE 4.
Observed diffusion path for couples Ti-Fe_{100-y}C_y, y > 6.5.

FIGURE 5

Enlargement of a section of figs. 3 and 4, showing the decarburisation for couples $\text{Ti-Fe}_{100-y}\text{C}_y$ with $y > 0.2$.

FIGURE 6

Diffusion paths in couples $\text{Ti-Co}_{100-y}\text{C}_y$ showing the decarburisation of the cobalt starting material.

The diffusion path in figure 5 for the case Ti-Fe_{100-y}C_y, $y > 6.5$ at.%, actually is a normal composition profile determined by point measurements (EPMA) of concentrations in the single-phased Fe_{100-y}C_y material. However, in case of a two-phased starting material, like Co_{100-y}C_y in figure 6, a concentration profile based on point measurements by EPMA only gives information on the composition in both phases, but not on the number of precipitates as a function of distance (in the diffusion direction). This number is decreasing strongly in the direction of the TiC reaction layer (fig. 6), showing the strong decarburisation needed to form titanium carbide. So, in this case, the use of a composition profile, which is averaged over the observed phases, is indispensable. A diffusion path is then obtained (per definition) by plotting the average composition profile on a phase diagram cross section, thereby omitting the kinetic information.

Exactly the same decarburisation profile as described in figs. 5 and 6 (for diffusion couples forming TiC) has been observed when TiC coatings were applied to Fe_{100-y}C_y or Co_{100-y}C_y substrates by CVD³. This strongly underlines the usefulness of (well-selected) diffusion couples as simulation experiments for CVD-treated samples.

4. CONCLUSIONS

Diffusion paths plotted on the isothermal cross sections Fe-Ti-C and Co-Ti-C reveal phenomenological information concerning the decarburisation process involved in the deposition of TiC on iron-carbon (or cobalt-carbon) substrates by CVD.

The usefulness of diffusion couples as analogs for CVD experiments has been demonstrated.

As diffusion paths do not contain inherent kinetical information, a complete study of decarburisation phenomena should include a synthesis of diffusion path and composition profile

(as a function of distance) determinations.

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