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Kinetics of the formation of metal binder gradient in WC–Co by carbon diffusion induced liquid migration

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Abstract

Cemented tungsten carbide (WC–Co) with a cobalt content gradient from the surface to the bulk of a sintered piece is an example of a functionally graded material, the mechanical properties of which are optimized by the unique gradient microstructure, giving rise to superior combinations of wear resistance vs. fracture toughness. A process for creating such cobalt gradients in WC–Co was developed recently based on heat treatments of fully sintered WC–Co materials in carburizing atmospheres. A study of the kinetics of the process is necessary to fully understand the mechanisms of the process in order to achieve desired or designed gradients. In this paper, a series of carburizing experiments were conducted to examine the effects of key process parameters including temperature, composition of the atmosphere, and time on the overall kinetics of the process. A kinetic model was established to predict the thickness of the gradient as a function of these process variables, enabling the design of functionally graded WC–Co through controlling atmosphere and time.

Keywords: Cemented tungsten carbide; Functionally graded material (FGM); Kinetic analysis; Carbon diffusion

1. Introduction

Cemented tungsten carbide (WC–Co), one of the most widely used industrial tool materials, consists of large volume fractions of tungsten carbide (WC) particles embedded in cobalt (Co) binder. The compatibility between the hard WC grains and the ductile Co binder phase enables the composites to have unique and superior combinations of mechanical properties including high modulus, hardness, wear resistance and moderate fracture toughness. These mechanical properties make WC–Co materials indispensable for a variety of manufacturing industries such as metal cutting, gas and oil drilling, mining, construction, and other applications requiring extreme wear resistance [1].

Typically the wear resistance and the fracture toughness of conventional WC–Co materials are inversely related to each other. The wear resistance is often improved at the expense of the fracture toughness, and vice versa. Such a trade-off between wear resistance and toughness limits the use of WC–Co for broader industrial applications. Functionally graded WC–Co (FG WC–Co) provides a viable solution to this trade-off by tailoring Co content and/or WC grain size within the microstructure. For example, a WC–Co with lower Co content near the surface and higher Co content in the core provides FG WC–Co with characteristics of a hard-surface, tough-core structure. Such a hard-surface, tough-core structure combines high wear resistance and high fracture toughness in a single component, giving rise to significant performance gains in comparison to homogeneous WC–Co materials [2–5]. It should be noted, however, that the Co gradient in WC–Co composites may also cause residual stresses within the material. The distribution of residual stresses will affect the performance of WC–Co materials. It has been found that in most cases when the cobalt content at the surface is lower than that in the interior, the residual stress on or near the surface is compressive, which is beneficial for enhancing the surface fatigue properties of components [6–9].

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Because of the potential advantages of FG WC–Co, there has been considerable research reported over the past decades on means for manufacturing WC–Co with microstructure gradient [5,10–21]. Typically WC–Co is manufactured via liquid phase sintering process. The liquid phase sintering process, however, cannot be used to manufacture FG WC–Co with graded Co composition because the liquid Co phase will homogenize through migration during the liquid phase sintering process. In a series of publications, Fang et al. [22–30] systematically investigated the key factors that affect migration of the liquid phase: the initial Co gradient; the grain size gradient; and the carbon gradient. In general, the liquid phase migrates from regions with a higher volume fraction of liquid Co phase to those with a lower fraction of the liquid Co phase, from coarse grain locations to fine grain locations, and from areas with a high carbon content to those with a lower carbon content.

Although the principles of the liquid migration phenomenon are now understood, the manufacturing of FG WC–Co remains a challenge. There is still to date no process that could be used to manufacture FG WC–Co in industrial scale except in special cases such as processes for making WC–Co with cobalt enriched surfaces [31–33] and so-called dual properties (DP) carbide [2–5], both of which form only under special conditions and generate only limited microstructure gradients. Other processes for making FG WC–Co that are available in literature rely on solid state sintering processes or premixing powder with different compositions, all of which have severe limitations with regard to their versatility and practicality [12,21,34,35].

Recently, a novel process has been developed based on controlling the volume fraction of liquid Co phase by introducing a carbon content gradient and the migration of liquid phase [36–39]. The new process is based on two principles: (i) liquid phase migrates from where the volume fraction of liquid Co is higher to where it is lower, and (ii) the relative volume fraction of liquid Co phase vs. that of solid Co phase varies from 0% to 100% within a triple phase field in which WC, solid Co, and liquid Co coexist as shown by the shaded area in Fig. 1 [40]. At a given temperature within the triple phase range, the volume fraction of liquid Co phase depends on the carbon content. It is thus possible to create a gradient of volume fraction of liquid Co by introducing a gradient of carbon content within the material. The process involves carburizing the material in a carbon-rich atmosphere such as a mixture of hydrogen and methane. Methane serves as the source of carbon. As a result of the surface carburization, the carbon content in the near surface region increases from the initial nominal carbon content (C_i as seen in Fig. 1), which drives the carbon diffusion inwardly from the surface into the interior of the parts. The diffusion of carbon causes the phase transformation of solid Co to liquid Co and an increase of volume fraction of liquid Co phase near the surface region. Consequently, the liquid Co migrates from the surface region with more liquid Co towards the core region that has less liquid Co. Thus a cobalt gradient with reduced Co content in the carburized surface region is created.

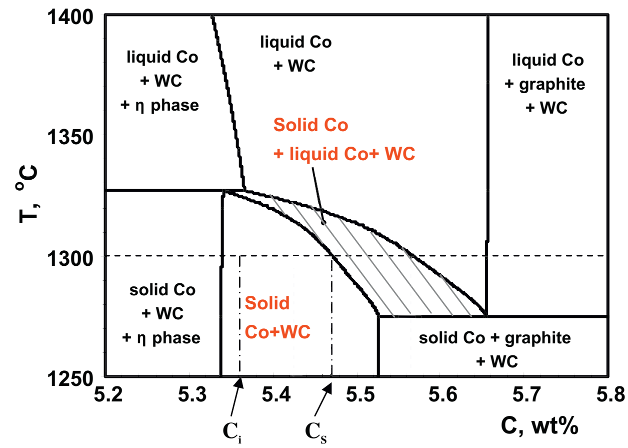

Fig. 1. Vertical section of the ternary phase diagram of W–Co–C at constant 10 wt.% Co.

The process as described above is a promising method for making WC–Co composite materials with gradient Co compositions. The general methodology may also be applicable to other material systems that are manufactured by liquid phase sintering and have similar liquid–solid-coexisting phase equilibriums. The effectiveness of the method, however, depends not only on the thermodynamic feasibility, but also on the kinetics of the process. As the basic principle suggests, there are several underlying subprocesses including: (i) surface carburizing reaction, (ii) carbon diffusion in the semi-solid–semi-liquid material, (iii) carbon diffusion in the fully solid material, (iv) phase transformation of solid Co to liquid Co, and (v) the migration of liquid Co. The complex interactions among these individual subprocesses will determine the gradients obtained in the final products. To achieve a desired or designed gradient, a study of the kinetics of the overall process is therefore important. From a practical point of view, it is also necessary to investigate the effects of key process factors including temperature, carbon potential of the atmosphere, and time so as to control the kinetics of the process.

In the present study, a series of carburizing experiments were undertaken to examine the effects of these factors. The aim of this study is to derive a kinetic model based on the results of the experiments to predict the formation of the gradient as a function of the process variables. In this article, we will first present the experimental results of the dependence of Co gradient near surface on temperature, atmosphere and time. The experimental data will then be used to determine the numeric parameters in the model. The model will be useful for understanding mechanisms and guiding practical implementations of the process.

2. Experimental

Commercially available WC–Co powder with 10 wt.% Co was used as raw materials for this study. WC–10 Co specimens with slightly sub-stoichiometric carbon content