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Phase evolution in synthesis of nanocrystalline WC-η composite powder by solid-state in situ reactions

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ABSTRACT

Replacement of Co with η phase (e.g. Co_6W_6C and Co_3W_3C) is proposed as an effective approach to resist against corrosion of WC-Co coatings in environment of molten zinc. In the present work, the nanocrystalline WC-η powder was firstly synthesized as the coating material by a novel method of in situ reactions using metal oxides and carbon black as raw materials. The phase evolution in the process of in situ synthesis was investigated by thermodynamic calculations and experiments. It was found that the initial WO_3, Co_3O_4 and C transformed firstly to $CoWO_4$, then to W and W_2C, and eventually to η and WC. The formation of η phase decreases the energy barrier for WC formation and hence the synthesis temperature for the composite powder. The duplex phase constitution of WC and η was obtained with optimized conditions, and the composite powder had a mean particle size of about 190 nm with inner grain size of about 50 nm. The amount of Co in the composite is controllable by adjusting the carbon addition to the starting materials.

1. Introduction

Wear and corrosion of the galvanizing components (e.g. the sink roll and stabilizing roll) have been a great challenge in the hot-dip galvanizing industry [1–6]. In the past two decades, the WC-Co coating was widely used as the surface protection material for these rolls. The corrosion resistance of WC-Co coating in molten zinc depends largely on the binder phase. As reported [7,8], the metallic Co could easily react with Al of the liquid zinc (including Zn, Al, Fe, Cr, etc.) and form the Co—Al intermetallic compound which would subsequently transit to Al-Fe-Zn-Co phase and eventually to stable Fe_2Al_5. The Fe—Al compound may be attached to the coating and is difficult to be removed. Also, it's suggested that the failure of WC-Co coating is resulted from the melting corrosion of Co [9].

Replacement of Co with the η phase (e.g. Co_6W_6C and Co_3W_3C) is considered to be an effectively approach to resist against the fast corrosion of WC-Co coating [5]. However, brittleness of η phase will result in the degradation of mechanical properties of the WC-based coatings [10–12]. Particularly, there is a higher tendency for cracks to initiate in the conventional coarse-grained coatings as compared with the nanocrystalline coating. The nanostructured WC-based coating has higher hardness and much higher toughness [13–15]. Thus, the nanostructured WC-η coating may be a better candidate material resisting against the wear and corrosion in environment of molten zinc. In order to prepare the nanostructured WC-η coating, the synthesis of nanoscale WC-η raw powder is the first important step.

For the W-C-Co system, the formation of η phase mainly depends on the carbon content and the temperature [16–18]. In case of lacking carbon and lower temperatures, W and W_2C may appear in the product and otherwise Co will coexist with the η phase. The temperature not only affects the stability of these phases, but also the particle size of the synthesized powder. It is a great challenge to realize the co-existence of nanoscale WC and η phase. In this work, a unique technique utilizing in situ reactions of metal oxides and carbon was used to prepare the nanocrystalline WC-η composite powder. The factors that affect the phase constitution of the powder were investigated in terms of the carbon addition to the raw materials and the reaction conditions. The phase evolution behaviors in the synthesis process of the powder will be clarified for better understanding the formation mechanisms of WC-η composite.

2. Experimental

The commercially available tungsten oxide (FSSS: 10–18 μm, > 99.95% purity, Ganzhou Grand Sea W & Mo Group Co. Ltd., China), cobalt oxide (D50: 1–5 μm, BET ≥ $1.0\ m^2/g$, 72.6–73.6% purity, Jiangsu Cobalt Nickel Metal Co. Ltd., China) and carbon black (D50: ~0.3 μm, 99.8% purity, PetroChina Southwest Oil and Gasfield

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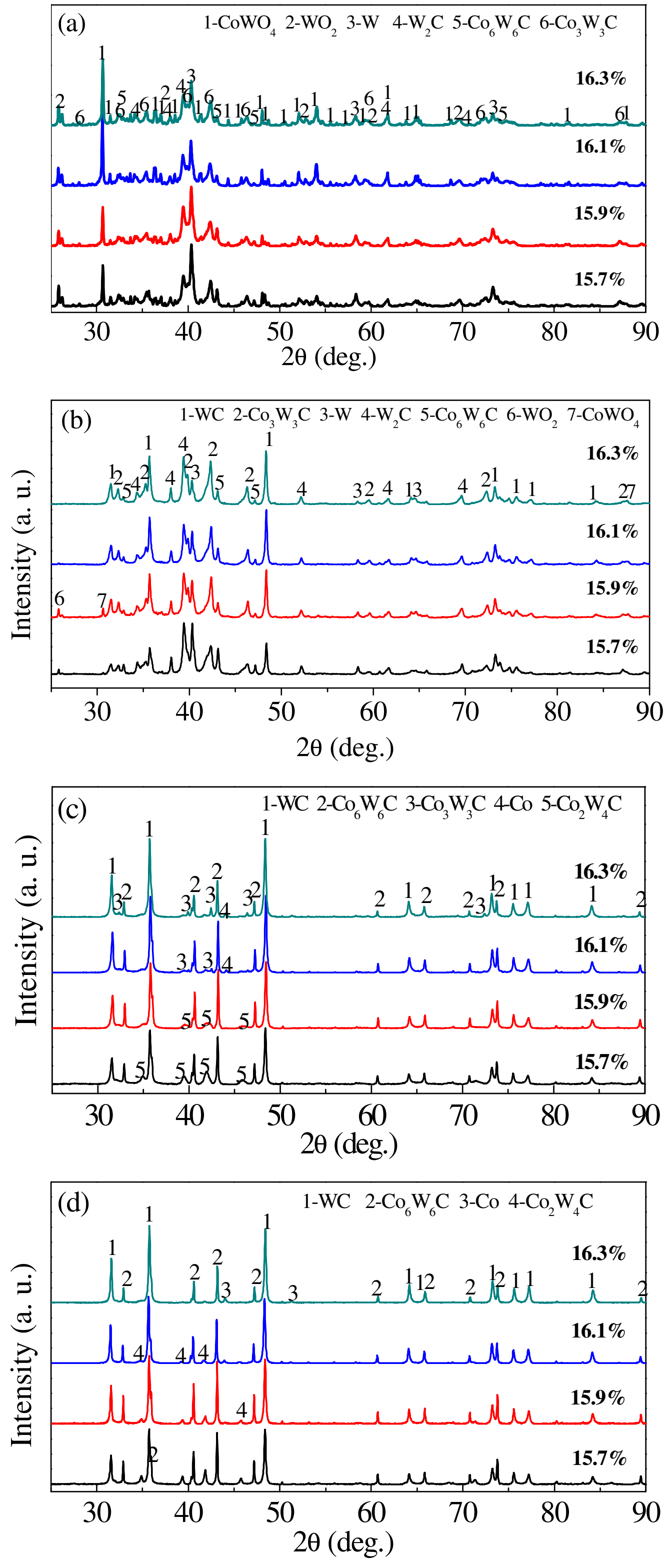

Fig. 1. XRD patterns of the powder synthesized at target temperatures of (a) 850 °C, (b) 900 °C, (c) 950 °C and (d) 1000 °C and a constant holding time of 1 h.

Company) were used as raw materials. With respect to various stoichiometric ratios of the η phases, the Co_6W_6C compound with the lowest carbon content among η phase, is chosen as the target products. The ratio of the raw materials is determined according to the following reaction equation:

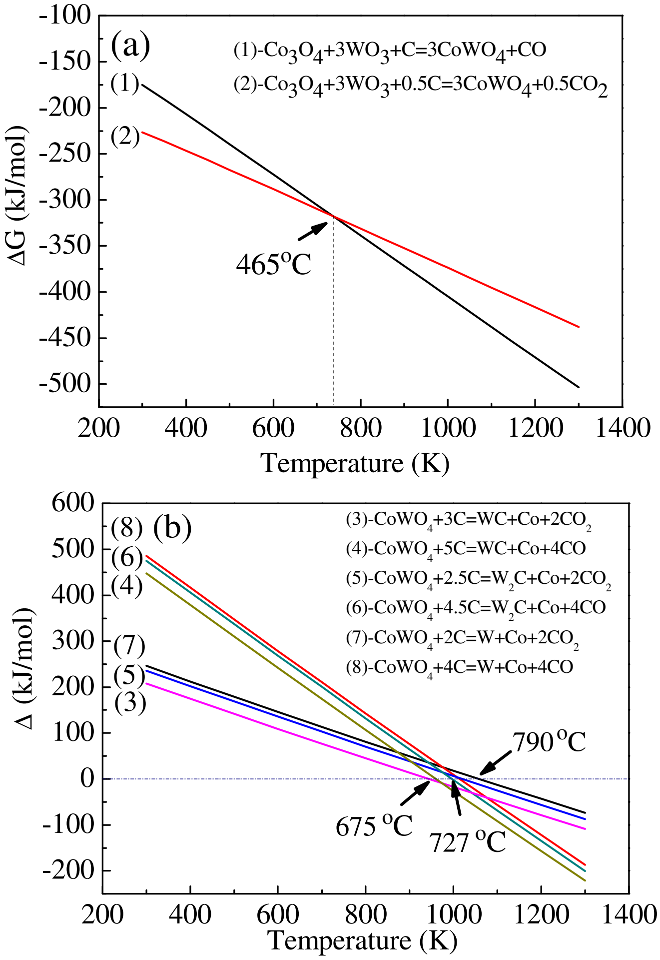

Fig. 2. Changes of Gibbs free energy of formation (a) and decomposition (b) reactions of $CoWO_4$ as a function of temperature.

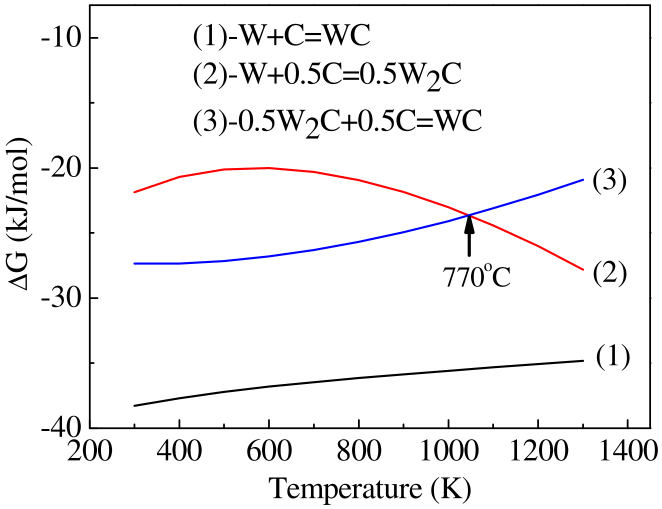

Fig. 3. Changes of Gibbs free energy of the carbonization reactions of W and W_2C as a function of temperature.

$$WO_3 + Co_3O_4 + C \rightarrow WC + Co_6W_6C + CO \qquad (1)$$

The theoretical Co content in the synthesized powder is designed as 12 wt%. In order to optimize the composition of the synthesized powder, the amount of carbon in the raw materials is adjusted from 15.7 wt% to 16.5 wt%. The raw powders were mixed by ball milling for