

In situ formation of RE_2S_3 and $\text{RE}_2\text{O}_2\text{S}$ phases on sinter skin of Cr–mischmetal co-doped WC–Co alloy

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Abstract: The as-sintered sinter skin of WC–11Co–0.71Cr₃C₂–0.06RE cemented carbide with WC+ β microstructure was analyzed by scanning electron microscope, energy dispersive X-ray spectroscopy and X-ray diffractometer. RE represents La-, Ce-, Pr- and Nd-containing mischmetal, and β is cobalt-based binder phase. It was discovered that La, Ce, Pr and Nd migrated directionally from the alloy to the sinter skin to combine with the impurity elements S and O from the sintering atmosphere during the sintering process. As a result, main dispersed phase RE_2S_3 and minor $\text{RE}_2\text{O}_2\text{S}$ were formed in situ on the sinter skin. The mechanisms for the stimulation of the migration activity and the directional migration of RE atoms were discussed in terms of the thermodynamics stability of Cr₃C₂, solubility characteristic of Cr in Co and the polarization or ionization of RE atoms.

Key words: RE_2S_3 ; $\text{RE}_2\text{O}_2\text{S}$; cemented carbide; sintering; rare earth directional migration; atom polarization

1 Introduction

The in situ formation of a layer-structured $\text{RE}_2\text{O}_2\text{S}$ phase (RE=La-, Ce-, Pr- and Nd-containing mischmetal) with lubricating function on the cutting faces of mischmetal doped WC–Co inserts was reported [1,2]. To realize this self lubricating function of rare earth doped cemented carbide tools by in situ stimulation in service, the prerequisite is that the rare earth must stay stably in the alloy during the sintering process. It is known that there is a huge difference in the atomic radius between La/Ce/Pr/Nd and W, La/Ce/Pr/Nd and Co, i.e., 32.8%–37.2% and 45.6%–50.4%. Therefore, it is an amazing phenomenon to observe the directional migration of La/Ce/Pr/Nd in the RE doped WC–Co alloy. Investigation of the way of the migration is the foundation for the stability control of rare earth in WC–Co alloys during the sintering process.

It is demonstrated that the behavior of La was stable in La₂O₃ independently doped WC–Co alloy [3]. During the sintering process of the alloy with WC+ β + η three-phase microstructure (cross section, the same in the following), La atoms close to the sinter skin could

migrate to the sinter skin; nevertheless, massive or long-range migration of La atoms and enrichment of La on the sinter skin have not been observed, where β is a cobalt-based binder phase and η is a carbon-deficient phase with a composition of Co₃W₃C. Nevertheless, we observed the massive directional migration of La in La₂O₃ and Cr₃C₂ co-doped WC–Co alloy with WC+ β + η three-phase microstructure and the in situ formation of La₂O₂S and LaCoO₃ phases on the sinter skin [4].

For La-, Ce-, Pr- and Nd-containing mischmetal (RE) independently doped WC–Co alloy, where RE was added in the form of RE–Co pre-alloyed powder, the situation was little complicated. For bulk alloy (in normal size) with WC+ β + η three-phase microstructure, La and Ce got separated and Ce predominantly migrated towards the sinter skin during the sintering process [5,6]. Nevertheless, the behavior of RE in WC–Co alloy with WC+ β two-phase microstructure followed a so called size effect. For WC–Co grainy alloy (less than 0.2 mm in diameter), La and Ce in the alloy migrated towards the sinter skin during the sintering process [7]; for WC–Co bulk alloy, both La and Ce stayed stably in the alloy during the sintering process [3].

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In this work, we demonstrate that the directional migration ability of La, Ce, Pr and Nd can be activated by the addition of Cr_3C_2 in WC–Co bulk alloy with WC+ β two-phase microstructure.

2 Experimental

Commercial powders of tungsten carbide (FSSS 7.0 μm), cobalt (FSSS 1.42 μm), chromium carbide (FSSS 1.45 μm) and RE–65%Co pre-alloyed powder (in mass fraction, the same in the following) were used to prepare the samples with a composition of WC–11%Co–0.71% Cr_3C_2 –0.06%RE (WC–11Co–0.71 Cr_3C_2 –0.06RE). The composition of mischmetal was La 29.91%, Ce 45.84%, Pr 5.65% and Nd 18.20%. Sintering of the samples was performed at 1430 °C for 60 min in a vacuum furnace. The final dimensions of the samples were approximately 5.25 mm in height, 6.5 mm in width and 20 mm in length. The polished cross-section etched with Murakami's reagent was observed by optical microscope. It turned out that the alloy had a WC+ β two-phase microstructure.

The sinter skin was analyzed by JEOL JSM–6490 LV scanning electron microscope (SEM) and the attached EDAX Genesis XM4 Neptune energy dispersive X-ray spectroscopy (EDS). Phase identification was conducted on Rigaku Dmax /2550VB X-ray diffractometer. EDS and XRD (X-ray diffraction) examinations were performed on the same sample with a surface area of 6.5 mm \times 20 mm. MDI Jade 6.0 analysis software developed by Materials Data Inc. was used to analyze the XRD spectrum.

3 Results and discussion

It was discovered that there is something quite different on the sinter skin of WC–11Co–0.71 Cr_3C_2 –0.06RE alloy, as shown in Figs. 1 (a) and (b). It can be observed that there exists a dispersedly distributed new phase with bulgy shape on the sinter skin. EDS analysis results of the micro zones shown in Fig. 1 are given in Fig. 2 and Table 1.

Table 1 indicates that La, Ce, Pr, Nd and W, Co, C, as well as impurity elements S, Ca and O were detected in zones 1–3; nevertheless, both S and Ca were not detected in the WC+ β matrix, i.e., zone 4 shown in Fig. 1. Therefore, it can be deduced that RE atoms have a strong ability to combine S and Ca atoms. It is notable that the average S content is as high as 23.96% in the RE enriched areas and the relative mass ratio of La, Ce, Pr and Nd is close to their original one in mischmetal. The oxygen contents in zones 1–4 are close to each other.

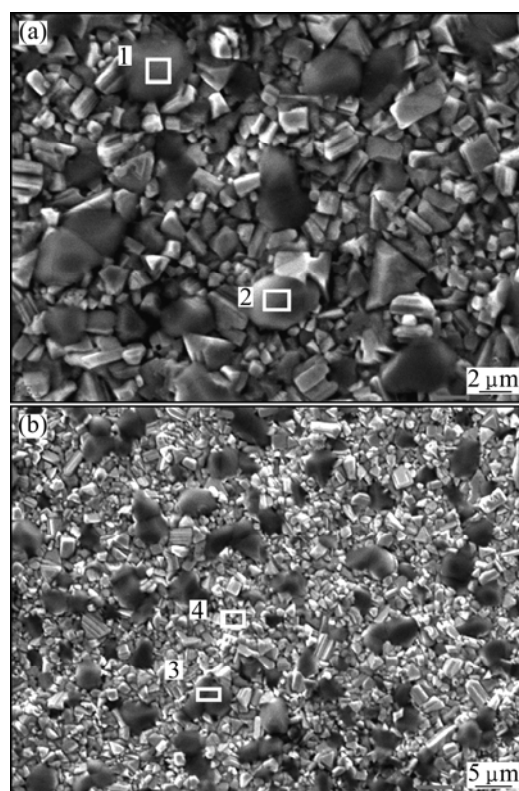


Fig. 1 SEM images of sinter skin of WC–11Co–0.71 Cr_3C_2 –0.06RE alloy

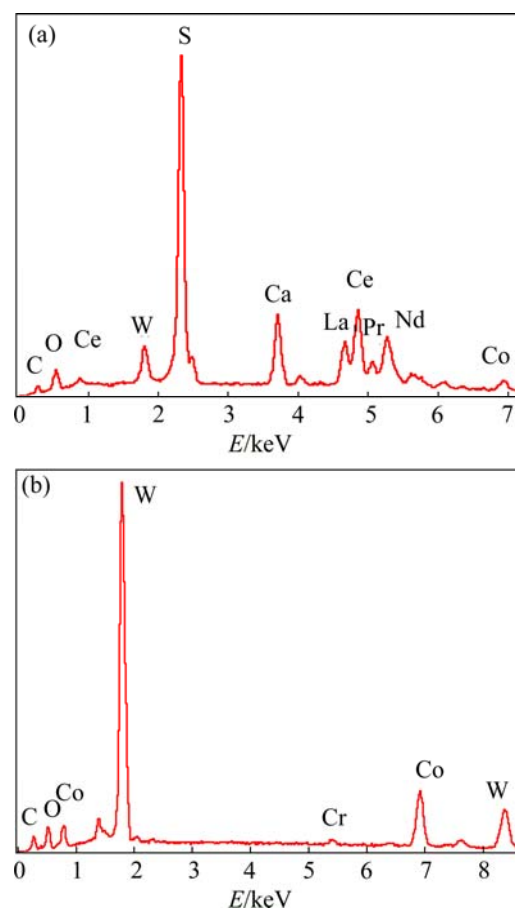


Fig. 2 EDX spectra corresponding to zones 1 and 4 in Fig. 1

Table 1 EDX analysis results of zones shown in Fig. 1

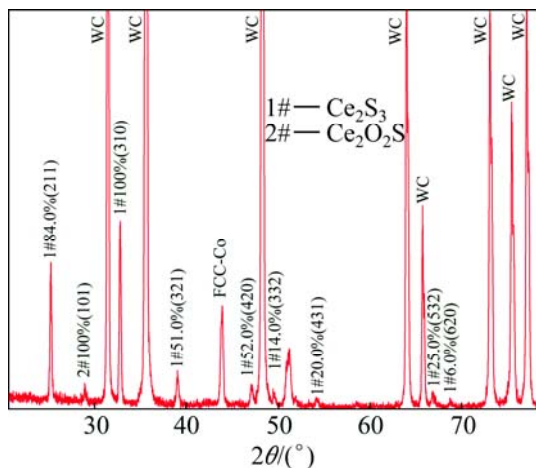
Zone	w(C)/%	w(S)/%	w(O)/%	w(La)/%	w(Ce)/%	w(Pr)/%
1	4.42	23.16	3.63	15.04	27.36	2.00
2	4.30	22.31	3.32	14.52	26.71	2.06
3	*	26.40	3.21	13.96	34.32	2.40
4	5.31	—	3.52	—	—	—

Zone	w(Nd)/%	w(Cr)/%	w(Co)/%	w(W)/%	w(Ca)/%
1	6.52	—	2.65	9.30	5.91
2	6.49	—	1.70	12.80	5.78
3	7.59	—	0.71	4.48	6.94
4	—	0.92	15.65	74.59	—

*: Not included in the analysis for the weak peak.

It is relatively easy to understand the existence of O in the sintering atmosphere for the vacuum level is limited. As for the other impurity elements, e.g. S and Ca, there were two kinds of resources. One was originally from the graphite tray and carbon fiber in the sintering furnace, and the other was from the volatiles deposited on the graphite tray and carbon fiber during the sintering process of cemented carbides.

For the new phase identification, the as-sintered sinter skin with dimensions of 6.5 mm×20 mm was examined by X-ray diffractometer, as shown in Fig. 3. Figure 3 indicates a good consistency between the detected diffraction peaks and the standard diffraction peaks of Ce_2S_3 , which means that the crystal structure of RE_2S_3 is a $\gamma\text{-Ce}_2\text{S}_3$ type and the substitution of Ce by La, Pr and Nd does not result in notable lattice distortion. Bigger Ce vacancy size than Ce cation in $\gamma\text{-Ce}_2\text{S}_3$ crystal is responsible for the small lattice distortion [8]. Only one diffraction peak, i.e. (101) main peak of $\text{RE}_2\text{O}_2\text{S}$ with the same crystal structure of $\text{Ce}_2\text{O}_2\text{S}$, was detected, which indicates that the amount of $\text{RE}_2\text{O}_2\text{S}$ is very small.

**Fig. 3** XRD pattern of as-sintered sinter skin of WC-11Co-0.71Cr₃C₂-0.06RE alloy

It can be summarized that together with hard phase WC and FCC-structured β phase, there are two new phases on the sinter skin, namely RE_2S_3 and $\text{RE}_2\text{O}_2\text{S}$.

Considering the fact that the La, Ce, Pr and Nd enrichment phenomenon has not been observed in RE independently doped WC-Co bulk alloy with WC+ β two-phase microstructure [3], it can be deduced that Cr plays a vital role in the directional migration. There are two kinds of hypothesis to decipher the Cr-induced migration activity stimulation mechanism, all related to the transiently existing free carbon atoms with high activity. Hypothesis one is based on the stability of high carbon type of chromium carbide. Due to the variability of valent states of chromium, there are different kinds of chromium carbides, i.e., CrC, Cr₃C₂, Cr₂C, Cr₇C₃ and Cr₂₃C₆ with carbon mass fractions of 18.75%, 13.33%, 10.34%, 9.0% and 5.68%, respectively. It is well established that the valence electron structures of rare earth elements are unique. It can be deduced that under the coexistence condition of RE atoms with high activity and Cr₃C₂, the stability of Cr₃C₂ with relatively high carbon content can be deteriorated due to the interaction among the valence electrons from RE and chromium carbide [4]. Another hypothesis is based on the high solubility of Cr in Co. During the sintering process of WC-11Co-0.71Cr₃C₂-0.06RE alloy, due to the high solubility of Cr in Co, as high as 30%–33% at the temperature of 1400 °C [9,10] and larger than 95% of the Cr additive is dissolved in the Co-based binder phase at room temperature [11], free carbon atoms can be released as a result of the solution of Cr in Co. Owing to the large difference in electronegativity between RE elements and carbon, there are strong interactions between the valence electrons from RE atoms and transiently existing free carbon atoms. As a result, the energy of RE atoms in the alloy can be substantially raised and the polarization or ionization of RE atoms can be realized. Similarly, the carbon-donation conjecture of Cr₃C₂ in WC-Co alloy was reported by LEE et al [12].

From the phase diagrams of La-Co and Ce-Co, it is known that the liquid emergence temperature of RE-65%Co alloy is around 1200 °C. Therefore, the migration of RE atoms could be in the liquid state during the sintering process. As is known that the electronegative parameters of S and O are much bigger than those of La, Ce, Pr and Nd, there is a strong tendency for S and O to interact and combine with La, Ce, Pr and Nd. Therefore, owing to the existence of S and O in the sintering atmosphere although in minor amount, RE atoms existing with high activity stimulated by carbon atoms can be attracted to the sinter skin.

$\text{RE}_2\text{O}_2\text{S}$ and RE_2S_3 are characterized with high melting point, e.g. La₂O₂S 2000–2200 °C [13], Ce₂O₂S (2000±200) °C [14], $\gamma\text{-La}_2\text{S}_3$ 2080 °C [15,16], $\gamma\text{-Ce}_2\text{S}_3$

1870–2296 °C [17,18]. Therefore, with the formation of the compounds, RE atoms migrated from the alloy can be locked on the sinter skin of the alloy.

According to the skeleton theory of the liquid phase sintering of powder metallurgy products, at the liquid phase sintering stage, it is very difficult for the long-distance migration of liquid phase with good wettability to the solid phase in the alloy. It was reported that when the amount of RE in metallic state in cemented carbide reached 0.2% or above, a RE-containing dispersed phase was formed, and good interface combining strength of RE-containing dispersed phase with the WC hard phase and the binder phase was confirmed in WC–Co alloy [19,20]. Therefore, it can be deduced that there is a good wettability of liquid RE to the WC phase. Although the fast directional migration behavior of RE in cemented carbide still remains a mystery, under the situation of the polarization or ionization of RE atoms accompanied by the substantial decrease in atom radius, it is possible for RE atoms in polarization or ionization state to pass through the WC solid phase during their directional migration process. It is supposed that at the liquid phase sintering stage, the RE atoms normally migrate through the interfaces between the WC and the liquid Co binder phase; if the migration paths are blocked by the WC solid phase, RE atoms in polarized or ionized state can diffuse directly into the WC lattice and pass through the WC solid phase.

4 Conclusions

1) During the sintering process of metallic mischmetal and Cr_3C_2 co-doped WC–Co alloy with WC+ β two-phase microstructure in the inner part of the alloy, La, Ce, Pr and Nd atoms in mischmetal migrated directionally from the alloy to the sinter skin, forming in situ RE-containing compounds, i.e. main RE_2S_3 and minor $\text{RE}_2\text{O}_2\text{S}$, with crystal structures of Ce_2S_3 and $\text{Ce}_2\text{O}_2\text{S}$ type, respectively.

2) Cr_3C_2 with carbon-donation ability and the impurity elements S and O from the sintering atmosphere with much larger electronegative parameters than La, Ce, Pr and Nd are thought to be the reason behind the directional migration of RE atoms.

3) At the liquid phase sintering stage, RE atoms normally migrate through the interfaces between WC and liquid Co binder phase; if the migration paths are blocked by WC solid phase, RE atoms in polarized or ionized state can diffuse directly into the WC lattice and pass through the WC solid phase.

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Cr–RE 共掺杂 WC–Co 合金 烧结体表面 RE₂S₃ 和 RE₂O₂S 相的原位形成

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摘 要: 采用扫描电镜、能谱仪以及 X 射线衍射仪对具有 WC+ β (β 为钴基粘结相)两相结构的 WC–11Co–0.71Cr₃C₂–0.06RE (RE 为含 La、Ce、Pr、Nd 的混合稀土)硬质合金烧结体表面进行观察与分析。结果表明, 在烧结过程中合金中的 La、Ce、Pr、Nd 通过定向迁移与烧结炉内气氛中的 S、O 等杂质元素结合, 在合金烧结体表面形成 RE₂S₃(主)和 RE₂O₂S(少量)弥散相。从合金中 Cr₃C₂ 的热力学稳定性、Cr 在 Co 中的溶解度特性以及稀土原子激发等 3 个方面, 对稀土迁移活性的激发机制和稀土原子的定向迁移机制进行分析与讨论。

关键词: RE₂S₃; RE₂O₂S; 硬质合金; 烧结; 稀土定向迁移; 原子极化

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