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原位反应法制备 Cr_2AlC-Fe 复合材料

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摘 要：采用原位反应法制备了 Cr_2AlC-Fe 系复合材料，并采用热分析、X 射线衍射、扫描电子显微镜和三点弯曲实验，研究了原位反应的烧结工艺对产物和显微结构的影响，以及对原料中 Cr_2AlC 的含量对复合材料性能的影响。结果表明：通过高温原位反应，原料中 Cr_2AlC 发生了分解，形成了网络状陶瓷增强结构，所制备的复合材料具有较好的强度和韧性，且随着 Cr_2AlC 含量的增加，复合材料的强度也在增加，但断裂韧性逐渐下降。当 Cr_2AlC 的体积分数达到 30%时，复合材料的抗弯强度达 1 417 MPa。

关键词：复合材料；原位反应；烧结；弯曲行为
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Fabrication of Cr_2AlC Fe-based Composites by *in-situ* Reaction Method

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Abstract: A Cr_2AlC-Fe composite, which could have potential applications in nuclear energy industry as engineering materials, was synthesized by an *in-situ* reaction method. The *in-situ* reactions between Cr_2AlC and Fe at different temperatures and ratios were analyzed by thermogravimetric analysis-differential thermal analysis, X-ray diffraction and scanning electron microscopy, respectively. The effect of s Cr_2AlC content on the bending behaviors was investigated. The results show that Cr_2AlC can *in-situ* react with Fe, and decompose to form chromium carbide. The synthesized composite exhibits a higher flexural strength and a greater fracture toughness at room temperature.

Key words: based composites; in situ reaction; sintering; bending behaviors

1 Introduction

Combine with the unique desirable properties of a single metal or ceramic material and offsetting each other's deficiencies, composites can be used as the engineering materials for extreme environment of nuclear energy industry, mining industry, chemical and metallurgical industry and so on.[1–3] The reinforcing ceramic particulates include Al_2O_3, TiC, Si_3N_4, WC, *etc*..[4–8] Although those traditional ceramic reinforcements own high strength, they have low fracture toughness, poor wetting, inconsistency of linear expansion coefficient with iron, and are hard to be machined by using normal tools.

Recently, Cr_2AlC and related composites have attracted increasing attention,[9–13] which belong to a new type of ternary structures advance ceramics so called MAX phase. Compared with traditional ceramic reinforcing agents, these kinds of ceramics possess unique crystal laminated structure as graphite. In the Cr_2AlC crystal structure, the Cr atoms and C atoms form two common edges Cr_6C tetrahedron with strong ionic bond are separated by Al atomic planes,[14] and the link between Al atomic planes and Cr_6C tetrahedron are weak Cr–Al metallic bond.[15–16] This structure lead the Cr_2AlC phase combinational properties of both metals and ceramics, such as low density, high modulus, easy machinability, good electrical and thermal conductivity, excellent thermal shock and high-temperature oxidation resistance, but also can react with Fe by the technique of in situ reaction method,[17–19] which is a process where

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reinforcements are synthesized in metallic matrix by chemical reactions, and ensured the introduction of chemical bonding force in the interface of the reinforcements and the metal matrix, and the high performance bonding will make the external applied stress transferred from the matrix to the reinforcements. Zhang *et al*.[20] nosed out that the reaction between Cu and Ti_3AlC_2 form TiC_x and Cu (Al) above 950 ℃. Our previous work[21–24] shows that the incorporation of Ti_3SiC_2 or Ti_3AlC_2 with Cu increase the strength and modulus as well as wear resistance without the loss of conductivity and meet the requirements of applications in electrical sliding contacts in high-speed railway. In fact, similar reactions also exist between the Cr_2AlC with Fe matrix.

Hence, this paper intends to report on processing and property of Fe-based Metal Matrix Composites (MMCs) using the Cr_2AlC, which is a type member of the MAX phase ceramics, as precursor in the raw material. By using this *in-situ* reaction method, the Cr_2AlC ceramic particles might decompose to fine chromium carbide reinforcing agents. Different from the traditional direct synthesis methods, this method has several advantages, such as the better link between the reinforcing agents with the matrix, and the easier distributed evenly of the reinforcing agents, and so on.

2 Experimental

Reduced iron powders (purity 99.5%, size < 74 μm, Beijing Chemical Reagent Company) and Cr_2AlC powders (purity > 97%, average size 5.197 μm, the details can be found elsewhere[10]) are mixed for 10 h in plastic cans to ensure homogeneous reactant mixtures. The Cr_2AlC particle powders size measurement was performed on laser diffraction particle size analyzer (Mastersizer 2000, Malvern, Britain). Then, the mixed powders were hot-pressed (HP) at 1 300 ℃ under 30 MPa for 30 min in flowing argon gas. The flexural strength of the composites was tested by three-point bending method by GB/T 6569–1986, and the fracture toughness was tested by single edge notched and three-point bending method (SENB). The final samples were cut into blocks with dimensions of 3 mm × 4 mm × 36 mm for bending tests, of 4 mm × 6 mm × 36 mm for SENB tests, the both tests were performed on a universal testing machine (ZWICK, Z005) at a loading speed of 0.5 mm/min. According to the standard force and displacement from the universal testing machine, the bending strength and fracture toughness of the composites are calculated from following equations respectively:

$$R_{tr} = \frac{3FL}{2bh^2} \tag{1}$$

$$K_{IC} = \frac{3FL}{2bh^2} \times \sqrt{a}\left(1.93 - 3.07\frac{a}{h} + 14.53\frac{a^2}{h^2} - 25.07\frac{a^3}{h^3} + 25.80\frac{a^4}{h^4}\right) \tag{2}$$

where R_{tr} and K_{IC} are the flexural strength and fracture toughness of the composites respectively, F is the force required to the fracture, L is the distance between the fulcrums, b and h are the width and thickness of the samples respectively, a is the crack length of the composites, here is 2.8 mm.

After the bending tests, the specimens were analyzed by a scanning electron microscopy (SEM)(JSM–6460).

3 Results and discussion

Figure 1 shows the TG–DTA curve of 30%Cr_2AlC/70%Fe system and the DTA curves of pure Fe. In the TG–DTA curve of 30%Cr_2AlC/70%Fe system, there are no obvious changes in the weight during the reaction between Cr_2AlC and Fe, which indicates that there is no obvious change in the weight during the reaction between Cr_2AlC and Fe. In the DTA curve 30%Cr_2AlC/ 70%Fe system, two endothermic peaks sat 763.5 ℃and 914.5 ℃ can be observed. For the endothermic peaks, compare to the DTA curves of pure Fe, one can notice that almost same endothermic peaks at 770.21and 915.24 ℃ are observed in the DTA curves of Fe. Hence, it can be concluded that two endothermic peaks at 763.1 ℃and 913 ℃ are probably ascribed to the phase transition of Fe. Indeed, according to the Fe–Al phase diagrams,[25] it can be seen the magnetic transition temperature (T_c) of Fe at 770 ℃and the transformation of α-Fe to γ-Fe at 912 ℃ are in good agreement with our results here. Above 914.5 ℃, the endothermic reaction is predominant and there was no new obvious peak. The different phase coposition at different temperatures were made certain by the analyzing of XRD.

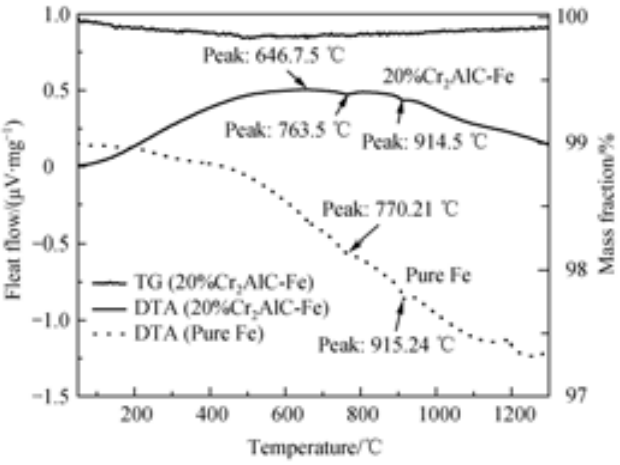


Fig. 1　TG–DTA curves for 30% Cr_2AlC/70%Fe and DTA curves for pure Fe powder in argon atmosphere

Figure 2 shows the XRD patterns of samples of 30%Cr_2AlC/70%Fe composites sintering at the temperatures from 1 000 ℃ to 1 400 ℃under 30 MPa for 30 min. The results show that, when the sintering temperature is between 1 000 to 1 300 ℃, the peaks from Cr_2AlC disap-

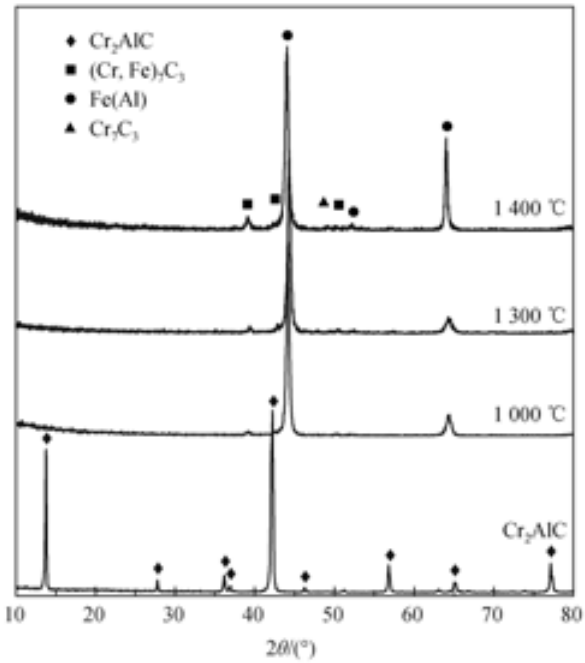


Fig. 2 XRD patterns of Cr_2AlC powders and samples of 30%Cr_2AlC/70%Fe composites sintered at 1 000 to 1 400 ℃

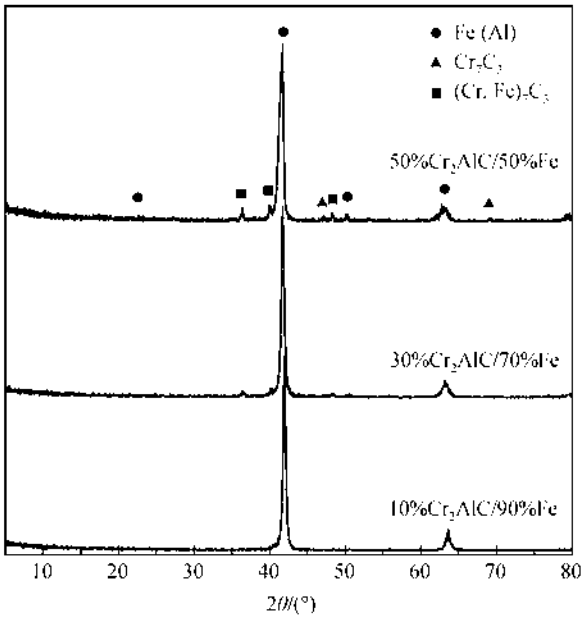


Fig. 3 XRD patterns of samples of Cr_2AlC-Fe mixtures with different Cr_2AlC contents after sintered at 1 300 ℃ for 30 min

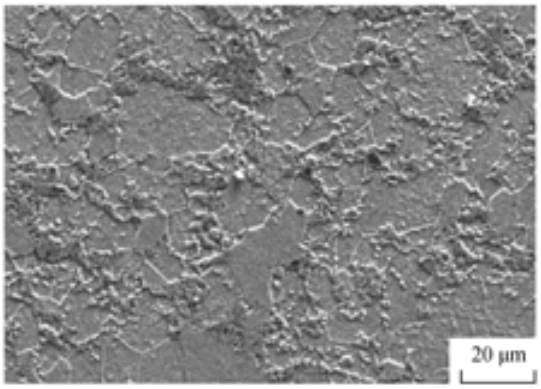
peared and the main phases were stability of $(Cr,Fe)_7C_3$ and Fe (Al). As the sintering temperature continued rise to 1 400 ℃, the intensity of the diffraction peaks from Fe (Al) was growing substantially, and great contraction deformation has emerged in the samples after sintering at 1 400 ℃, this phenomenon indicating that the ceramic segregation had occurred at this high temperature. So the temperature from 1 000 to 1 300 ℃ is the appropriate sintering temperature range.

Figure 3 shows the XRD patterns of samples of Cr_2AlC-Fe mixtures with different Cr_2AlC contents after sintered at 1 300 ℃ under 30 MPa for 30 min. When the Cr_2AlC contents in the mixtures below 30%, no new phases can be detected besides Fe (Al) and $(Cr, Fe)_7C_3$. As the Cr_2AlC contents increasing to 50%, the diffraction peaks from Cr_7C_3 became higher. The main reason of the reactions can be contributed to the *in-situ* reaction between Cr_2AlC and Fe. This *in-situ* reaction can be described as this: At high sintering temperature, Al atoms can strip from Cr_2AlC due to the weak Cr–Al metallic bond in Cr_2AlC, and dissolve in the metal matrix, forming Cr_7C_3 grains and Fe (Al) solid solution. At the same time, Fe will through into the ceramics particles by the Al vacancies. When the Cr_2AlC contents increasing to 50%, the liquid Fe are insufficient and results in some Cr_7C_3 phase remaining. The reaction can be described as following:

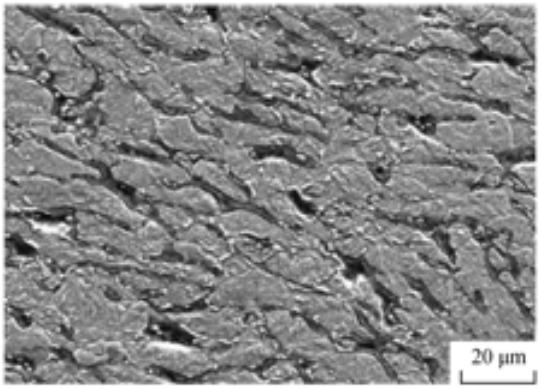
$$Cr_2AlC + Fe \longrightarrow Cr_7C_3 + Fe(Al) \quad (1)$$

$$Cr_7C_3 + Fe \longrightarrow (Cr, Fe)_7C_3 \quad (2)$$

Figure 4 shows the microstructure of samples of 30%



(a) Polished surface



(b) Polished surface which was etched in nital

Fig. 4 Microstructure of samples of 30%Cr_2AlC/70%Fe sintered at 1 300 ℃ under 30 MPa for 30 min

Cr_2AlC/70%Fe sintered at 1 300 ℃ under 30 MPa for 30 min. Choose a notable ceramics area in a bulk 30%Cr_2AlC/70%Fe composites' polished surface, and its SEM

image shows as Fig. 4(a). In the composites, the ceramic particulates are uniformly distributed in the matrix, and the ceramic particulates with shapes of needle, spindle, and flake. Figure 4(b) is a representative SEM image of the bulk 30%Cr_2AlC/70%Fe system composites' polished surface which was etched in nital. This typical micrograph exhibits that the composites with a compact texture, and the ceramic particulates are uniformly distributed in the Fe matrix with the average thickness size of 1.3 μm, form a hard continuous skeleton. This structure can be contribute to the microstructure genetic effects from the superimposed shape of the platelet microcrystalline Cr_2AlC in the of Cr_2AlC polycrystalline grains.

The sample of 30%Cr_2AlC/70%Fe sintered at 1 300 ℃ for 30 min in argon atmosphere, and its flat well-polished surface analyzed by EDS are shown in Fig. 5. It clearly shows that the Cr_2AlC particles almost turned into Cr_7C_3. We can also observe that Fe had diffused into the Cr_2AlC particles, Al, Cr and C can be detected in the Fe matrix.

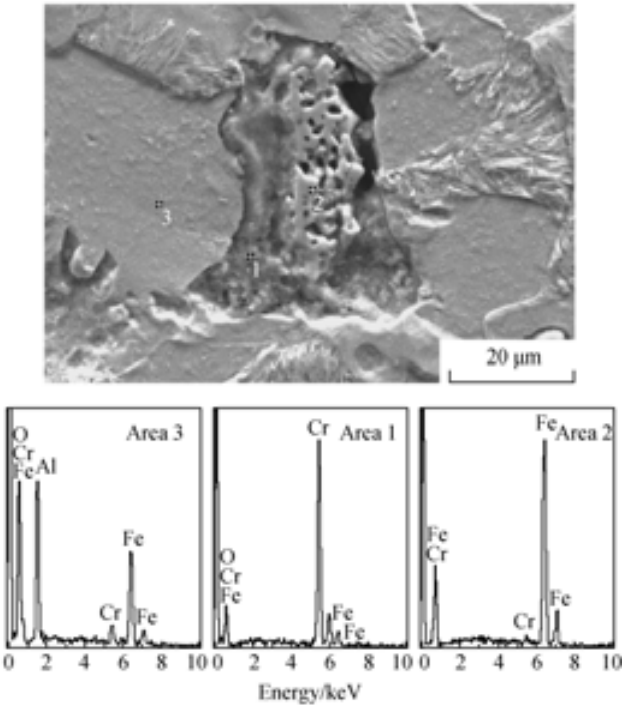


Fig. 5　EDX of samples of 30%Cr_2AlC/70%Fe sintered at 1 300 ℃ under 30 MPa for 30 min

Figure 6 shows the relationship between the flexural strength, fracture toughness and the volume content of Cr_2AlC for Cr_2AlC-Fe composites sintered at 1 300 ℃for 30 min. The flexural strength of the sample was increased greatly, but the fracture toughness was decreased while raising Cr_2AlC content. When the Cr_2AlC content was 50% in the starting materials, the flexural strengths of 50%Cr_2AlC/50%Fe can reach 1417.05 MPa, however, its fracture toughness drop to 18 MPa·$m^{1/2}$. A most remarkable feature is the strengths of Cr_2AlC-Fe composites not only much stronger than the strengths of pure Fe bulk, but

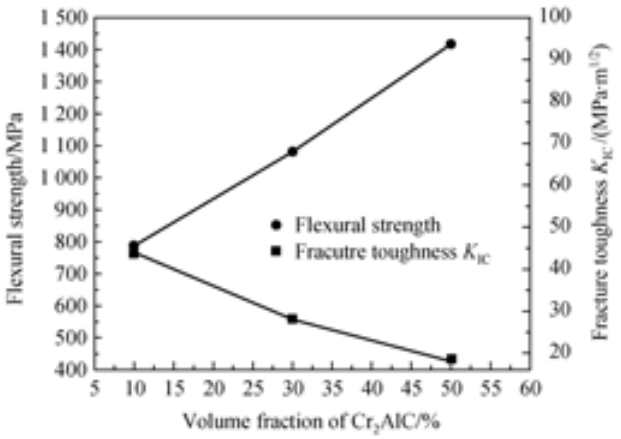


Fig. 6　Relationship between the flexural strength, fracture toughness and the volume content of Cr_2AlC for Cr_2AlC- Fe composites sintered at 1 300 ℃ for 30 min

also much stronger than the strengths of Cr_2AlC bulk (which flexural strengths is about 378 MPa). This phenomenon can be contributed to the hard continuous skeleton microstructure and strong interface bonding between the reinforce particulates and the metal matrix in the composites.

Figure 7 shows the typical bending site specimen photograph of 30%Cr_2AlC/70%Fe sample sintered at 1 300 ℃ for 30 min after the bending tests. A lot of slip bands are formed in the matrix at about 45 °with respect to draw axis. This result indicates that the interfacial bond between the ceramic reinforcements and metal matrix are strong. After in situ reaction, the chemical bond is formed in the interface between the chromium carbide particulates and matrix. During deformation, the ceramic particles not only can resist the passing dislocations, but also can induce drag force to the grain boundaries of the matrix. As a result, the external applied stress will be transferred from the matrix to chromium carbide particulates, and undoubtedly, the load bearing capacity of the composites with

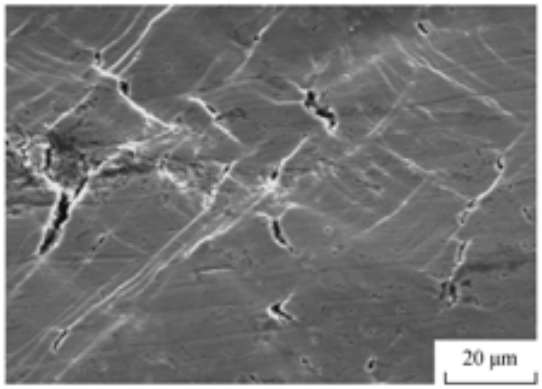


Fig. 7　Typical bending site specimen photograph of 30%Cr_2·AlC/70%Fe sample sintered at 1 300 ℃ for 30 min after bending tests

more ceramic reinforcement will be greater during the period of elastic deformation.

4 Conclusions

The chromium carbide reinforces Fe (Al) composites can be prepared by *in-situ* reaction method using Cr_2AlC powders as precursor. The *in-situ* reaction between Cr_2AlC and Fe completed above 1 000 ℃, and the products main phases keep stable in the 1 000–1 300 ℃ sintering temperature range. As the Cr_2AlC content increasing, the flexural strength of the sample is increased greatly, but the toughness is decreased.

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