Microstructure evolution and in-situ-formed mechanism of dual-scale WC-Fe reinforced iron matrix composites

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Abstract. Dual-scale WC–Fe reinforced iron matrix composites were prepared by hot pressing sintering under a pressure of 10 MPa at 1250 ± 5 °C for 6, 10, and 14 h using low-cost ferrotungsten, graphite, and Fe powders as raw materials. The microstructure and in-situ-formed mechanism of composites were studied by X-ray diffraction, scanning electron microscopy, and differential scanning calorimetry. The mixed powders with ferrotungsten and graphite comprised W, Fe₂W, Fe₇W₆, and Gr, which showed agglomeration after 48 h milling. When the hot pressing sintering time was prolonged from 6 h to 14 h, the W₂C and Fe₃W₃C phases emerged as intermediate phases. The main composite phases included WC and α-Fe, where dual-scale WC–Fe reinforcements were distributed uniformly within the α-iron matrix. The average size of irregularly shaped WC particles in WC–Fe reinforcements totaled 5 µm, and the volume fraction of WC reached 76.40%. The amount of local liquid phase decreased with decreasing carbon content, improving the capillary driving force and promoting the Fe₃W₃C formation. Finally, sufficient carbon content ensured that the intermediate phases W₂C and Fe₃W₃C transferred to WC completely.

1. Introduction
Tungsten carbide (WC) particles find application in metal matrix composites (MMCs) and cemented components because of their extremely high melting point (2870 °C), high hardness, (16–23.5 GPa) and Young’s modulus (691–710 GPa), low thermal expansion (a 5.2×10⁻⁶/°C, c 7.3×10⁻⁶/°C, 20 °C), and excellent wettability between WC and molten metals [1, 2]. Compared with Co matrix, Ni matrix, and other WC-reinforced MMCs, WC reinforced steel or iron matrix composites are desirable materials due to their low cost and good mechanical properties [3, 4].

Two primary methods are currently used in preparing WC reinforced steel or iron matrix composites. The first method is an ex-situ procedure that adds WC particles into the matrix directly; it is applied in many techniques, such as casting [5], hot isostatic pressing [6], laser melting deposition [7], and plasma melt injection [8]. For example, normal sand casting is used to prepare white cast Fe carbide particle reinforced wear-resistant composites [5]. The casting technology ensures the chemical bonding between the white cast Fe and particle reinforcements. The wear behavior of the white cast Fe-based composite is considerably better compared with that of the standard materials used in industrial
applications. The second method is an in-situ synthesis approach that can obtain fine grain size and uniform distribution of reinforcements\cite{9-11}. For example, the reactive cast-infiltration technique was used to produce an Fe–WC surface composite layer on an Fe casting, in which the WC particulates were formed in situ from the reaction of W with C. The surface composite featured three basic phases, namely, α-Fe, WC, and Fe₃W₃C, and the volume fraction of WC particles reached 30\%\cite{12}. Meanwhile, the primarily unresolved problems can be understood from two aspects. First, W is a weak carbide-forming element compared with Fe\cite{13, 14}; hence, finding a method to promote the in-situ reaction elements in the Fe–W–C system remains an intractable issue. Second, WC reinforcements, whether ex-situ or in-situ synthesized, are prone to dissolve into a molten pool owing to their low free generation enthalpy at high temperature. During solidification, the WC particles become the main points for the initiation of solidification due to their high heat capacity. Owing to the partial dissolution of WC particles and the resulting interdiffusion of elements, such as W, Co, Fe, C, and Cr, carbides containing Fe, Cr, W, and Co are formed\cite{5}. Thus, the volume fraction of WC in steel or iron matrix composite is restricted.

In the present paper, dual-scale WC–Fe reinforced iron matrix composites were prepared by hot pressing sintering under a pressure of 10 MPa at 1250 ± 5 °C at different times using ferrotungsten, graphite, and Fe powders as raw materials. The microstructural evolution of the composite at different times was studied by X-ray diffraction (XRD) and scanning electron microscopy (SEM). In-situ-formed mechanism of dual-scale WC–Fe reinforcement was discussed by analyzing the differential scanning calorimetry (DSC) results and the relationship between carbon content, the amount of local liquid-phase, and capillary driving force.

2. Experimental procedure
The dual-scale WC–Fe reinforced iron matrix composite was prepared by hot pressing sintering of raw materials consisting of commercial ferrotungsten (WFe70, 70 wt\%, W), Fe (99.5\%, Fe), and graphite (99.3\%, C) powder with a particle size of 200 mesh and a mass ratio of 22:7:1. Ferrotungsten and graphite powders were mixed by ball milling at 300 r/min for 48 h to blend homogeneously due to their large density difference (MITR, China). Before hot pressing sintering, Fe powder was added into the mixed ferrotungsten/graphite powder and mixed for 30 min using a mixer (MSK-SFM-11, China). After pre-press shaping under 20 MPa for 1 h, a hot pressure sintering furnace (BTLM×1400 °C, China) was used to produce the composites. The sample with 5 mm diameter and approximately 3–4 mm height was sintered with a pressure of 10 MPa at 1250 ± 5 °C for 6, 10, and 14 h under the protection of argon gas.

The specimens of dual-scale WC–Fe reinforced iron matrix composites were ground and polished for phase compositional analysis and microstructure observation. To analyze the 3D morphology of WC grain, we etched one of these samples with HCl etchant (HCl:C₂H₅OH = 3:1) to remove the metal matrix and reveal the WC grains.

The phases of mixed powder and composites were analyzed by XRD, which was performed on the sample surface using CuKα radiation over a 2θ range of 30°–90° (for mixed powder) and 20°–80° (for bulk composite) on a PW 1730 X-ray diffractometer (Philips, Netherlands) at 40 kV and 40 mA. The microstructure of mixed powder and composites was observed by a scanning electron microscope (VEGA TESCAN, Czech) equipped with an energy dispersive X-ray spectrometer. DSC was performed on a Q600 SDT (TA, Instruments, USA). The specimen was heated at 10 °C/min up to a maximum temperature of 1400 °C with argon gas protection.

3. Results and discussion

3.1. Mixed powder and DSC results
The ferrotungsten/graphite powder should be milled before mixing with the Fe powder due to the density difference between them. Moreover, homogeneous blending of the mixed powders was necessary for the in-situ reaction. Figure 1 shows the XRD result and SEM micrograph of
ferrotungsten and graphite mixed powder after milling for 48 h. The mixed powder comprised W, Fe₉W, Fe₇W₆, and Gr (graphite), where W, Fe₉W, and Fe₇W₆ were contributed by ferrotungsten, and Gr originated from graphite. Based on the X-ray patterns, milling could not affect the phase type of raw materials. The result coincides with the work of Mansour Razavi [15]. In his study, extremely weak WC appeared and was intensified by the increase in 75 h milling as 1 wt% tungsten carbide was nucleated during ball milling. The particle size of the mixed powder decreased from 200 mesh (<74 μm) to ~1.2 μm. The mixed powder showed agglomeration after milling for 48 h. Ferrotungsten is brittle and was broken by starting milling. When milling was prolonged, the local temperature increased, and several agglomerations formed in the mix. These agglomerations will not be broken unless hard phases arise after prolonged milling times [15]. The decrease in particle size and distribution in homogenization are beneficial to densification and in-situ reaction during hot pressing sintering. Moreover, the agglomeration caused by milling is the foundation for in-situ-formed dual-scale WC–Fe reinforcements, which will be discussed later.

The DSC analysis of ferrotungsten, graphite, and Fe mixed powder was performed to restrict hot pressing sintering temperature and clear phase transformation during temperature increase. The results are shown in figure 2. Two endothermic peaks at 1123 °C and 1301 °C and an exothermic peak at 1154 °C were observed. The endothermic peak at 1123 °C showed a eutectic temperature for the Fe–WC–Fe₃C system [16]. The other endothermic peak at 1301 °C arose from the four-phase intersection points with liquid η/γ-Fe/ W. The exothermic peak at 1154 °C is attributed to the Fe–C eutectic temperature, which is 1148 °C in the Fe–C equilibrium diagram [17]. The authors set the in-situ synthesized temperature as 1250 ± 5 °C. The temperature was lower than 1301 °C to avoid the generation of primary phases, forming as much WC as possible during the insulation and subsequent cooling. Moreover, the temperature was higher than the Fe–C eutectic temperature (1148 °C), which is conducive to exhibit liquid–solid interface due to uneven local composition. In this situation, solute redistribution at liquid–solid interface promoted the stability of WC.

Figure 1. The XRD result (a) and SEM micrograph (b) of ferrotungsten and graphite mixed powder after milling for 48 h.
3.2. Microstructural evolution of the composite at different sintering times

Figure 3 indicates the XRD patterns of dual-scale WC–Fe reinforced iron matrix composite sintered at 1250 °C for 6, 10, and 14 h. The presence of W, WC, α-Fe, Fe₃W₃C, W₂C, and Gr in the composite with 6 h sintering and WC, α-Fe, Fe₃W₃C, and Gr in the composite with 10 h sintering was detected. After 14 h sintering, only WC and α-Fe were detected in the composites. The sudden disappearance of W peaks after heat treatment at 1250 °C for 10 h confirmed that all W atoms were consumed by their reaction with graphite in the matrix. Moreover, the disappearance of W₂C peaks confirmed the existence of excess carbon atoms near the reaction zone, which promoted the conversion of W₂C to WC. The amount and intensity of peaks for the Fe₃W₃C phase decreased and disappeared after 10 and 14 h heat treatment, respectively, indicating that the Fe₃W₃C phase was the intermediate phase. Local formation of the Fe₃W₃C phase was evidenced at the interface of the two layers (WC base and Fe/C mixture) heated at 1300 °C for 60 min by powder metallurgy [18]. Finally, two phases (i.e., WC and α-Fe) and WC–Fe reinforced iron matrix composite can be obtained under the current conditions.

Figure 2. DSC result of ferrotungsten, graphite and iron mixed powder.

Figure 3. The XRD results of dual-scale WC–Fe reinforced iron matrix composite sintering at 1250 °C for 6, 10, and 14 h.

Figure 4 presents the SEM images of dual-scale WC–Fe reinforced iron matrix composite after sintering at 1250 °C for 14 h. WC particles agglomerated and were uniformly distributed within the α-iron matrix (figure 4(a)). Detailed observation showed that the dual-scale WC–Fe reinforcement was formed by WC and α-Fe (figure 4(b)). The average size of the dual-scale WC–Fe reinforcement approximated 54 μm, whereas the average grain size of irregularly shaped WC particles reached 5 μm. No defects were observed at the interface between the reinforcement and α-iron matrix due to the same phases present in the dual-scale reinforcement and matrix. The volume fraction of WC particles in the composite reached 76.40%, which was calculated by image method using ImageJ software.

Figure 4(c) shows the SEM morphologies of the in-situ-formed WC grains. Only the WC grains were observed due to the dissolution of α-Fe into the HCl etchant and agglomeration of WC grains. The WC grains featured rectangular and triangular prism shapes, consistent with the results reported by other researchers [19-21]. The rectangular shape reveals the (0001) lattice plane involvement in the WC grains, whereas the triangular prism shape shows the inclusion of (0001) plane and [0001] direction. The nucleation and growth process of WC grain occurred on the (0001) lattice plane. The triangular prism shape is considered the equilibrium shape of WC due to its considerably low surface energy [19]. Alloying elements, such as Co, Fe, and Ni, affect the morphology of WC grain by changing the dimensions of its surface facets [20, 21]. During the hot pressing sintering in this study, the presence of Fe affected the morphology of WC grain by increasing the diffusivity of W and carbon atoms, especially in the local liquid-phase zone.
Figure 4. The SEM micrograph of dual-scale WC–Fe reinforced iron matrix composite after sintering at 1250 °C for 14 h.

The microstructural evolution of the composite must be discussed considering the main phases of the raw material before heating (W, Fe₂W, Fe₇W₆, α-Fe, and Gr). After 14 h holding at 1250 °C, the main phases of the composite were WC and α-Fe. Figure 5 presents the SEM micrographs of the composites after sintering at 1250 °C for 6 and 10 h, respectively. As discussed, the main phases in ferrotungsten were W, Fe₂W, and Fe₇W₆.

After 6 h heat treatment, a reaction layer formed around the W particles. According to EDS and XRD analysis, the white phase in the center was W, whereas the light gray phase at the boundary was W₂C with a thickness of 0.5 μm (figures 5(a) and 5(b)). The white particles were WC particles inlaid in the gray Fe₃W₃C matrix (figures 5(b) and 5(c)). After 10 h sintering, W and W₂C phases disappeared, and Fe₃W₃C and WC existed in the aggregate zone (figure 5(d)).

Figure 5. The SEM micrograph and EDS results of dual-scale WC–Fe reinforced iron matrix composite after sintering at 1250 °C for 6 h (a, b, c) and 10 h (d).

Fe₂W is the low-temperature stable, intermetallic phase; it will not form at 1250 °C [22]. At 1051 °C, peritectoid reactions occurred as follows: Fe₂W+η ↔α+η+μ, where phase μ is Fe₇W₆, and the phase transition temperature of Fe₇W₆ is as high as 1398 °C [23]. Fe₃W₃C and WC formed completely after 10 h due to the diffusion of carbon atoms. Antoni-Zdziobek [23] discussed four ternary eutectic microconstituents in the Fe–W–C system and explained why metastable microconstituents can readily be formed experimentally and by calculations. In this work, the weight fractions of Fe, W, and C totaled 40.58%, 55.79%, and 3.63% in the aggregate zone, respectively, which conformed to the high W/low C zone.
3.3. Formation mechanism of WC in WC–Fe reinforced iron matrix composite

W, Fe₂W, Fe₇W₆, and Gr in the mixed powder were transferred to WC and α-Fe completely after heat treatment at 1250 °C for 14 h. During sintering, W₂C and Fe₃W₃C were in-situ produced as the intermediate phases. Thus, the relationship between the final products and intermediate phases, that is, the formation mechanism of dual-scale WC–Fe reinforcements, must be discussed extensively. First, all the reactions during hot pressing sintering can be divided into two categories: high- and low-carbon content reactions.

High-carbon-content reactions:

\[ W + C \rightarrow W_2C \]  \hspace{1cm} (1)

\[ W_2C + C \rightarrow WC \]  \hspace{1cm} (2)

\[ Fe_3W_3C + C \rightarrow Fe + WC \]  \hspace{1cm} (3)

Low-carbon-content reactions:

\[ W + Fe + C \rightarrow Fe_3W_3C \]  \hspace{1cm} (4)

Figure 6 shows the carbon concentration change schematic, local Fe–C phase diagram, and the variation in capillary driving force for the changes in liquid phase. The localized liquid phase appeared because the sintering temperature (1250 °C) was slightly higher than the Fe–C binary eutectic temperature (DSC: 1154 °C). Under the action of capillary force, the liquid phase permeated the surface of the aggregate, which was rich in W. Carbon atoms easily diffused into W due to their small atomic radius. W₂C formed on the surface W zone by in-situ reaction (1). The existence of a local liquid phase allowed the carbon atoms to achieve extremely high diffusion rates [24]. In-situ reactions (1) and (2) consumed carbon atoms and caused a decrease in the carbon concentration in the liquid phase, as shown in figure 6(a). Combined with the local uneven distribution of the liquid components and the solubility of W in the liquid phase, the amount of liquid phase reduced. Figures 6(a) and 6(b) show that if the carbon concentration decreased from \( c_{L1} \) to \( c_{L2} \), then the melting point increased from \( T_{L1} \) to \( T_{L2} \), and the amount of liquid phase decreased from \( u_1 \) to \( u_2 \). At the same time, WC was immersed in the liquid phase (low carbon concentration), which is prone to dissolve into molten pools owing to its low free generation enthalpy at the high temperature [5]. At high concentration gradient, the diffusion rate of W atom was slower than that of carbon, forming a higher concentration of W and lower carbon [25], which can be expressed as reaction (4). The rapid diffusion of carbon from the interface led to the relative enrichment of W, forming the Fe₃W₃C phase [16]. The corresponding carbon concentration and the amount of liquid phase increased to \( c_{L3} \) and \( u_3 \), respectively, whereas the melting point decreased to \( T_{L3} \). The carbon content consumed by in-situ reactions (1) and (2) was higher than that released by reaction (4), that is, \( c_{L1} - c_{L3} > 0 \). Thus, the carbon content in liquid phase gradually decreased with prolonged sintering times.

Given in-situ reaction (1), reaction (2), and reaction (4), the carbon content in the liquid phase fluctuated as the reaction progressed, thus further affecting the amount of liquid phase. The capillary driving force is directly related to the liquid content. Under the action of capillary force, the locally generated Fe liquid migrated to the W-enriched large particles. The evolution of this process was driven by the decreased excess free energy, \( F \), associated with interfaces. The liquid-phase distribution under semi-liquid temperature can be written as follows [26]:

\[
-\left(\frac{d\bar{F}}{dV_l}\right)_{V_s,n_c} = -\frac{\partial \bar{F}}{\partial u} \frac{\partial u}{\partial V} = -\gamma_s V_p^{-1/3} k_{cc}^{-2/3} (1 - u)^{4/3} \left[ \frac{\partial k_i}{\partial u} + \frac{2 k_i}{3(1 - u)} \right]
\]

where

- \( V_l \) and \( V_s \) are the volume of the liquid and solid phases, respectively;
- \( V_p \) is particle volume, \( V_p = V / n_c \), where \( n_c \) is the average particle coordination in the aggregate;
- \( u \) is the liquid-phase volume fraction;
\( k_{VC} \) and \( k_i \) are three non-dimensional shape factors; and \( \gamma_{sl} \) is the solid/liquid interface tension.

Denoting angle,

\[
\psi = 2 \arccos \left( \frac{2 \gamma_{sl}}{\gamma_{ss}} \right)
\]

when \( \psi/2 \) takes on different values, the relationship between \( dF/dV_l \) and \( u \) can be expressed as figure 6(c), where \( dF/dV_l \) is negative at low liquid-phase volume fraction, showing persistence of a driving force.

Carbon content affects the volume fraction of the liquid phase. When the carbon content increased, the liquid phase showed accelerated diffusion, and the difference in the total carbon on both sides of the reaction layer resulted in varying liquid volume fractions on both sides of the reaction interface and large driving force of the liquid phase during inward migration. Carbon diffusion continued, allowing the liquid phase at the interface to exist, because Fe was consumed in the reaction zone around the W-enriched large particles (reaction (4)), the liquid phase volume fraction in the reaction zone was still low, and the capillary force persisted. The interface was pushed inward until W particles were consumed. At this point, the carbon concentration of the system gradually decreased, the liquid phase disappeared, and the capillary force gradually weakened until disappearing.

Carbon atom diffusion led to the formation of more liquid \([25]\), and thus, W was constantly consumed. \( W_2C \) was simultaneously transferred to WC due to the increased carbon atom diffusion into its interstitial sites. After the large W-enriched particles were completely consumed, reaction (1) cannot occur, and \( W_2C \) continually transformed into WC given the sufficient carbon levels. Gradual decreases occurred in the carbon concentration of the system, which consisted of WC, Fe\(_3\)W\(_3\)C, and graphite, and the liquid phase. After 14 h heat treatment, all Fe\(_3\)W\(_3\)C was transferred to WC particles regardless of whether they were formed from the local liquid zone or from Fe\(_3\)W\(_6\) (figures 4(b)). During the transformation, carbon atoms were consumed by reaction (3).

\[\text{Figure 6. Schematic of carbon concentration change (a), local Fe–C phase diagram (b), and variation in the capillary driving force during changes in the liquid phase (c).}\]

4. Conclusion

Dual-scale WC–Fe reinforced iron matrix composites were prepared by hot pressing sintering process under a pressure of 10 MPa at 1250 ± 5 °C for 6, 10, and 14 h using low-cost ferrotungsten, graphite, and Fe powder as raw materials. The microstructure of the mixed powder and microstructural evolution and in-situ-formed mechanism of the composite were studied by XRD, SEM, and EDS analysis.

(1) The mix powders with ferrotungsten and graphite were composed of W, Fe\(_3\)W, Fe\(_7\)W\(_6\), and Gr. The particle size of mixed powders decreased from 200 mesh (<74 μm) to ~1.2 μm and showed agglomeration after 48 h milling.

(2) When hot pressing sintering time increased from 6 h to 14 h, W\(_2\)C and Fe\(_3\)W\(_3\)C phases arose as intermediate phases and finally transferred to WC and α-Fe phase due to excess carbon. The dual-scale
WC–Fe reinforcements with an average size of 54 µm were uniformly distributed within the α-iron matrix. The average size of irregularly shaped WC grains was 5 µm. The volume fraction of WC in the composite reached 76.40%.

(3) The volume of local liquid-phase zone decreased with the decrease in carbon content due to consumption by the in-situ reactions, which would improve the capillary driving force and the formation of Fe₃W₃C. Finally, sufficient amount of carbon ensured that the intermediate phases W₂C and Fe₃W₃C were transferred to WC.

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