Microstructural characteristics of TiC and (TiW)C iron matrix composites

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The present work investigated microstructures of *in situ* synthesized 10 vol% TiC-Fe and 10 vol% (TiW)C-Fe composites. The results show that in the TiC-Fe composite, as only second phase, TiC is in two kinds of morphologies, i.e., spherulic and rod-like ones. It is thought that the spherulic TiC is a proeutectic phase and the rod-like one is a eutectic phase. *In situ* synthesis of the 10 vol% (TiW)C-Fe composite in liquid iron is feasible. In the composite, the (TiW)C reinforcements as only one second phase are more homogeneously distributed in iron matrix, and most of them are spherulic and the few rod-like. Within the spherulic (TiW)C phase, there is an inhomogeneous distribution of titanium and tungsten. Its core is rich in titanium, while the periphery rich in tungsten. Such the characteristic microstructure is closely related with its formation during solidification. Comparing with the TiC, the (TiW)C phase has a density matchable for iron melt, which makes it more suitable as *in situ* synthesized reinforcements in large size ingots of iron matrix composites. © *2002 Kluwer Academic Publishers*

1. Introduction

Insertion of high strength and high hardness ceramic particles into metal matrices, developing metal matrix composites (MMCs), can improve mechanical properties, especially, wear resistance of metallic materials substantially. In fact, various sintered cobalt-, iron- and nickel-base alloys with a larger volume fraction of added coarse carbide particles have been applied to cutting, machining and wear resistance. They have usually been produced through powder metallurgy. However, the process has intrinsic limitations for product size, production costs and material qualities. Considering the materials qualities, there are usually a high volume fraction of microvoids in such materials, and the higher the density required, the greater is the consolidation pressure and the smaller the size of the product. Furthermore, such materials usually have low ductility and impact resistance. However, most cast products can overcome those drawbacks, and solidification processing seems to be a more economical and versatile technique for producing the MMCs, which has been widely used in production of light metal matrix composites such as Al and Mg etc. In contrast, relatively little work had been conducted on the solidification processing of the MMCs with high melting points until *in situ* synthesis technique in melts was developed recently, for the high melting points would make it difficult addition of reinforcements into melts by stirring mechanically.

For the last decade, much attention has been paid to the *in situ* synthesis technique of the MMCs. Its eminent advantage is in that eliminates interface incompatibility of matrices with reinforcements by creating more thermodynamically stable reinforcements based on their nucleation and growth from the parent matrix phase. Although it was developed firstly for preparation of aluminum matrix composites, the technique has been applied lately to synthesize iron matrix composites, mainly TiC-Fe [1–4]. Spherulic and uniformly distributed TiC reinforcements could successfully be synthesized in iron matrices. This opened a door for solidification processing of iron matrix composites. However, it should be noted that there is great difference in density between TiC and iron melt. Relatively light TiC particulates are formed firstly and tend to float up during solidification, resulting in their segregation in cast composites. (TiW)C phase seems to be more prospective candidate for reinforcements synthesized *in situ* in iron melt, for its density is a little higher than that of TiC, and approaches that of iron melts [5, 6].

The present work investigated microstructural characteristics of both *in situ* synthesized 10 vol% TiC and 10 vol% (TiW)C iron matrix composites. It is expected that the results can be significant in promoting

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the development and applications of the *in situ* synthesized iron matrix composites.

2. Experimental procedure

Commercial powders of titanium, tungsten, graphite and iron were used for the preparation of batches. A batch, Fe-4.528wt%Ti-1.132wt%C, was prepared to obtain 10 vol% TiC-Fe composite. Titanium and carbon powders were at a ratio corresponding to that of stoichiometric TiC. The other batch, Fe-2.264wt%Ti-8.692wt%W-1.132wt%C, was prepared to obtain 10 vol% (TiW)C-Fe composite. It is assumed that a half of titanium atoms in TiC are substituted by tungsten atoms, forming a $(Ti_{50}W_{50})C$ carbide in iron matrix. In order to get a homogeneous mixed powder, the weighted powders were mechanically stirred in a cup for 10 minutes, and then were uniaxially compacted in a die of 25 mm in diameter under a pressure of 270 MPa. Sample weighing 10 g was melted in an electric arc furnace using a non-consumable W electrode. The reaction product was weighed, cut, ground and polished for metallographic observation.

Scanning electron microscopy (SEM) in combination with energy dispersive X-ray spectroscopy (EDS) was employed to examine microstructure and perform compositional microanalysis. MEF4A Image Analysis System was used to analyze the volume fraction and uniformity of distribution of carbides in iron matrix. In order to identify the nature of the formed phases, X-ray diffraction analysis with Cu K_α radiation was done on the samples. The metallographical samples were prepared and etched in an ethanol solution containing 5 vol% HNO_3.

3. Results

3.1. Microstructures of the TiC-Fe composite

Fig. 1a is the back-scattered electron image of the 10 vol%TiC-Fe composite. It can be seen that some large spherulic titanium-rich particulates are distributed in the matrix. At a higher magnification (Fig. 1b), a great number of thin rod-like phases can be observed, which seems to be a eutectic morphology. EDS demonstrates that the rod-like phases also contain an amount of titanium and carbon atoms, as shown in Fig. 2. But, at the same time, iron peaks in the spectroscopy are noticeable. As the rod-like phases are too thin, it is unable to conclude if the iron peaks come from the phases or the matrix. Fig. 3 shows the X-ray diffraction pattern of the composite. Besides the peaks of the iron matrix, there are exclusively prominent peaks of TiC phase. This indicates that the TiC is the only second phase in the composite and no surplus carbides such as cementite (Fe_3C) are formed. In the composite, the TiC phase appears in two morphologies, i.e., spherulic and rod-like. Unlike the particulates, the TiC rods are undesirable as far as mechanical properties of materials are concerned.

3.2. Microstructures of the (TiW)C-Fe composites

Fig. 4a is the microstructure of the 10 vol% (TiW)C-Fe composite. It can be seen that a lot of fine particulates
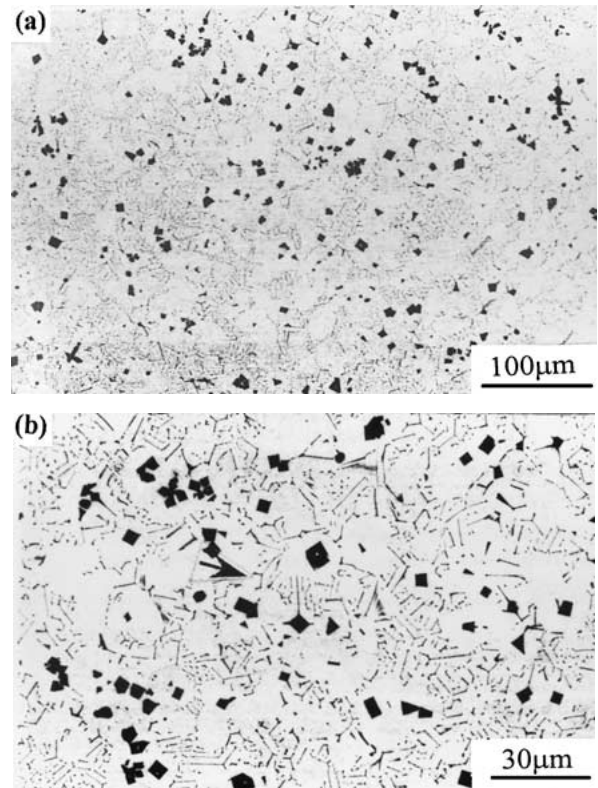

Figure 1 Back-scattered electron images of the 10 vol%TiC-Fe composite, (a) low magnification and (b) high magnification.
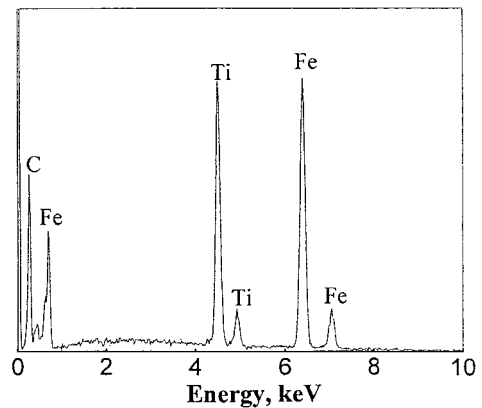

Figure 2 EDS of the rod-like phase in Fig. 1b as indicated by an arrow.
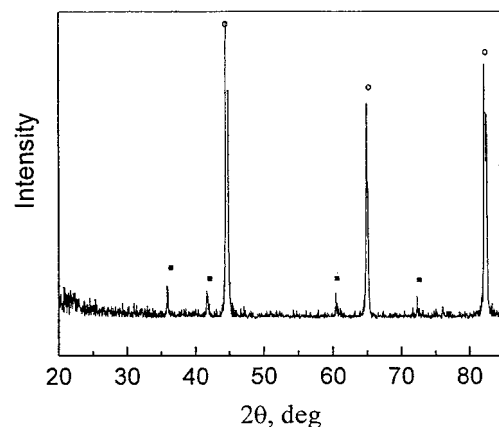

Figure 3 X ray diffraction pattern of the 10 vol% TiC-Fe composite. (○), Fe; (■), TiC.
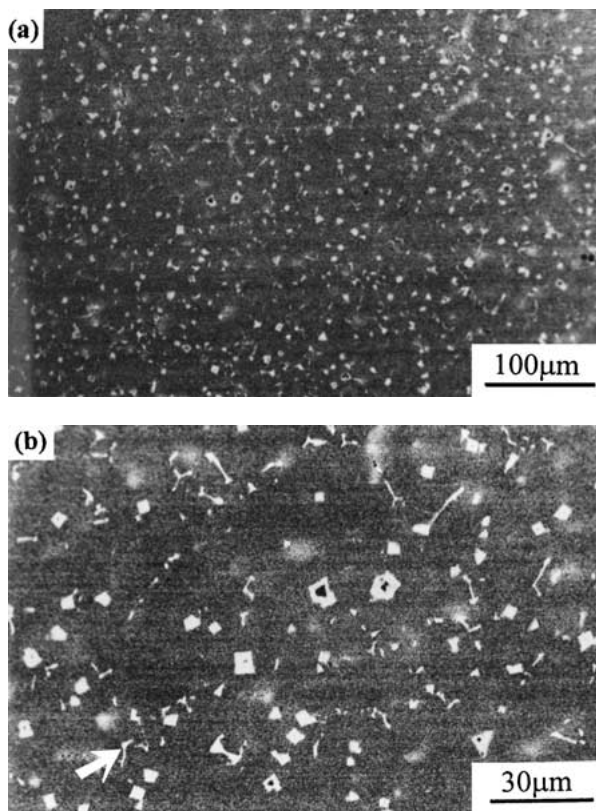
Figure 6 The spherulic phase in the 10 vol% (TiW)C composite; the line indicates the location of line scanning.

Figure 4 Back-scattered electron images of the 10 vol% (TiW)C-Fe composite, (a) low magnification and (b) high magnification.

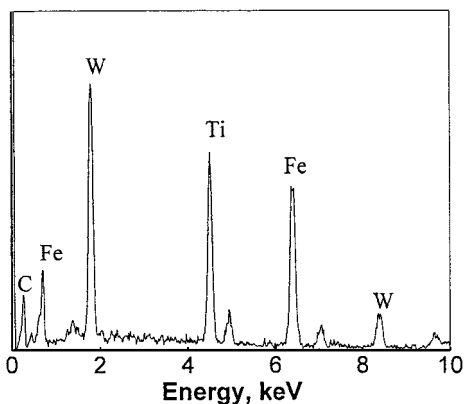Figure 7 EDS line scan across the spherulic phase shown in Fig. 6.

Figure 5 EDS of the rod-like phase in Fig. 4b as indicated by an arrow.

Figure 8 X ray diffraction pattern of the 10 vol% (TiW)C-Fe composite. (○), Fe; (■), TiC/(TiW)C.

are more homogenously distributed in the iron matrix than that in the TiC composite. Fig. 4b shows that the majority of the second phases are spherulic, and the minority in rod-like form. In these back-scattered electron images, all the second phases are brighter than the iron matrix, indicating that they are rich in tungsten. EDS was performed on the rod-like phases and a typical result is shown in Fig. 5. It demonstrates that they are carbides rich in titanium and tungsten. As the case of the TiC-Fe composite, these rod-like phases are too thin to make sure if they contain iron atoms.

Interestingly, however, a darker core was observed in the most spherulic phase, as shown in Fig. 6. The line scanning across such a particulate was conduced with EDS and the result is shown in Fig. 7. Evidently, the phase substantially consists of titanium, tungsten and carbon atoms, and does not contain iron. But, it is noticeable that titanium and tungsten atoms are un-
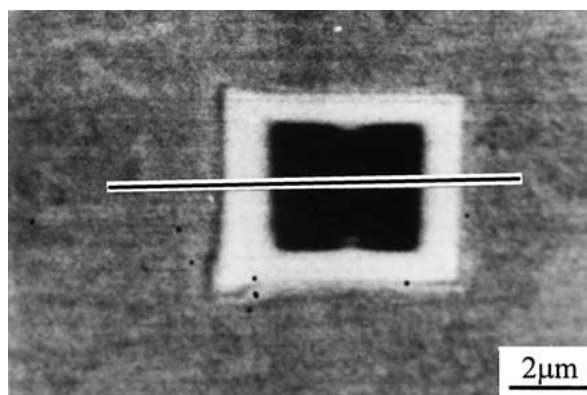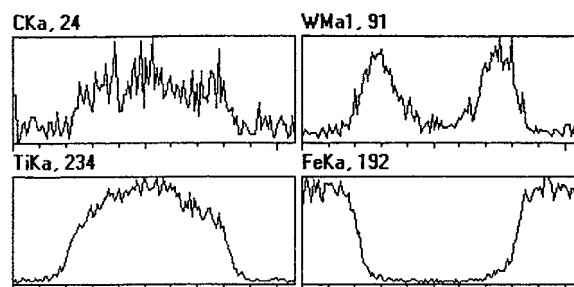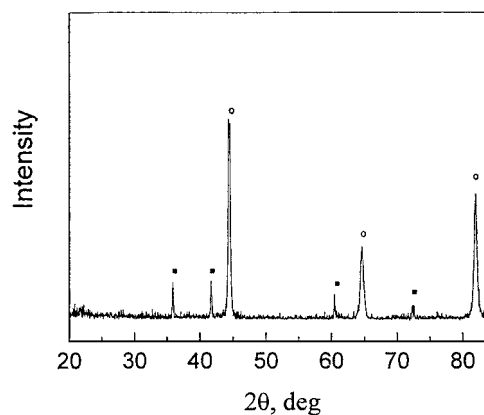
evenly distributed within the phase. In the dark core of the phase, there are most titanium and least tungsten atoms, while at the periphery of the phase, there are least titanium and most tungsten atoms. It seems that there are positive and negative gradient distributions of titanium and tungsten from the core outward, respectively.

Fig. 8 is X-ray diffraction pattern of the 10 vol% (TiW)C-Fe composite. Besides iron peaks, there are exclusively prominent peaks of second phases, TiC and/or (TiW)C. Those of TiC and (TiW)C phases exactly overlap and no distinction can be made between them. In combination with the microstructural observations and compositional microanalysis with SEM and EDS, it can be concluded that they are the (TiW)C rather than the TiC. The (TiW)C is only second phase in the (TiW)C-Fe composite and no other second phase is formed, that is expected.

Image analyses show that the volume fraction of TiC in the TiC-Fe composite is about 9.5%, and the (TiW)C in the (TiW)C-Fe composite is 9.3%. Several local areas analyses show that the (TiW)C in the (TiW)C-Fe composite is more homogeneously distributed in the iron matrix than TiC in the TiC-Fe composite. The little lower volume fraction of reinforcements than that we designed may come from two aspects: first, not all graphite we added has been changed into alloying carbon, second, some tiny or burred carbide phases cannot be properly detected by image analysis system. But the measured volume fractions is quite close to the value that we designed, we believe that TiC and (TiW)C are the only second phases in the TiC-Fe and (TiW)C-Fe composites, respectively.

4. Discussion

Despite that exact melting temperature cannot be measured, it is believed that a batch is heated to an extraordinarily high temperature with an electric arc furnace, resulting in its complete melting. In the present work, therefore, the formation of the TiC and (TiW)C phases in the composites occurred during cooling of the melts. As the two kinds of the composites experienced the same melting process, their microstructural differences must result from their different chemical compositions.

As is expected, in the 10 vol% TiC-Fe composite, the TiC as an exclusively second phase is formed and roughly homogeneously distributed in the iron matrix. But, it appears two kinds of morphologies, i.e., spherulic and rod-like ones. Although it usually appears in the form of fine equiaxed particulate in metals and alloys, the other morphologies such as rod, cross and dendritic forms were observed in iron matrix composites synthesized *in situ* by a liquid route [2]. This indicates the complexity of its formation in iron melts. The amount of Ti and C, their ratio as well as processing parameters all may be the important affecting factors of its morphology.

Considering that Ti and C in the batch of the TiC-Fe composite correspond to stoichiometric TiC and the resultant composite is composed of only TiC and Fe, the formation of solidification microstructure may be followed on a Fe-TiC binary phase diagram. Fig. 9 is the Fe-TiC phase diagram reproduced from Ref. 7. It is shown that there is a eutectic reaction near iron rich
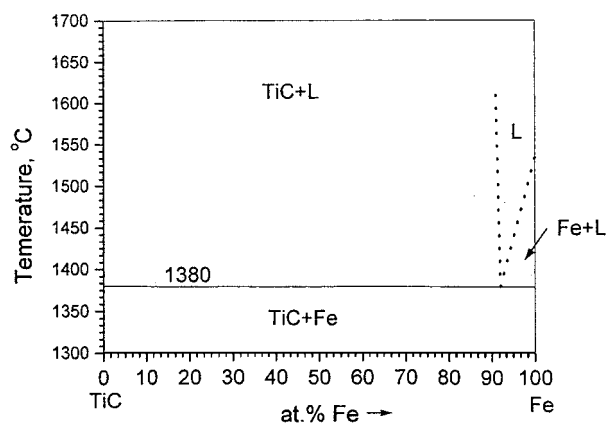
corner. The 10 vol% TiC-Fe composite is located at hypoeutectic zone and thus, its microstructure is hypoeutectic, and composed of a proeutectic phase and a eutectic. Evidently, the spherulic TiC as the proeutectic phase precipitates firstly during solidification, while the rod-like TiC is formed later as the eutectic product.

In the 10 vol% (TiW)C-Fe composite, the (TiW)C phase is only second phase and no surplus phase exists in the iron matrix. This work demonstrates that *in situ* synthesis of the (TiW)C in the iron matrix and development of the *in situ* synthesized (TiW)C-Fe composites are feasible. Comparing with the 10 vol% TiC-Fe composite, the 10 vol% (TiW)C-Fe composite seems to contain more spherulic and less rod-like reinforcements. such microstructure is favorable to the improvement of mechanical properties, especially wear resistance.

Initial aim of the development of the *in situ* synthesis of the (TiW)C reinforcing iron matrix composites is to overcome the larger difference in density between reinforcements such as TiC and iron matrix so as to improve homogeneity of distribution of the reinforcements in iron matrix. At present, since the actual chemical constitution of the synthesized (TiW)C phase is unknown, the exact calculation of its density is impossible. Here, a rough evaluation is made. It is assumed that titanium and tungsten in the batch all enter into the (TiW)C phase, as is expected. Therefore, in the phase, their atomic ratio is 1:1 and the corresponding formula is $(Ti_{0.5}W_{0.5})C$. Considering that the (TiW)C has the same crystal lattice and lattice constant as TiC, the density of the $(Ti_{0.5}W_{0.5})C$ is calculated. The result shows that it is 9.07 g/cm^3, while those of TiC and iron are 4.25 and 7.8 g/cm^3, respectively. This indicates that the $(Ti_{0.5}W_{0.5})C$ does have a density closer to iron than TiC. Undoubtedly, the $(Ti_{0.5}W_{0.5})C$ would alleviate the segregation of the reinforcements in a melt, and can be more homogeneously distributed in the iron matrix than TiC.

Like the TiC in the TiC-Fe composite, the (TiW)C also has two kinds of morphologies, i.e., spherulic and rod-like ones. But, the spherulic is predominant in number and the rod-like is few. Since Fe-Ti-W-C and Fe-(TiW)C phase diagrams are unavailable presently, the exact formation mechanism of such the microstructure fails to be determined. However, it seems to be reasonable to assume a similarity of the Fe-(TiW)C phase diagram with that of the Fe-TiC. Therefore, the spherulic and rod-like phases are taken as proeutectic and eutectic phases, respectively. Then, the relatively smaller number of the rod-like phase in the (TiW)C-Fe means that a eutectic point of the Fe-(TiW)C phase diagram is shifted to the iron-rich corner in comparison with that of the Fe-TiC phase diagram. This results in a marked increase of the spherulic (TiW)C and corresponding decrease of the rod (TiW)C, respectively.

It is worthy of noting that there is an uneven distribution of elements of titanium and tungsten within spherulic (TiW)C phase (Figs 6 and 7). This demonstrates that the phase is in a thermodynamical nonequilibrium. Indeed, an electric arc furnace characterizes rapid heating and cooling and thus, few products are in a thermodynamical equilibrium during cooling process. But, this characteristic feature of the spherulic (TiW)C

Figure 9 Fe-TiC phase diagram [7].

may provide a clue to know how the phase is formed. Like the TiC-Fe composite, the formation of the phases of the (TiW)C-Fe composite also occurred during solidification. When the melt cools, the TiC phase first is formed through a direct reaction between solute titanium and carbon in the melt, for it has the highest melting point among all the compounds consisting of two or more of Fe, Ti, W and C. Indeed, this is confirmed by the titanium-rich core of the (TiW)C. With temperature dropping further, the solubility of tungsten in the melt decreases and tungsten atoms are expelled from the melt. They enter into the growing TiC phase by substituting titanium ones. This produces the spherulic (TiW)C phase with the titanium-rich core and the tungsten-rich periphery. As is well known, the TiC phase is indeed a very effective heterogeneous nucleus of metal and alloy melts and has been widely used to refine solidifying microstructures of castings. Evidently, the roughly uniform distribution of the spherulic (TiW)C phase in the composite is closely related to the heterogeneous nucleation of the TiC phase. When the eutectic temperature is reached, the rod-like (TiW)C is formed as a eutectic product. The small number of the rod-like phase indicates that the eutectic point is much near the iron-rich corner.

The present work shows that the 10 vol% TiC could be synthesized *in situ* in liquid iron and the TiC as reinforcements is only second phase in the composite. But, the large number of the rods makes the microstructure unfavorable for mechanical properties. So, some measures need to be taken to modify the rod-like into the spherulic TiC before the 10 vol% TiC-Fe composite is put into use. In contrast, the microstructure of the 10 vol% (TiW)C-Fe composite is more desirable. The (TiW)C reinforcements are also only second phase, which are more homogeneously distributed in the iron matrix than the TiC in the TiC-Fe composite. Furthermore, most of them are spherulic and few the rod-like. The more important is the (TiW)C phase, having a density matchable for iron melts. Considering that it is formed in the melt, this makes it more appropriate as reinforcements synthesized *in situ* in iron melts for large size composite ingots where they take a much longer time to solidify. This results reveal the possibility of producing large size ingots of (TiW)C-Fe composites using bulk form metals or alloys.

5. Conclusions

1. As only second phase, the TiC could be synthesized *in situ* in 10 vol% TiC-Fe composite. It takes two kinds of morphologies, i.e., spherulic and rod-like ones.

2. According to the Fe-TiC phase diagram, it is learnt that the spherulic and rod-like TiC phases are proeutectic and eutectic phases, respectively.

3. *In situ* synthesis of 10 vol% (TiW)C-Fe composite in liquid iron is feasible. In the composite, the (TiW)C reinforcements as only one second phase are more homogeneously distributed in iron matrix, and most of them are spherulic and the few rod-like.

4. Within the spherulic (TiW)C phase, there is an inhomogeneous distribution of titanium and tungsten. Its core is titanium rich and periphery tungsten rich. Such the characteristic microstructure is closely related with its formation during solidification.

5. Comparing with the TiC, the (TiW)C phase has a density matchable for iron melt, which makes it possible to use as *in situ* synthesized reinforcements in large size ingots of iron matrix composites.

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