Fabrication of Steel Matrix Composite Locally Reinforced with in Situ TiC Particulate via SHS Reaction of (Ti, Fe)–C System during Casting

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The low-alloy steel matrix composites locally reinforced with in situ TiC particulates have been successfully produced utilizing the self-propagating high-temperature synthesis (SHS) reaction of (Ti, Fe)–C systems during casting. Two types of TiC particulates synthesized by different mechanisms exhibit a relatively uniform distribution in the local reinforcing region. The large rectangular TiC particulates with an average size of \(-2 \mu m\) or more, which are formed by the nucleation-growth mechanism through the contact reaction process, are mainly present in the local reinforcing region of the composites fabricated by \((28Ti, Fe)–C\) system and the matrix region nearby the interface between the steel matrix and reinforcing region. The fine spherical/near-spherical TiC particulates, which are synthesized by reaction, solution and precipitation mechanisms during the SHS reaction, are mainly existent in the reinforcing region. Moreover, the average size of spherical/near-spherical TiC particulates increases from \(-0.1 to -0.5\) and then to \(-1 \mu m\) with the increase in Ti content from 28 to 48, and then to 68 wt% in \((Ti, Fe)\) powders. The interfaces of the composites are clean, which results in a good metallurgical bonding between steel matrix and reinforcing region in the composites. Moreover, the micro-hardness and wear resistance of the local reinforcing region of the composites are significantly higher than those of the unreinforced steel matrix.

KEY WORDS: metal-matrix composites (MMCs); particulate; locally reinforced composites; TiC.

1. Introduction

It is well established that the incorporation of hard ceramic particulates to ferrous matrices can significantly improve certain material properties, e.g. hardness and wear resistance.\(^{1,2}\) In recent years, therefore, metal matrix composites (MMCs) reinforced with ceramic particulates have received considerable attention.\(^{3-7}\) For example, particulate reinforced steel matrix composites have been proposed for use as wear and corrosion resistant parts in the chemical and process industry, or as substitutes for the more expensive cemented carbides (e.g. WC–Co).\(^{5}\)

The common ceramic materials used for reinforcing iron and steel matrices are \(Al_2O_3, TiC, ZrO_2, Si_3N_4, Cr_2C_3, TiB_2, B_4C, WC, VC, etc.\)^{1,7,9,10} Among them, TiC has proved suitable in iron and steel matrices due to its high hardness, good wettability, low density, and its relative chemical stability with iron and steel matrices.\(^{1,5,6,9,11-16}\) Unfortunately, the synthesis of TiC via in situ reaction of elemental powders is relatively expensive due to the very high cost of pure Ti powder. Therefore, the application of TiC ceramics has been limited. In this case, some studies\(^{3,12-16}\) have used mineral ilmenite (FeTiO\(_3\)), ferrotitanium (Ti, Fe), and titanium dioxide (TiO\(_2\)) powders as reactants to synthesize TiC ceramics.

The FeTiO\(_3\) powders were used to produce TiC particulates with carbon in flowing argon or under vacuum in the temperature range of 1 100–1 400°C by Brown et al.\(^{3}\) Uniformly dispersed TiC particulates were formed in the matrix, but long cracks also propagated around the grain boundaries through the metal body.\(^{3}\) Whereas Raghunath et al.\(^{11}\) attempted to introduce (Ti, Fe) and C mixtures into a melt of cast iron to produce in situ MMCs reinforced with TiC. The (Ti, Fe) to TiC transformation was achieved but considerable foaming, exothermic reactions, and a low viscosity of the melt/particulate mixture impaired the castings.\(^{12}\) Furthermore, a similar transformation was also achieved with (Ti, Fe) and carbon by hot-isostatic pressing and an in situ transformation by Bens and Wewers.\(^{13}\) They reported that the steel composites reinforced with in situ TiC particulates have excellent properties of hardness and abrasion resistance at room temperature or elevated temperature.\(^{13}\) More recently, D. S. Gowtam et al.\(^{15}\) have produced a Fe–Mn-based austenitic steel composites with in situ TiC particulates, utilizing aluminothermic reduction (also termed as aluminothermic SHS) of iron oxide (Fe\(_2O_3\)), manganese dioxide (MnO\(_2\)) and titanium dioxide (TiO\(_2\)) powders in the presence of C. Although iron- and steel-matrix MMCs reinforced with TiC particulates have been investigated widely, there are still some areas which lack understanding, e.g. the formation mechanism of ceramics and fabrication techniques of composites.\(^{16-18}\) So, further re-
searches and more focuses are still needed.

Generally, MMCs can be produced by techniques of powder metallurgy, conventional melting and casting, as well as combustion synthesis, also termed self-propagating high-temperature synthesis (SHS), etc.17) However, most of them are monolithic composites. In view of application, the service life of products usually depends on the local region property such as hardness and wear resistance, so the local region of casting rather than all the casting is desired to be reinforced by ceramic particulates.19,20) In the previous studies, starting material systems of Ni–Ti–C,21) Ni–Ti–B22) were used to produce locally reinforced steel matrix composites. More recently, Zhao et al.23) have fabricated in situ TiC particulate locally reinforced steel MMCs with an increase in micro-hardness by SHS reaction of (Ti, Fe)–C–Al system utilizing high-frequency induction process, and proposed that the addition of Al promoted the TiC formation process under differential thermal analysis (DTA) condition.24) In addition, the locally reinforced composites can reduce processing cost and improve the poor castability of the monolithic composites to some extent.25)

The principal objective of the present study is to examine the feasibility of fabricating of steel matrix composites locally reinforced with TiC particulates synthesized by utilizing the heat of the liquid steel during casting to trigger the SHS reaction of (Ti, Fe)–C system utilizing high-frequency induction process, and proposed that the addition of Al promoted the TiC formation process under differential thermal analysis (DTA) condition.24) In addition, the locally reinforced composites can reduce processing cost and improve the poor castability of the monolithic composites to some extent.25)

2. Experimental

The starting materials for the preforms were commercial powders of ferrotitanium (Ti, Fe) (~44 μm) and carbon (99.5 % purity, ~38 μm). Three kinds of ferrotitanium powders of (28Ti, Fe), (48Ti, Fe) and (68Ti, Fe) were selected, which contain ~28, ~48 and ~68 wt% Ti contents, respectively. The impurities in the (28Ti, Fe) powders are mainly ~2.5 wt% Si and ~1.0 wt% V together with <0.1 wt% C, and those in (68Ti, Fe) powders are mainly 4.5 wt% Al, 1.5 wt% Si, ~2.5 wt% V together with <0.15 wt% C. Note that the (48Ti, Fe) powders are the mixtures of (28Ti, Fe) and (68Ti, Fe), containing ~48 wt% Ti. The (Ti, Fe) powders were mixed with carbon powders at a ratio corresponding to stoichiometric TiC. After dry-blending for 6 h in a cylindrical stainless steel jar containing stainless-steel balls with a ball to powder weight ratio of about 5 : 1 by mechanical rotation at 40 rpm, the mixed powders were uniaxially pressed into cylindrical preforms (20 mm in diameter and 8 ± 1 mm in length) by using a stainless steel die under pressures ranging from 70 to 75 MPa.

The preforms, after being dried in a vacuum oven at about 300°C for 3 h to remove any trace of moisture, were placed and fixed on the bottom of the sand mold, which was described elsewhere22) in detail. The low-alloy steel was selected as the matrix alloy, whose chemical composition, measured by an ARL4460 Metals Analyzer, is listed in Table 1.

Table 1. Compositions of the low-alloy steel matrix (wt%).

| Mn | Si | C  | Cr | Ti | V  | Fe |
|----|----|----|----|----|----|----|
| 1.763 | 0.455 | 0.359 | 0.020 | 0.010 | 0.009 | Bal. |

The steel melt, prepared in a 5 kg medium-frequency induction furnace with a temperature of ~1600°C, was poured into the mold to ignite the SHS reaction of the preforms. After solidification and cooling, the reinforcing regions of the composite castings were sectioned and polished.

Metallographic samples were prepared according to standard procedures of metal samples, and etched with 5 vol% HNO3 for 5–10 s at 25°C. As the TiC particulates are more difficult to be etched than the steel matrix, the main purpose of etching is to distinctly display the TiC particulates in the composites. Subsequently, both the phases and microstructures of the reinforcing regions of the locally reinforced steel matrix composites were investigated. Vickers micro-hardness values of reinforcing regions of the composites, as well as the unreinforced steel matrix, were tested under a load of 50 g with an indentation time of 10 s on Buehler Omnimet Vickers hardness tester. Every sample was tested for 10 times at different positions and then the average value was calculated. Sliding abrasive wear resistance was tested using a pin-on-disc apparatus with a load of 25 N. Both unreinforced steel matrix and reinforcing regions of the composites were machined into cylindrical specimens with about 6 mm in diameter and 12 mm in length for the sliding abrasive test, in which two types of SiC abrasive papers (600 and 1 000 grit sizes) were used as the counterface. The cylindrical specimens were carefully cleaned with ethanol and were weighted before and after the tests using an electronic balance with an accuracy of 0.1 mg. The densities of the steel matrix and the composites were measured by Archimedes water immersion method.

The phase analysis was conducted by X-ray diffraction (XRD) using CuKα radiation (Model D/Max 2500PC Rigaku, Japan). The microstructure analysis of the samples was investigated by using field emission scanning electron microscope (FESEM) (Model FEI-XL30, America) equipped with energy-dispersive spectrometer (EDS) (EDAX-Genesis2000, America).

3. Results and Discussion

3.1. Phase and Microstructure

When molten steel with a temperature of ~1600°C was poured into the mold, the preforms placed in the mould were heated rapidly by the heat release of liquid steel. After a short time delay, the temperature of preforms reached to ignition temperature of (Ti, Fe)–C system; subsequently, the SHS reaction occurred to form an amount of TiC particulates in the local region of the castings.

Figure 1 shows the XRD patterns of local reinforcing regions of the steel matrix composites fabricated by (a) (28Ti, Fe)–C, (b) (48Ti, Fe)–C and (c) (68Ti, Fe)–C systems, respectively. According to XRD results, the reinforcing region of the composite fabricated by (28Ti, Fe)–C sys-
tem only consists of TiC and α-Fe phases, indicating that the reaction was complete between (28Ti, Fe) and C to form TiC (Fig. 1(a)). Besides TiC and α-Fe phases, however, a small amount of unknown phase is also found in reinforcing regions of the composites fabricated by (48Ti, Fe)–C and (68Ti, Fe)–C systems, which is ascribed to the use of commercially pure (68Ti, Fe) powders.

Figure 2 shows the as-cast microstructures of the reinforcing region of the locally reinforced steel matrix composites fabricated by (28Ti, Fe)–C system. The low magnification microstructures of the in situ processed composites reveal a relatively uniform distribution of TiC particulates in the local reinforcing region (Fig. 2(a)). It is interesting to note that the local reinforcing region contains two types of TiC, i.e. spherical/near-spherical and rectangular shapes (Fig. 2(b)). The rectangular TiC particulates, located in Fe-rich area, are relatively large but in a small quantity, while the spherical/near-spherical ones are fine and in large quantities. This result is attributed to the different formation mechanisms of TiC particulates, and it will be discussed later.

Figure 3(a), 3(b) and 3(c) show the typical FESEM micrographs of local reinforcing regions of the composites fabricated by (28Ti, Fe)–C, (48Ti, Fe)–C and (68Ti, Fe)–C systems, respectively. Note that the large rectangular TiC particulates with an average size of ~2 μm are mainly present in the composites fabricated by (28Ti, Fe)–C system. Moreover, the average size of spherical/near-spherical TiC particulates increases from ~0.1 to ~0.5, and then to ~1 μm with an increase in Ti content from 28 to 48, and then to 68 wt% in (Ti, Fe) powders.

According to the previous study, the propagating combustion wave of the SHS reaction is fast and the dwell time of the material in the combustion zone is very short. Although the combustion zone is of high temperature, the growth time of the crystals is very short, resulting in the formation of fine spherical/near-spherical particulates. The SHS reaction in (Ti, Fe)–C system can be summarized as

\[(\text{Ti, Fe}) + C \rightarrow \text{TiC} + \text{Fe} \]  

Consequently, the formation of fine spherical/near-spherical TiC particulates in the local reinforcing region is assisted by the reaction, solution and precipitation mechanism during the SHS reaction. Generally, the combustion temperature of the SHS reaction increases with the increase of Ti, and C atoms per unit volume in the reactants. The increase in temperature or reactant concentration is favorable for the growth of TiC crystals, and therefore, the size of spherical/near-spherical TiC particulates increases with Ti content in (Ti, Fe) increasing (Figs. 3(a)–3(c)).

Due to the high temperature in the combustion zone, some Ti in (Ti, Fe) and C atoms will diffuse and dissolve in
the liquid steel, forming [Ti] and [C]. As the concentrations of [Ti] and [C] in the melts reach the saturation state, the TiC nuclei tend to precipitate out of the melts by the nucleation-growth manner. In this case, the TiC formation mechanism can be characterized as contact reaction process, which can be summarized as follows

\[ [\text{Ti}] + [\text{C}] \rightarrow \text{TiC} \] ..............................(2)

Under this condition, the TiC crystals are in favor of growing into large rectangular particulates due to the relatively long solidification time of the steel melts. As a result, the large TiC particulates are generally entrapped inside Fe-rich area in local reinforcing region (Fig. 2(a)). This result is in well agreement with our previous study, in which large particulates are also formed and located in Fe-rich area in locally reinforced steel matrix composites fabricated by Ni–Ti–B4C system.5)

3.2. Interface between Steel Matrix and Reinforcing Region

Figures 4(a) and 4(b) show the interfaces between steel matrix and reinforcing region of the composites fabricated by (28Ti, Fe)–C and (68Ti, Fe)–C systems, respectively. It can be seen that the interfaces are clean, which results in a good metallurgical bonding between steel matrix and reinforcing region in the composites. Note that some large irregular TiC particulates locate in the matrix region nearby the interface between the steel matrix and reinforcing region, as shown in the insert of Fig. 4. Although the size of the TiC particulates located in the matrix region is lightly larger than that of the ones entrapped inside Fe-rich area in local reinforcing region (Figs. 2(a) and 2(b)), the formation mechanism of the former is similar to that of the latter, which are also formed by the nucleation-growth mechanism through the contact reaction process.

It should be mentioned that significant micro-porosities are present at the interface and the local reinforcing region in the composites produced by (68Ti, Fe)–C system (Fig. 4(b)), while only minimal micro-porosities are existent in the composites fabricated by (28Ti, Fe)–C system (Fig. 4(a)). Moreover, the micro-porosities in the composites produced by (48Ti, Fe)–C system are less than those in the composites synthesized by (68Ti, Fe)–C system, while more than those in the composites fabricated by (28Ti, Fe)–C system. The reason is ascribed to both the combustion temperature and the heat release increase with the increase of Ti content in (Ti, Fe) reactant, which result in the increase of gas evaporation generated by the SHS reaction and the micro-porosity in the composites.

3.3. Density, Micro-hardness and Wear Resistance

Table 2 shows the measured densities of steel matrix, and local reinforcing regions of the composites fabricated by (28Ti, Fe)–C, (48Ti, Fe)–C and (68Ti, Fe)–C systems, respectively. Note that the local reinforcing regions of the composites fabricated by (48Ti, Fe)–C and (68Ti, Fe)–C have relatively low densities, which indicates some micro-porosities are present in these two composites.

| Materials | Low-alloy steel | Local reinforcing regions of the composites |
|-----------|----------------|------------------------------------------|
|           |                | (28Ti,Fe)-C                               |
| Measured density (g/cm³) | 7.88 | 5.34 | 4.60 | 4.38 |

Figures 5 and 6 show the micro-hardness and wear resistance of steel matrix as well as local reinforcing regions of the composites fabricated by (28Ti, Fe)–C, (48Ti, Fe)–C and (68Ti, Fe)–C systems, respectively. It can be seen that the micro-hardness of the reinforcing region is significantly higher than that of the unreinforced steel matrix. Improvement of micro-hardness of the local reinforcing region in the composites is mainly attributed to the presence of high volume fraction of hard TiC ceramic particulates. Although the amount of TiC increases with the increase of Ti content from 28 to 68 wt%, the average micro-hardness value goes down slightly rather than increases, which may be attributed to the presence of micro-porosity in the composites.

It is obvious that the wear resistance of the reinforcing region of the composite is higher than that of unreinforced steel matrix. It is interesting to note that the composites
synthesized by (28Ti, Fe)–C and (68Ti, Fe)–C systems are of similar wear resistance, although they have different volume fraction of TiC particulates. The steel composite synthesized by (48Ti, Fe)–C system has relatively poorer wear resistance than the other two composites.

Figure 7 shows the abrasive surface of the steel matrix and the local reinforcing regions of steel composites fabricated by (48Ti, Fe)–C and (68Ti, Fe)–C systems, respectively. Note that the abrasive surface was formed against SiC abrasive papers of 600 grit size. It can be seen that the steel matrix has a relatively rough abrasive surface compared to the reinforcing regions. Moreover, many parallel and deep slots are cut or grooved by the hard SiC particulates through the surface of the steel matrix, and large steel chips are cut away from the steel surface (Fig. 7(a)). However, the local reinforcing regions of the composites have relatively smooth abrasive surfaces with slight slots and small steel chips due to the presence of hard TiC particulates, which are shown in Figs. 7(b) and 7(c). According to Refs. 2, 5, 29, 30, the increase of wear resistance of the composites is mainly attributed to load bearing by the hard second phase particles. Therefore, it is concluded that the load bearing capability of the in situ formed TiC ceramics retained at the sliding surface improves the wear resistance of the composites.

4. Conclusions

The low-alloy steel matrix composites locally reinforced with in situ TiC particulates were successfully fabricated utilizing the SHS reaction of (Ti, Fe)–C systems during casting. Two types of TiC particulates synthesized by different mechanisms exhibit a relatively uniform distribution in the local reinforcing region. The large rectangular TiC particulates with an average size of ~2 μm or more, which are formed by the nucleation-growth mechanism through the contact reaction process, are mainly present in the local reinforcing region of the composites fabricated by (28Ti, Fe)–C system and the matrix region nearby the interface between the steel matrix and reinforcing region. The fine spherical/near-spherical TiC particulates, which are synthesized by reaction, solution and precipitation mechanism during the SHS reaction, are mainly existent in the reinforcing region. Moreover, the average size of spherical/near-spherical TiC particulates increases from ~0.1 to ~0.5, and then to ~1 μm as the Ti content increases from 28 to 48, and then to 68 wt% in (Ti, Fe) powders.

The interfaces of the composites are clean, which result in a good metallurgical bonding between steel matrix and reinforcing region in the composites. Although only minimal micro-porosities are present in the composites fabricated by (28Ti, Fe)–C system, the micro-porosities increase with the Ti content further increasing in the composites produced by (48Ti, Fe)–C and (68Ti, Fe)–C systems. Moreover, the micro-hardness and wear resistance of the local reinforcing region of the composites are significantly higher than those of the unreinforced steel matrix.

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Fig. 5. Micro-hardness of the low-alloy steel matrix and the locally reinforced steel matrix composites fabricated by (28Ti, Fe)–C, (48Ti, Fe)–C and (68Ti, Fe)–C systems.

Fig. 6. The wear resistance of the low-alloy steel matrix and the locally reinforced steel matrix composites fabricated by (28Ti, Fe)–C, (48Ti, Fe)–C and (68Ti, Fe)–C systems.

Fig. 7. Typical FESEM morphologies of abrasive interface (against SiC abrasive papers of 600 grit size) of (a) low-alloy steel matrix, (b) locally reinforced composites fabricated by (b) (48Ti, Fe)–C and (c) (68Ti, Fe)–C systems.
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