Original Article

An Al–7Si alloy/cast iron bimetallic composite with super-high shear strength

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A new composite technology is presented consisting of the surface pretreatment of cast irons, the hot-dipping in a Zn–0.2 wt.% Bi melt and the Al/Fe composite process. The shear strength of Al/Fe (Al–7Si/cast iron) bimetallic composites fabricated by the technology is up to 32 MPa that is far more than the shear property obtained by composite technology reported in literatures. The super-high shear strength is mainly attributed to the formation of a peculiar concave–convex interface (CCI) structure. The addition of 0.2 wt.% bismuth into the zinc melt can promote the formation of Zn-rich regions at the surface layer of cast irons, leading to the formation of Al–Fe phases at these Zn-rich regions. Reducing the amount of Al–Fe phases appearing in the ferrite–graphite interface in cast irons can benefit improving the shear property of Al/Fe bonding interface. Further analysis of the stress state confirms that the CCI can enhance the shear strength of Al/Fe bonding interface.

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1. Introduction

The situation that involves energy waste, emission pollution induced by the lower energy efficiency of automobiles impels researchers to focus on fabricating automobiles with lightweight, better fuel-economy and less fume emissive properties [1,2]. One innovation in the automobile industry is proposed that is to use a multi-material as car body structure for reducing the automotive deadweight [3–7]. Al/Fe bimetallic composites, as one of the multi-material series, have a good combination of both high strength, wear resistance from the Fe (cast irons/steels) and high heat conductivity, corrosion resistance and lightweight properties from the Al (pure Al/aluminum alloys). They have attracted an extensive attention on the applications in automobile body, such as engine blocks [8,9] and pistons [10] etc. However, the greater physico-chemical differences between the Al and the Fe restrict the large-scale applications of Al/Fe bimetallic composites in the automobile body. For example, the Al melt wettability of cast iron is easily weakened because of a solder melt oxidation [11], leading to the difficulty of triggering the metallurgical reaction of Al/Fe [12]. The thicker rich-Al phase (Al3Fe, Al7Fe3) layer [13] or the thinner total Al–Fe phase layer [1] can generate a great threat to the bonding property of Al/Fe composite interface. Thus, during the manufacture process there are still
some challenges on how to obtain a sound metallurgical bonding, even a better interface shear property, by overcoming physicochemical differences between Al and Fe [14]. Although lots of methods at the laboratory scale have been developed in present to join Al with Fe, such as friction stir welding (FSW) [15–17], laser welding-brazing (LWB) [18–20], cold metal transfer (CMT) [21,22], rolling [23,24] and riveting [25], these methods are applied difficulty to join complex-shape components [1]. Composite casting technique that can combine liquid metals with solid metals by a solid–liquid metallurgical reaction has a great flexibility of joining complex-shape components [26] (Fig. 1). For example, Liu et al. [27] developed a new composite casting method characterized by hot-dipping in Zn–2.2 wt.% Al melt to obtain a metallurgical bonding of aluminum alloys/mild steels. Furthermore, most of methods including the above [15–25] are mainly focused on joining aluminum alloys with steel. Methods of connecting aluminum alloys and gray cast iron are rarely reported.

Increasing interface shear property plays a positive role in the application of Al/Fe bimetallic composites in automobiles. However, a limited number of literatures have an investigation on optimizing interfacial shear property of Al/Fe bimetallic composites, and the improved shear strength value is not very high. Jiang et al. [28] investigated the effects of surface pretreatments to steel on the shear property of Al/Fe (aluminum alloy/mild steel) bonding interface, and reported that the improved interfacial shear strength reached 10.4 MPa. Sun et al. [29] reported that the improved shear strength of Al/Fe (aluminum alloy/casting iron) bonding interface reached 19.53 MPa. Contrast to the already reported shear property of Al/Fe bimetallic composites in literatures [28–30], the shear property obtained by our technology is far more than that, as shown in Table 1.

In this work, a new composite casting technology is developed consisting of the surface pretreatment of cast irons, the hot-dipping in Zn–Bi (Zn–0.2 wt.% Bi) melt, the Al/Fe composite process to obtain an Al/Fe (Al–7Si alloy/casting iron) bimetallic composite with super-high shear strength. Relationships between the super-high shear strength and the interface microstructure were investigated with comparison to hot-dipping in Al–7.2 wt.% Si melts (from [24]), pure Zn melts, and Zn–2.2 wt.% Al melts (from [31]). The effect of interface morphology on the shear property of Al/Fe bimetallic composites was also investigated. Finally, the further analysis on the stress state of Al/Fe bonding interface was shown to account for the effect of interfacial morphology on interface shear property.

2. Materials and methods

2.1. Materials

The cast iron (Table 2) stripes of 4 mm × 9 mm × 75 mm were prepared by using wire cut equipment to cut engine block cylinders. The Al–7Si alloy (Table 2) placed in the crucible was melt by medium-frequency induction furnace, acting as the liquid matrix of liquid/solid composite system. The Zn–0.2 wt.% Bi alloy used as coating alloy was prepared by
adding bismuth (99.99 wt.%) into the pure zinc (99.95 wt.%) melt during the heating of medium-frequency induction furnace, and then was charged into the resistance furnace to keep the temperature at 753 ± 5 K for 15 min at least.

2.2. Methods

2.2.1. Hot-dipping and Al/Fe composite process

Prior to the Al/Fe composite process, the cast iron stripe as Fe matrix needs to be coated with Zn–Bi (Zn–0.2 wt.% Bi) alloy and then is connected with Al–7Si alloy. The major process is as follows: firstly, Zn–Bi melt in a crucible was enough stirred mechanically before immersing the Fe matrix into the hot-dipping melt at a bath temperature of 753 ± 5 K for 120 s (Table 3). Then, Fe matrix was extracted from the Zn–Bi melt at the speed of 1.5 m/min [32] and put into the mold at 453 ± 10 K. Finally, Al–7Si alloy melt (in Table 2) was poured immediately onto the Zn–Bi coating cladded Fe matrix in the mold at 453 ± 10 K. After the above steps, the Al/Fe bimetallic composites were then cooled to the ambient temperature in air. The hot-dipping processes were then repeated as the schedule in Table 3.

2.2.2. Characterizations of the mechanical properties and the microstructure of Al/Fe bimetallic composites

For the convenience of testing and detection, Al/Fe bimetallic composites were cut into specimens of 5 mm × 7 mm × 20 mm in the wire cut equipment. The shear strength of Al/Fe bimetallic composite from each group of parameters in Table 3 was the average value of shear strength from using five specimens. The width of Al/Fe reaction layer was measured by optical microscopy. The scanning electron microscope (SEM) with an energy dispersive spectrometer (EDS) was used to analyze the microstructure and the morphology of Al/Fe bonding layer. Al/Fe intermetallic phases in the bonding interface were detected by X-ray diffraction (XRD) analysis on the fracture surface of the Al/Fe composite specimens.

3. Results

3.1. Microstructure and shear strength of Al/Fe bimetallic composites produced by hot-dipping in Al–7.2 wt.% Si alloy melt, pure Zn melt, Zn–2.2 wt.% Al melt, Zn–0.2 wt.% Bi melt

We conducted the EDS analyses (Table 4) on the Al/Fe composite interface shown in Fig. 2(a)–(d). XRD analyses (Fig. 3) were also performed in order to further make certain the constitution of intermetallic phases in Al/Fe composite interface. Hot-dipping parameters and the detailed information about interface microstructure is exhibited in Table 5, Table 6, respectively.

Fig. 2(a) presents the thickest Al/Fe reaction layer with the dominant phase-the bigger, coarser polyhedral Al3Fe2Si (Table 6). It is well known that the thicker Al-rich phase layer readily leads to the fast fracture of Al/Fe bonding interface [13]. Therefore, the above features of interface microstructure should be responsible for the lowest shear strength of about 11MPa in Fig. 4. Fig. 2(b) describes the Al/Fe bonding interface with the same hot-dipping time and temperature as shown in Fig. 2(c). It can be seen that the width and the phase constitution of Al/Fe reaction layer in Fig. 2(b) are nearly identical to that in Fig. 2(c). However, Fig. 2(b) presents more brittle-hand needle-like phases in Al matrix around Al/Fe interface, which is the main factor rendering shear strength (approximating 18MPa) lower than 20.0MPa of Al/Fe bonding interface in Fig. 2(c).

| Table 2 - The composition of cast iron and Al–7 Si alloy (wt.%). |
|-----------------|-----|-----|-----|-----|-----|-----|-----|-----|
|                 | C   | Si  | Mn  | S   | P   | Mg  | Al  | Fe  |
| Cast iron       | 3.16–3.30 | 1.79–1.93 | 0.89–1.04 | 0.09–0.12 | 0.12–0.17 | –   | –   | Bal |
| Al–7Si alloy    | –   | 6.5–7.5 | –   | –   | –   | –   | 0.2–0.4 | Bal |

| Table 3 - Experiment parameters of hot-dipping Zn–Bi melt. |
|-----------------|-----------------|
| Hot-dipping times (s) | Hot-dipping temperature (K) |
| 120 ± 5          | 753 ± 10          |
| 180 ± 5          | 753 ± 10          |
| 240 ± 5          | 753 ± 10          |
| 480 ± 5          | 753 ± 10          |
| 600 ± 5          | 753 ± 10          |

| Table 4 - The compositions (at.%) detected by EDS at red-color 1–9 site in Fig. 2. |
|-----------------|-----|-----|-----|-----|-----|-----|-----|
|                 | Al  | Fe  | Si  | Mn  | site | Al  | Fe  | Si  | Mn  |
| site            |     |     |     |     |      |     |     |     |     |
| 1               | 69.51 | 28.31 | 1.41 | 0.77 | 6    | 65.7 | 24.25 | 9.33 | 0.72 |
| 2               | 70.13 | 23.54 | 6.20 | 0.13 | 7    | 70.73 | 13.38 | 14.43 | 1.01 |
| 3               | 74.12 | 18.24 | 7.9  | 0.15 | 8    | 65.97 | 25.13 | 8.28  | 0.62 |
| 4               | 68.7  | 24.68 | 6.5  | 0.12 | 9    | 73.73 | 10.23 | 16.01 | 0.03 |
| 5               | 71.73 | 11.81 | 16.43 | 0.03 |      |      |      |      |      |

| Table 5 - Hot-dipping parameters of the hot-dipping Zn–Bi melt and the control groups of another three hot-dipping melts. |
|-----------------|-----------------|-----------------|
| Hot-dipping melt | Hot-dipping temperature (K) | Hot-dipping time (s) |
| Zn–0.2 wt.% Bi melt | 873 ± 10         | 600 ± 5         |
| Al–7.2 wt.% Si melt | 953 ± 10         | 600 ± 5         |
| Pure zinc melt     | 873 ± 10         | 600 ± 5         |
| Zn–2.2 wt.% melt   | 873 ± 10         | 600 ± 5         |
Fig. 2 – Images (a), (b), (c) and (d) represent the morphology of Al/Fe bonding interface produced by hot-dipping Al–7.2 wt.% Si melt, pure Zn melt, Zn–2.2 wt.% Al melt and Zn–0.2 wt.% Bi melt, respectively.

Fig. 3 – XRD analysis on Al/Fe composite interface in Fig. 2(a)–(d).

| Table 6 – The detailed information on the microstructure of Al/Fe bonding interface in Fig. 2. |
|-----------------------------------------------|-----------------|-----------------|-----------------|-----------------|
| Image                                         | (a)             | (b)             | (c)             | (d)             |
| Hot-dipping melt                               |                 |                 |                 |                 |
| The phase constitution in the bonding interface| Al$_5$Fe$_2$, Al$_5$Fe, Al$_5$Fe$_2$Si | Al$_5$Fe$_2$, Al$_5$FeSi | Zn–2.2 wt.% Al melt | Zn–0.2 wt.% Bi melt |
| Width of intermetallic reaction layer          | 45–50 μm        | 15–17 μm        | 17–20 μm        | 9–14 μm         |


3.1. Effects of hot-dipping parameters in different melt on the interface microstructure of Al/Fe bimetallic composites

Compared to Fig. 2(c), Fig. 2(d) shows a major difference that refers to the peculiar serrated morphology of Fe matrix. The serrated morphology differs obviously from the relatively flat Fe matrix in Fig. 2(c). The brittle-hard $\text{Al}_5\text{FeSi}$ phase, acting as the exacerbation of the fracture behavior, almost does not prevent the highest shear strength being possessed by the Al/Fe bonding interface in Fig. 2(d). All of these phenomena indicate that the formation of the concave-convex interface (CCI) is beneficial to increasing the shear strength of Al/Fe bonding interface.

3.2. Effects of hot-dipping parameters in Zn–0.2 wt.% Bi melt on the interface microstructure of Al/Fe bimetallic composites

Fig. 5 shows the cross-section of Al/Fe bimetallic composites with the hot-dipping time 480s at 873 K. Region (A) and
(B) surrounded by yellow dotted line are detected as Zn-rich regions by EDS and EMPA. The EDS detection on sites marked by 1, 2, 3, 4 presents that Zn content firstly decreases and then increases, indicating the segregation of Zn element at the region (A). The red dotted line-surrounded region (C) at the graphite–ferrite interface is Al–Fe phases in Fig. 5(a). The black-color zone in the region (A) in Fig. 5(a) is amplified in Fig. 5(b). The black-color zone is the cataclastic zone of ferrite corroded by elemental zinc, rather than the graphite because its coarse, semi-circle ends are distinguished from the blade-like ends of the graphite. In Fig. 5(c), region (D), (E), (F) that are detected as Zn-rich regions by EDS demonstrates that Zn-rich regions cause a degradation to the ferrite in cast iron.

Considering distinctive materials and their corresponding manufacturing process, it is well-known that metallurgical and micromechanical aspect are controlled by the resulting microstructure, unsoundness, strength and ductility. Based on this fact, the microstructure parameters are of high order to determine the resulting properties of materials (e.g., mechanical and corrosion responses of a number of distinctive alloys and materials). Therefore, the microstructure array induced by hot-dipping parameters in present work is necessary to be exploited.

Fig. 6 exhibits six different interface morphologies from Al/Fe bimetallic composites with various shear strengths. The six interfacial morphologies display the different depth value of Al–Fe phases inserted in the graphite–ferrite interface of cast irons – 50 μm, 34 μm, 22 μm, 18 μm, 15 μm, and 12 μm. The shear strength from image (a)–(f) corresponds to 9 ± 2 MPa, 14 ± 3 MPa, 18 ± 2 MPa, 22 ± 3 MPa, 26 ± 2 MPa, 29 ± 3 MPa, respectively. Thus, the shear strength increases gradually with decreasing depth value of Al–Fe phases inserted in the graphite–ferrite interface. The width of Al/Fe reaction layer in image (a)–(f) almost stays within the range of 9–14 μm. Changing hot-dipping parameters does not generate an obvious effect on the width of Al/Fe reaction layer.
Image (a) illustrates the typical interface morphology with a low shear strength (8 MPa) – Zn-rich regions in the ferrite, the bare graphite in the Al matrix as well as the largest inserting depth of Al–Fe phases in the graphite–ferrite interface. The intermetallic phase in the Al/Fe reaction layer in image (a)–(d) consists of AlFeSi phase. Image (f) exhibits the typical interface morphology with a high shear strength (about 29 ± 3 MPa) – the smallest inserting depth, the serrated cast iron matrix with a relatively even Al/Fe reaction layer. From image (a)–(d), zinc content is found to appear in the Al–Fe phase inserted in the graphite–ferrite interface and decrease gradually along the Al–Fe phase toward the iron matrix. There may be a relationship between the Zn element and the formation of Al–Fe phases at the graphite–ferrite interface. The phenomenon that the increased inserting depth of Al–Fe phases in the graphite–ferrite interface can decrease the maximum shear stress necessary to damage Al/Fe bonding interface can be also understood by the fracture behavior of Al/Fe bonding interface.

From Fig. 7(b) and (c), it can be seen that cracks always occur at the position in which Al–Fe phases appear. Although cracks also occur at the Al/Fe interfacial reaction layer when Al–Fe phases form in the ferrite–graphite interface, the damage induced by shear stress is mainly concentrated in the graphite–ferrite interface – is to separate parts of ferrite from the cast iron (Fig. 7(b)). Thus, the formation of Al–Fe phases at the graphite–ferrite interface can weaken the bonding performance between the ferrite and the cast iron matrix. The greater inserting depth of Al–Fe phases in the graphite–ferrite interface can generate a stronger weakening effect on Al/Fe bonding performance, resulting in a decreased maximum shear stress necessary to damage the Al/Fe bonding interface.

We also exploited the percentage of the fiber-like graphite distribution in Fig. 6 by using the software ‘IMAGE J’. Fig. 8(a)–(f) presents the analysis images of the percent of fiber-like graphite and correspond successively to the Fe matrix shown in Fig. 6(a)–(f), respectively. The percent of fiber-like graphite from Fig. 8(a)–(f) is about 10.21%, 9.16%, 6.53%, 5.36%, 5.69%, and 5.5%. Although the increasing of shear property is seemingly accompanied with the decreasing of the percent of fiber-like graphite in Fe matrix around the Al/Fe interface, there is actually not the relation between the percent of graphite in Fe matrix and the shear property because the fracture exists only in a very narrow area with the center of Al/Fe interface.

4. Discussion

4.1. Effects of Bi element on the interface morphology of Al/Fe bimetallic composites

From Fig. 9(a) and (b), we can find that no Al–Fe phases appear in the graphite–ferrite interface under the condition of hot-dipping in pure Zn melt. In Fig. 9(c) and (d), there are Al–Fe phases found to form in the graphite–ferrite interface around the Al/Fe bonding interface induced by hot-dipping in Zn–Bi melt. Several white-color stripes marked by red-color arrows in Fig. 9(d) are detected by EMPA as Zn-rich regions which appear at the internal of Al–Fe phases. From the relative positions of both them, it can be seen that the emergence of Zn-rich regions in the cast iron matrix is earlier than Al–Fe phases. In particular, Al–Fe phases at the graphite–ferrite interface is always accompanied with zinc element (Fig. 6), suggesting that Al–Fe phases form at the graphite–ferrite interface with a premise of the presence of Zn element. The guess may be understood by the following process. Since Zn-rich regions have a dilatation coefficient differing from cast iron matrix, spatial sparseness is created due to the difference in the thermal strain between Zn-rich regions and cast iron matrix under the high temperature, and then the Al element diffuses rapidly into the vacant sparser regions toward the cast iron matrix by creating the resultant ternary phases – Al–Fe phases with a small amount of Zn element.

Only under the condition of hot-dipping in Zn–Bi melt do Zn-rich regions appear at the surface layer of cast iron. The
addition of Bi element into Zn melt plays a positive role in the formation of Zn-rich regions at the surface layer of cast iron, because adding a trace of Bi element into zinc melt enhances the liquidity of zinc melt [37], and thus enhances the Zn melt’ erosion-corrosion effect on cast iron. The enhanced penetration of zinc element toward the cast iron matrix causes the zinc accumulation at the surface layer of cast iron.

4.2. **Formation process of concave-convex interface caused by the serrated cast iron matrix during Al/Fe composite process**

The formation of CCI is closely related to the formation of Al-Fe phases at the graphite-ferrite interface. Firstly, Zn-Bi coatings fuse into the hyperthermia aluminum alloy melt in Fig. 10(a). A thin Al-Fe phases layer form primarily on the
cast iron with an Al/Fe metallurgical reaction in Fig. 10(b). Gradually, Al–Fe phases grow along the graphite–ferrite interface corroded by Zn-rich regions toward the cast iron matrix in Fig. 10(c). At this time, two types of graphite morphology avail to form the CCI, which are the I graphite morphology called by us that has both ends connected to Al/Fe interface reaction layer in Fig. 10(g) and the II graphite morphology that is a graphite group having two graphite intersected with each other in Fig. 10(h). With Al–Fe phases going gradually deep into the graphite–ferrite interface, the bonding interface of graphite (I and II graphite)/ferrite is substituted with a new bonding interface between Al–Fe phases and graphite in Fig. 10(d). Affected by a temperature fluctuation in the high temperature aluminum alloy melt, the new bonding interface is readily destroyed owing to Al–Fe phases re-melts, and parts of ferrite surrounded already by Al–Fe phases is forced to migrate and separate gradually from cast iron matrix (Fig. 10(e) and (f)). Fig. 10(g) and (h) displays the actual processes that the ferrite surrounded already by Al–Fe phases fails to be separated completely from cast iron matrix owing to cooling Al/Fe composite system too fast. After the ferrite is separated completely from the cast iron matrix, aluminum alloy melt flows into those positions lacking of ferrite, consequently resulting in a specular structure of the serrated cast iron attached with a relative even Al–Fe phase layer, called the concave–convex interface (CCI).

### 4.3 Analysis of stress state in concave–convex interface region to enhance the shear strength of Al/Fe bimetallic composites

Al/Fe composite specimens prepared by dipping Zn–0.2 wt.% Bi melt is subjected to a pair of shear forces near the interface in the experiment. The fracture surface of the specimens is nearly a plane parallel to the direction of the shear force. Thus, the state of stress on the interface of the specimen under the action of shear forces is nearly in pure state of shear and the state of plane stress. The state of stress acting on the small element of the interface is shown in Fig. 11(a). Only the shear stresses exist on faces of the small element, which are parallel and perpendicular to the x-axis, respectively (Fig. 11(a)). Based on the analysis of stress state, the stress acting on the element oriented at an angle $\alpha$ from the x-axis can be determined by the following equation [38].

$$\sigma_x = -r \sin 2\alpha$$

$$T_x = T \cos 2\alpha$$
5. Conclusions

In present work, a new composite technology consisting of the surface pretreatment on cast iron matrix, the hot-dipping in Zn–Bi (Zn–0.2 wt.% Bi) melt and the Al/Fe composite process, is developed to obtain an Al/Fe (aluminum alloy/casting iron) bimetallic composite with a super-high shear strength of 32 MPa. The shear strength of Al/Fe bimetallic composites induced by hot-dipping in Al–7.2 wt.% Si melt, pure Zn, Zn–2.2 wt.% Al melt, can be approximately up to 11 MPa, 19 MPa, 22 MPa, respectively. The increase of shear strength is mainly attributed to the formation of concave–convex interface (CCI) structures caused by the serrated cast iron matrix. This kind of CCI differs from the irregular Al reaction layer with dominant phases – big, blocky Al₃Fe₂Si induced by hot-dipping in Al-Si (Al–7.2 wt.% Si) melt. The addition of Bi element into the zinc melt promotes the formation of Zn-rich regions in the graphite–ferrite interface and surface layer of parts of ferrite, consequently leading to the formation of Al–Fe phases at the graphite–ferrite interface. With Al–Fe phases at the ferrite–graphite interface propagating toward the cast iron matrix, a new bonding interface between graphite and Al–Fe phases is established, weakening the bonding performance between ferrite and the cast iron matrix.

Conflicts of interest

The authors declare no conflicts of interest.

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