Diffusion bonding of Ti-15 mol% Sn alloy to various iron materials was carried out in the temperature range of 1 073–1 273 K for 0.9–14.4 ks in a vacuum to verify interface separation, a phenomenon that has been observed between Ti-20 mol% Al alloy and high-carbon steel after bonding treatment at 1 273 K for 3.6 ks. Four types of carbon steel and one type of cast iron were used as an opposite material for the Ti-15 mol% Sn alloy. In the case of steel having a relatively low carbon content, a sound joint without defects like a gap at the interface was obtained through bonding treatment at 1 273 K for 3.6 ks. However, the joints with high-carbon steel and cast iron, which were fabricated at 1 273 K for 3.6 ks, had gaps at the interfaces, and several specimens separated near the interface promptly after bonding treatment. The separated surfaces of the high-carbon steel and cast iron were relatively smooth. A microstructure corresponding to the grain boundary and pearlite was observed in the surfaces. It was found that this phenomenon depended on the heating temperature and the holding time. These features were consistent with those of interface separation previously reported in the case of Ti-20 mol% Al alloy. Therefore, it is concluded that the separation phenomenon was caused by interdiffusion across the interface between the titanium alloy and the iron material.

KEY WORDS: Ti-15 mol% Sn alloy; carbon steel; cast iron; diffusion bonding; interface separation.

1. Introduction

Titanium aluminides, typified by Ti3Al and TiAl, can be used as high-temperature structural materials in the aerospace and automobile industries, because they have low densities and high strengths at elevated temperatures. To encourage the effective use of these materials, they have been joined to themselves and other materials by various joining methods, such as diffusion bonding,1,2) brazing,3) friction welding,4) and electron beam welding.5) The authors have previously investigated the interfacial microstructures and the bonding strengths of Ti–Al alloy/iron material joints produced by diffusion bonding,6–9) because steel is a dominant structural material in industrial products. It has been reported that, when Ti-20 mol% Al (Ti-20Al, i.e. Ti-12.3 mass% Al) alloy is bonded to carbon steel containing 0.82 mass% C at 1 273 K for 3.6 ks in a vacuum, a gap with a thickness of a few micrometers is observed at the interface.7) Several specimens had already separated near the interface at the time of removing them from an electric furnace. Interestingly, the joint bonded at 1 073 K for 3.6 ks had a sound interface, and showed a bonding strength of 166 MPa.7) We refer to the phenomenon occurring at 1 273 K as “interface separation”. This phenomenon would be of use in recyclable composite materials with a reversible bonding/separating ability. In addition, the surface of the Ti-20Al alloy undergoing the separation was covered with titanium carbide (TiC), which was formed by reactions with the steel. Therefore, this phenomenon also shows promise as the basis of a new surface modification technique to overcome the poor wear resistance of titanium materials.

It is thought that the interface separation is attributed to the preferential diffusion of iron into the Ti-20Al alloy, which transforms from an α-titanium + Ti3Al duplex structure to an α-titanium single-phase structure in the vicinity of 1 273 K.7–9) If this hypothesis is correct, the interface between titanium alloy, which shows an increase in the ratio of the α-titanium phase with increasing heating temperature, and carbon steel containing 0.82 mass% C has the potential to cause the separation phenomenon. To verify this, Ti–Sn alloy was selected as a binary titanium alloy. Tin is an α-stabilizer for titanium, as well as aluminum. According to the Ti–Sn binary phase diagram,10) Ti-10–20 mol% Sn alloys have an α-titanium + Ti3Sn duplex structure at room temperature, and the ratio of the α-titanium phase in the duplex structure increases with temperature. At 1 273 K, these alloys become a β-titanium + Ti3Sn duplex structure. We previously attempted to join several Ti–Sn alloys to carbon steel containing 0.82 mass% C.11) In Ti-15 mol% Sn (Ti-15Sn, i.e. Ti-30.4 mass% Sn) and Ti-20 mol% Sn (Ti-38.3 mass% Sn) alloys, a phenomenon similar to that in the case of the
Ti-20Al alloy was observed at heating temperatures of 1173 K and 1273 K.

In the present study, diffusion bonding of Ti-15Sn alloy to various iron materials was carried out, and the influences of the carbon content in the iron material, the heating temperature, and the holding time on the separation behavior at the interface were investigated. The origin of the separation phenomenon is discussed on the basis of a comparison with the case of the Ti-20Al alloy.

2. Experimental Procedures

Ti-15Sn alloy was produced by using an arc melting process. The obtained ingot was homogenized at 1273 K for 86.4 ks in a vacuum of less than 3 mPa and then cut into square plates with dimensions of 5 mm × 5 mm × 1 mm. Four types of carbon steel, which were designated as SS400, S45C, SK5, and SK3 according to the Japanese Industrial Standards, and one type of cast iron were used as an opposite material for the Ti-15Sn alloy. The chemical compositions of these iron materials are shown in Table 1. The materials are hereafter referred to by their carbon content, e.g., Fe-0.09C means steel with 0.09 mass% C (SS400). The iron materials were machined into square blocks with dimensions of 10 mm × 10 mm × 5 mm. The bonding surfaces of all materials were finished with #1200 emery paper. Before bonding treatment, they were degreased in acetone using an ultrasonic cleaner and dried with hot air.

The Ti-15Sn alloy was placed on top of each iron material. The couples were fixed in a jig consisting of two molybdenum rods and two austenitic stainless steel blocks. The assemblies were held at temperatures in the range from 1073 to 1273 K for 0.9 to 14.4 ks in a vacuum of less than 3 mPa and then cut into square plates with dimensions of 1 mm × 5 mm × 5 mm. The bonding surfaces of all materials were finished with #1200 emery paper. The obtained ingot was homogenized at 1273 K for 86.6 ks in a vacuum of less than 3 mPa and then cut into square plates with dimensions of 5 mm × 5 mm × 1 mm.

The specimens were mounted in polyester resin and cut in half to reveal the microstructures around the interfaces. When the Ti-15Sn alloy had already separated from the iron material at the time of removing the specimen from the furnace, both materials were recombined into the shape of the material at the time of removing the specimen from the furnace. The origin of the separation phenomenon is discussed on the basis of a comparison with the case of the Ti-20Al alloy.

The Ti-15Sn alloy adhered firmly to the Fe-0.47C, and a reaction layer was observed between these materials. The Ti-15Sn alloy/Fe-0.96C joint also had a reaction layer at the interface. However, a gap indicated by white arrows existed along the interface. Figure 2 shows SEM micrographs of the interfaces in various Ti-15Sn alloy/iron material joints bonded at 1273 K for 3.6 ks. Two reaction regions, indicated as I and II, were observed around the interfaces in all cases. In addition, the formation of a gap at the interface, surrounded by two white arrows, seems to be related to the carbon content in the iron material.

The results of elemental mapping for the Ti-15Sn alloy/Fe-0.09C joint are shown in Figs. 3(a) to 3(e). The Ti-15Sn alloy consisted of gray and relatively white regions. These were distinguished by the concentration of titanium and tin. According to the Ti–Sn binary phase diagram, it is thought that the gray and relatively white regions correspond to α-titanium and TiSn, respectively. On the other hand, titanium and carbon were detected in region I in Fig. 2(a). Since it was difficult to accurately determine the carbon content, the compositional ratio of titanium, tin, and iron was examined in this region and the following values were obtained: 86.6 mol% Ti, 0.3 mol% Sn, and 13.1 mol% Fe. Considering these results, the reaction layer should be composed mainly of TiC, and may include a small amount of Fe–Ti intermetallic compounds. In addition, the formation of a TiSn region, which is indicated as II in Fig. 2(a), is probably due to the elimination of tin from region I. At

<table>
<thead>
<tr>
<th>Material</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Cu</th>
<th>Cr</th>
<th>Ni</th>
<th>Mg</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-0.09C (SS400)</td>
<td>0.09</td>
<td>0.04</td>
<td>0.68</td>
<td>0.017</td>
<td>0.017</td>
<td>0.02</td>
<td>0.03</td>
<td>–</td>
<td>–</td>
<td>Bal.</td>
</tr>
<tr>
<td>Fe-0.47C (S45C)</td>
<td>0.47</td>
<td>0.21</td>
<td>0.74</td>
<td>0.025</td>
<td>0.027</td>
<td>0.02</td>
<td>0.10</td>
<td>0.01</td>
<td>–</td>
<td>Bal.</td>
</tr>
<tr>
<td>Fe-0.82C (SK5)</td>
<td>0.82</td>
<td>0.18</td>
<td>0.40</td>
<td>0.013</td>
<td>0.021</td>
<td>0.08</td>
<td>0.10</td>
<td>–</td>
<td>–</td>
<td>Bal.</td>
</tr>
<tr>
<td>Fe-0.96C (SK3)</td>
<td>0.96</td>
<td>0.20</td>
<td>0.64</td>
<td>0.015</td>
<td>0.053</td>
<td>0.14</td>
<td>0.16</td>
<td>0.07</td>
<td>–</td>
<td>Bal.</td>
</tr>
<tr>
<td>Cast iron, Fe-3.71C</td>
<td>3.71</td>
<td>2.70</td>
<td>0.49</td>
<td>0.012</td>
<td>0.46</td>
<td>0.026</td>
<td>–</td>
<td>0.037</td>
<td>Bal.</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 1. Optical micrographs of the interfaces in (a) Ti-15Sn alloy/Fe-0.47C and (b) Ti-15Sn alloy/Fe-0.96C joints bonded at 1273 K for 3.6 ks. Two white arrows in (b) show a gap formed at the interface.
the Fe-0.09C side, there was no significant change of the microstructure, whereas small amounts of titanium and tin were detected. The Ti-15Sn alloy/Fe-0.47C joint should also show an elemental distribution similar to that of the Ti-15Sn alloy/Fe-0.09C joint, although voids were observed along the interface, as shown in Fig. 2(b).

Figures 2(c), 2(d), and 2(e) show the interfacial microstructures of the joints with high-carbon steel and cast iron. A gap located between the two white arrows was observed in each case. This indicates the occurrence of interface separation. In some cases, the Ti-15Sn alloy had already separated from the iron material at the time of removing the specimen from the electric furnace. Therefore, both materials were recombined into the shape of the joint and fixed in the resin to reveal the microstructure. For this reason, the thickness of the gap differed from specimen to specimen, and resin and grinding swarf remained in this position. Since these joints had the reaction layer along the interface, as well as region 1 in Fig. 2(a), the separation could have been caused in the holding or cooling steps in the bonding process.

As a typical result of compositional analysis, the results of elemental mapping for the Ti-15Sn alloy/Fe-0.09C joint are shown in Figs. 3(f) to 3(j). A high-carbon region in the Fe-3.71C indicated graphite, whereas the distribution of carbon in the gap along the interface reflected resin and grinding swirl. The reaction layer was observed in most of the Ti-15Sn alloy close to the gap, although it did not form on the opposite side from the graphite in the Fe-3.71C. As shown in Figs. 3(g) and 3(j), titanium and carbon were mainly detected in the reaction layer. The compositional ratio in this layer, excluding carbon, was 96.8 mol% Ti, 0.6 mol% Sn, and 2.6 mol% Fe. Therefore, the reaction layer was identified as TiC. In fact, when XRD measurement was carried out on the separated surface at the Ti-15Sn alloy side, the main diffraction peaks corresponded to TiC. Since tin and iron were almost eliminated from the TiC layer, the concentration of these elements increased in regions close to this layer.

It is noteworthy that the distribution of iron in the Ti-15Sn alloy, which is known to be a β-stabilizer for titanium, is more noticeable in Fig. 3(i) than in Fig. 3(d). This was also confirmed by quantitative analysis. Since the remarkable diffusion of iron into the Ti-15Sn alloy was recognized in the joint with Fe-0.82C,11) such a tendency is considered to be a common feature in joints showing interface separation. On the other hand, there was no microstructural change in the Fe-3.71C near the interface where small amounts of tita-
nium and tin were detected.

### 3.2. Evaluation of Separated Surfaces

The separated surfaces in the Ti-15Sn alloy/Fe-0.96C joint after bonding treatment at 1273 K for 3.6 ks were examined by SEM observation and XRD measurement. Figure 4(a) shows an SEM micrograph of the separated surface at the Ti-15Sn alloy side. A straight line-like pattern on the surface is related to a trace of the grinding process performed before the bonding treatment. An XRD pattern of this surface is presented in Fig. 5(a). As expected from the separation position in Fig. 2(d), diffraction peaks of TiC and Ti3Sn were observed. In addition, peaks corresponding to Ti5Sn3 and Fe3Sn were detected, although these materials were not recognized through cross-sectional observation. Since tin was hardly contained in TiC, as shown in Figs. 3(f)–3(j), it is thought that the elimination of tin from that region led to the formation of Ti5Sn3 and Fe3Sn. These results were also confirmed in the case of the joints with Fe-0.82C and Fe-3.71C.

The separated surface of the Ti-15Sn alloy was hardened because it was covered with TiC. Its Vickers hardness was HV = 800 or more, much higher than that of the bare Ti-15Sn alloy, which had an average hardness of HV = 337.

On the other hand, the separated surface at the iron material side in the Ti-15Sn alloy/Fe-0.96C joint is shown in Fig. 4(b). The surface was relatively smooth, and a microstructure corresponding to the grain boundary and pearlite was observed. As shown in Fig. 5(b), almost all diffraction peaks in the XRD pattern of this surface were identified as α-iron.

Figures 6(a) and 6(b) show SEM micrographs of the separated Fe-0.82C and Fe-3.71C surfaces after bonding treatment at 1273 K for 3.6 ks, respectively. These surfaces were also relatively smooth, and the XRD results were almost identical to those in Fig. 5(b).

### 3.3. Effects of Heating Temperature and Holding Time

Figure 7 shows an SEM micrograph of the interface in the Ti-15Sn alloy/Fe-3.71C joint bonded at 1073 K for 14.4 ks. The Ti-15Sn alloy adhered firmly to the Fe-3.71C, and the reaction layer, which is thought to be TiC, was observed at the interface, except for the graphite region in the Fe-3.71C. This indicates that separation like Fig. 2(e) did not occur after bonding treatment at 1073 K. In addition, the interfacial microstructures in the Ti-15Sn alloy/Fe-3.71C joints bonded at 1173 K for 0.9 and 3.6 ks are shown in Fig. 8. In both cases, sound joints were obtained, and the reaction layer formed at the interface. It should be noted that
4. Discussion

Despite being subjected to bonding treatment, the Ti-15Sn alloy/iron material joint can break near the interface. This phenomenon depended on the carbon content in the iron material, the heating temperature, and the holding time. Furthermore, we have previously reported on the dependency of the chemical composition in Ti–Sn alloys.11) These features were consistent with those of interface separation previously observed in Ti-20Al alloy/iron material joints. In the joints with the Ti-20Al alloy, it is thought that the occurrence of interface separation is associated with interdiffusion across the interface. Thus, we tried to explain the reason why such a phenomenon occurred in the Ti-15Sn alloy/iron material joints. Thermal stress, brittle-compound formation, and diffusion are considered as factors influencing the interface separation.

First, the influence of thermal stress occurring in the bonding process is discussed. The bonding treatments were conducted with the same heating and cooling rates. In addition, separation did not occur with a short holding time, when the Ti-15Sn alloy was bonded to Fe-3.71C at 1 173 K. The thermal expansion coefficients of the four types of carbon steel used in the present study are estimated to be $14.7 \times 10^{-6} \, /K$ to $15.0 \times 10^{-6} \, /K$ (at 273–973 K). At a bonding temperature of 1 273 K, these carbon steels become austenitic, and their thermal expansion coefficients are unlikely to make much difference. Therefore, the differences in the coefficients of thermal expansion between Ti-15Sn alloy and carbon steel should be approximately equal regardless of the carbon-steel type. These facts indicate that thermal stress has little influence on the interface separation.

Second, it is assumed that the formation of a brittle reaction phase, such as one involving Fe–Ti compounds, leads to interface separation. However, as shown in Figs. 4(b) and 6, the separated surfaces at the iron material side were relatively smooth, and a microstructure corresponding to the grain boundary and pearlite was observed. Also, almost all diffraction peaks in the XRD patterns for these surfaces corresponded to $\alpha$-iron. Furthermore, since the kinds of reaction products between Ti-15Sn alloy and carbon steel should be basically identical regardless of the carbon-steel type, we cannot explain the dependency on the carbon content in iron materials well. Therefore, it is extremely difficult to conclude that the brittle compound formed by interfacial reactions directly induced the interface separation.

Finally, we note the importance of the diffusion of iron into the Ti-15Sn alloy, as expected from Fig. 3. Considering this factor, we can explain not only the separated surface of the iron material, which is shown in Figs. 4(b) and 6, but also the void formation at the interface, which is shown in Fig. 8.

According to the Ti–Sn binary phase diagram,10) the Ti-15Sn alloy is composed of $\alpha$-titanium and Ti$_3$Sn at room temperature, and the ratio of $\alpha$-titanium in the duplex microstructure increases with increasing temperature. At 1 273 K, this alloy becomes a $\beta$-titanium + Ti$_3$Sn duplex structure. It is well-known that iron diffuses rapidly into $\alpha$- and $\beta$-titanium.13,14) At the same temperature, the diffusion coefficient of iron into $\beta$-titanium is larger than that into $\alpha$-titanium.15) In addition, judging from Figs. 3(f)–3(j), the diffusion coefficient of iron into $\beta$-titanium seems to be larger than that into Ti$_3$Sn at a heating temperature of 1 273 K. Therefore, the diffusion flux of iron into the Ti-15Sn alloy may further increase with increasing temperature by an increase in $\alpha$-titanium and subsequent phase transformation from $\alpha$-titanium to $\beta$-titanium. On the other hand, titanium and tin atoms, which are known to be ferrite formers for iron, diffuse into the iron material. Since titanium reacts with carbon to form the TiC layer, tin can diffuse mainly through it.
into the iron material. However, the titanium and tin contents were very small, even in the iron material close to the interface. Consequently, it is thought that the diffusion of iron into the Ti-15Sn alloy occurs preferentially, and the formation and accumulation of voids results from such a unidirectional diffusion.

A TiC layer formed at the titanium/steel interface is known to act as a barrier for interdiffusion across the interface.\(^{(16,17)}\) However, the TiC layer, which was observed in the present study, did not hinder the diffusion of iron into the Ti-15Sn alloy. Like the Ti-20Al alloy/Fe-0.82C joint,\(^{(7)}\) the reason for this may be that the TiC layer was composed of fine grains, which had a great number of grain boundaries acting as a diffusion path. On the other hand, the Ti-15Sn alloy was bonded to Fe-0.09 and Fe-0.47C, as shown in Figs. 2(a) and 2(b). In these cases, the reaction layer consisting mainly of TiC formed at the interface. Because a relatively high iron concentration was detected in the reaction layer, the formation of Fe-Ti compounds was also suggested. Although the difference in constituent phase and grain size of TiC in the reaction layer is thought to be one of the reasons why the remarkable diffusion of iron into the Ti-15Sn alloy was not observed, the details are still under investigation.

Considering the experimental results for the Ti-15Sn alloy/iron material and Ti-20Al alloy/iron material joints,\(^{(7–9)}\) it is concluded that the interface separation is attributed to the preferential diffusion of iron into the titanium alloy.

5. Conclusions
Diffusion bonding of Ti-15Sn alloy to various iron materials was carried out in the temperature range of 1 073–1 273 K for 0.9–14.4 ks in a vacuum to verify “interface separation”. The main results were as follows.

(1) The bonding of Ti-15Sn alloy to relatively low-carbon steel was achieved through bonding treatment at 1 273 K for 3.6 ks. However, the separation phenomenon was observed in the Ti-15Sn alloy/high-carbon steel and Ti-15Sn alloy/cast iron joints fabricated under the same conditions. In these cases, the separated surfaces at the iron material side were relatively smooth, and a microstructure corresponding to the grain boundary and pearlite was observed in these surfaces.

(2) In the Ti-15Sn alloy/cast iron joint, a sound joint without a gap at the interface was obtained at a bonding temperature of 1 073 K. At 1 173 K, small voids were formed at the interface adjacent to the cast iron with a short holding time, and their numbers and/or sizes increased with increasing holding time. Finally, the joint bonded at 1 173 K for 8.1 ks showed the separation phenomenon in the vicinity of the interface.

(3) The features of the interface separation in the Ti-15Sn alloy/iron material joints were consistent with those previously reported in Ti-20Al alloy/iron material joints. Therefore, it is concluded that this phenomenon is caused by interdiffusion across the interface between the titanium alloy and the iron material.

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