

Effect of Microstructure of Surface Layer in Steel Vessel Used for Sponge Titanium Manufacturing on Fe Elution

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Abstract

To make clear factors affecting Fe elution into molten Mg during sponge titanium production process and reasons why Fe elution from the steel vessel in the first use is high while it considerably reduces in the second use in the actual mill, immersion experiments into molten Mg at 950°C were conducted using specially designed specimens simulating the first and the second uses of the vessel, and microstructure change of the steel during the use was investigated in detail. TiFe, TiFe₂ and Ti-diffused steel layers formed on the surface of the steel specimen after the treatment similar to the first use of the vessel. The outermost portion of Ti-diffused steel contained 3mass% Ti, which should have transferred to the α phase at this temperature. Fe elution from TiFe and TiFe₂ was almost zero, while Fe elution from Fe-3mass%Ti was 1/4 of that from the unused steel. By taking the information on the phases appeared on the surface of the actual vessel into account, Fe elution from the vessel at the second use was estimated as 1/16 of that at the first use, which is well consistent with the value in the actual production mill.

1. Introduction

Fe, one of the impurities contained in titanium, strongly influences mechanical properties as well as corrosion resistance, and it is quite important to properly control Fe content. Fe contamination in titanium is mainly caused by Fe elution from a steel vessel into molten Mg in reduction process [1-3], in which TiCl₄ reacts with Mg and forms sponge titanium. According to the phase diagram of Mg-Fe system shown in Fig.1[4], solubility of Fe in molten Mg strongly depends on temperature, and it is higher at higher temperature. For example, solubility of Fe at 700, 800 and 900°C is 0.03, 0.08% and 0.17%, respectively.

In the reduction process in an actual production mill, Fe content in sponge titanium, which is transmitted from a steel vessel through molten Mg, is high when the vessel is used for the first time. However, there is a tendency that Fe content decreases to 1/10 - 1/20 at an opportunity of the repeated use twice or more times. It suggests that the nature of the inner surface of the steel vessel varies by contacting with newly precipitated sponge titanium and it may contribute to reduce Fe elution into molten Mg.

In this study, to clarify the details of this phenomenon, specially designed experiments were conducted, in which the circumstances where the inner surface of the vessel is actually exposed were reproduced in the laboratory cells, and microstructures of the surface layers of the steel specimens exposed to the simulated circumstances were closely analyzed. After that, an effect of microstructure changes of the steel on Fe elution into Mg was discussed based on the obtained experimental results and the information on the actual mill.

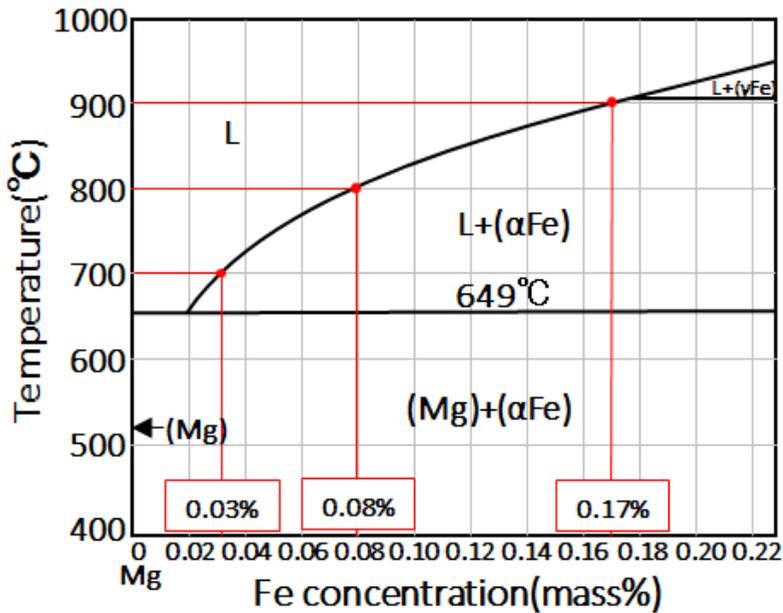


Fig.1 Fe solubility in molten Mg depicted on the binary phase diagram of Mg-Fe system [4]

2. Experimental Procedures

2.1 Materials Used

A plain steel (JIS SS400) plate was used in this study, which is the same material as that used for the vessels in actual sponge titanium manufacturing process. The plate was subdivided into 20x20mm cut pieces, and the following treatments were employed to simulate the first and the second uses of the vessel.

- Specimen A : To simulate the first use of the vessel, the cut pieces were used without employing any additional treatment.
- Specimen B : To simulate the second use of the vessel, specimens having the same nature as the inner surface of the vessel after the first use (before the second use) were prepared. At first, Ti powders of 10 to 45 μm in size were placed on Specimen A and heat treated in vacuum at 1000°C for 10h, which is similar to the heat pattern in the actual vacuum separation process in which residual MgCl_2 is separated from sponge titanium. An appearance of Specimen B is shown in Fig.2. Microstructures of Specimen B were closely investigated with SEM and EPMA.
- TiFe, TiFe_2 , Fe-3mass%Ti : As explained later in the “Results”, TiFe, TiFe_2 and Ti-diffused steel layers were recognized on the surface of Specimen B. Maximum Ti concentration in the Ti-diffused layer was 3 mass%. To examine effects of each substance on Fe elution into molten Mg, TiFe, TiFe_2 and Fe containing 3 mass%Ti (Fe-3mass%Ti) were prepared by arc melting. Brittle TiFe and TiFe_2 were easily crushed with a hammer and blocks of around 10mm in size were obtained. From the ingot of Fe-3mass%Ti, 20x20mm cut pieces were taken.

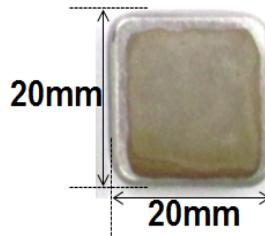


Fig.2 Appearance of Specimen B, which was prepared by coating Ti powders on plain steel specimen (Specimen A) and heat treated at 1000°C for 10h.

2.2 Immersion experiment into molten Mg

To grasp Fe elution into molten Mg, specimens described in 2.1 were immersed into molten Mg and eluted Fe content was measured. It is noted that Ti powders as well as some brittle intermetallics formed on the steel surface of Specimen B was removed before the immersion by a scraper to correctly simulate the second use of the steel vessel, which is termed as Specimen B'.

Before the immersion, ceramic coating was conducted on the surfaces except 10x10mm area for Specimen A, Specimen B' and Fe-3%Ti, which were 20x20mm in size. As the ceramic is quite stable in molten Mg and acts as a barrier of Fe elution, Fe elution from 10x10mm area of each specimen was correctly evaluated. An appearance of ceramic coated Specimen A is shown in Fig.3. The blocks of TiFe and TiFe₂ were directly immersed into molten Mg.

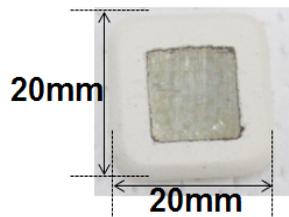


Fig.3 Appearance of ceramic coated specimen (Specimen A) used for immersion experiment into molten Mg. Ceramic coating was employed for all surfaces of the specimen except 10x10mm area on one surface.

The apparatus used for the immersion experiments is schematically shown in Fig.4. Several crucibles made of magnesia were placed in the furnace and one specimen was put in one crucible. 200g of Mg was inserted on the specimen in each crucible and heated in Ar to 800°C. Once temperature reached 800°C, molten Mg was stirred and then temperature was raised to 950°C. A crucible was taken out one by one after prescribed time elapsed, and cooled down to room temperature. Fe content in 200g Mg was measured by ICP atomic emission spectrophotometry, which was used as an index of Fe elution.

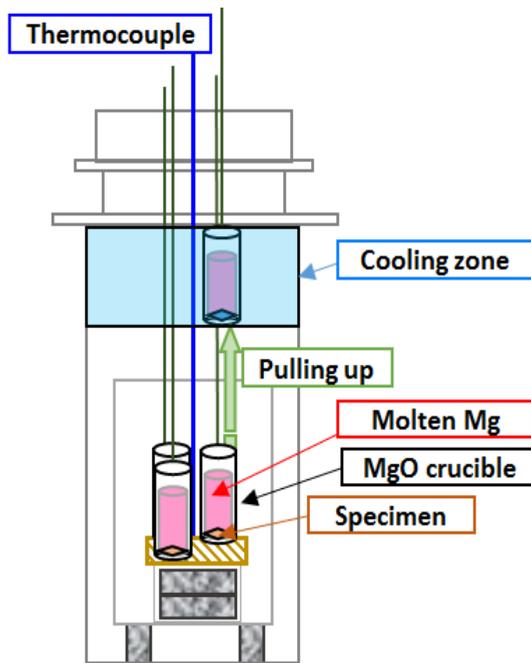


Fig.4 Schematic representation of apparatus used for immersion experiments into molten Mg.

3. Results

3.1 Microstructure after reaction with Ti (Specimen B)

Fig.5 is a backscattered electron image of the cross section of Specimen B. In the steel, three layers having different contrast can be seen, which are designated as “a”, “b” and “steel”. In Ti powders coated on the steel, two phases having different contrast can be seen. They are considered as the α phase and the Fe concentrated β phase. Fig.6 shows Ti (a) and Fe (b) distributions detected by EPMA near the steel/Ti powder interface. In Fig.6(a), it is clearly shown that Ti diffused into the steel for more than 200 μm , and Fe concentration was discontinuously distributed near the steel/Ti powder interface. It is considered that the layer “a” is TiFe and “b” is “TiFe₂”.

Fig.7 is closer look of Ti distribution near the steel/Ti powder interface. Line analysis of Ti indicates that Ti diffused around 200 μm into the steel and the most outer surface of the steel, which is just beneath the TiFe₂ layer shown in Figs. 5 and 6 as “b”, was 3mass% Ti.

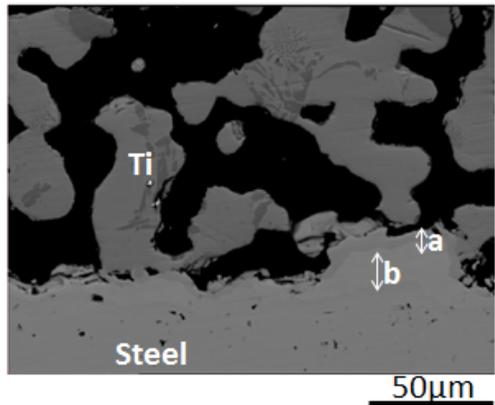


Fig.5 Backscattered electron image for cross section of Specimen B, simulating the steel vessel after the first use for sponge titanium production (Ti powders were coated and heat treated at 1000°C for 10h).

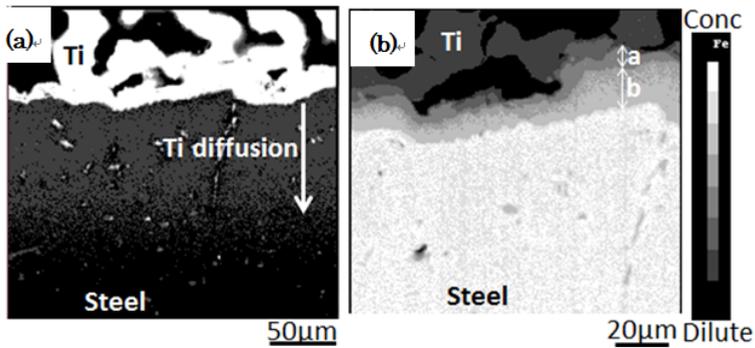


Fig.6 Distributions of (a) Ti and (b) Fe detected by EPMA for the area shown in Fig.5.

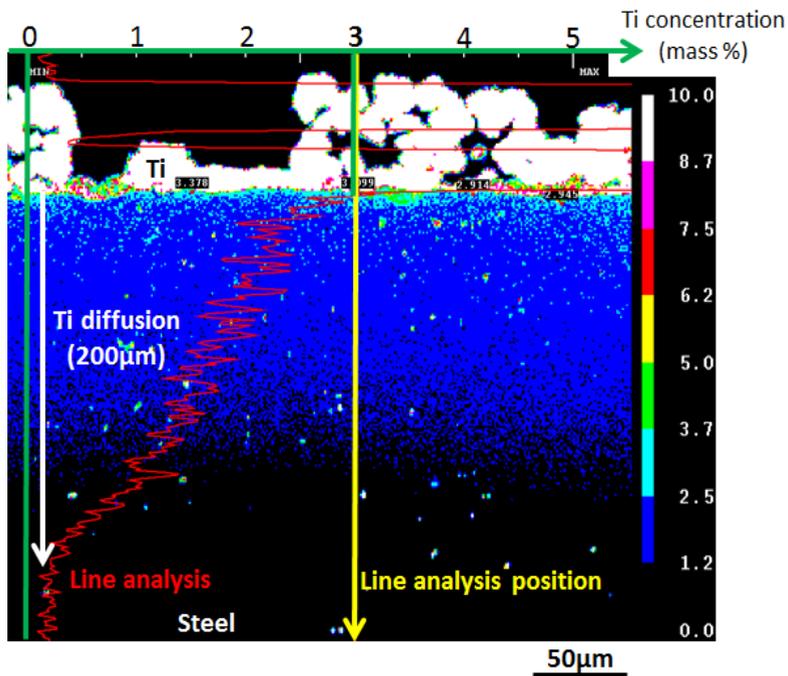


Fig.7 EPMA quantitative analysis of Ti distribution for the area near the steel/Ti powder interface in Specimen B.

3.2. Immersion experiment into molten Mg

Fig.8 (a) shows Fe elution of Specimen A and Specimen B', and Fig.8 (b) shows that of the other substances formed on the steel after the treatment similar to the first use (TiFe, TiFe₂ and Fe-3%Ti).

As shown in Fig.8 (a), Fe elution from Specimen B', which simulates the second use of the steel vessel, is drastically reduced compared to Specimen A, which simulates the first use. This is consistent with the actual situation.

Although the surface was cleaned in Specimen B' before the immersion, the surface should be covered with remnant of TiFe and/or TiFe₂ and the newly emerged steel surface on which 3%Ti is contained as shown in Fig.7. It is clearly shown that those substances had high resistance against Fe elution in Fig.8 (b), especially, TiFe and TiFe₂, which were almost immune against molten Mg.

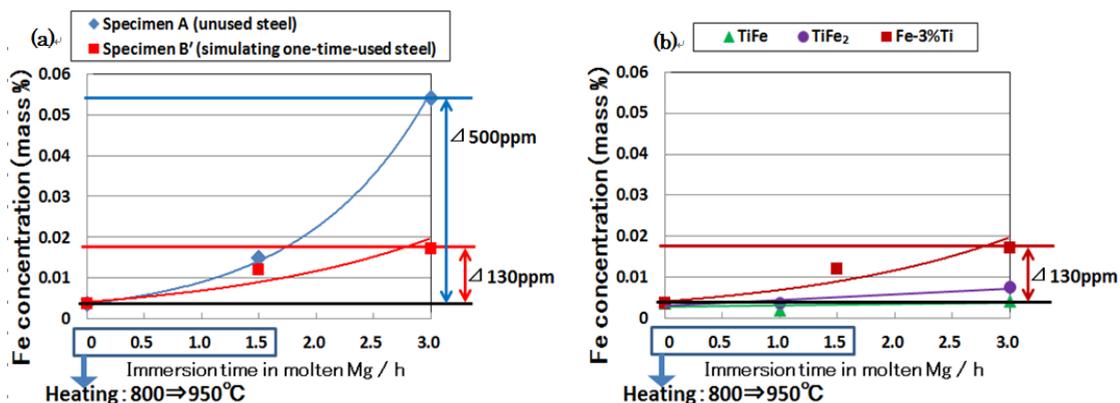


Fig.8 Fe elution into 200g molten Mg at 800-950°C from (a) Specimen A and Specimen B' which simulate the first and the second use of steel vessel, respectively, and (b) TiFe, TiFe₂ and Fe-3mass%Ti which form on the surface after the treatment similar to the first use of steel vessel.

4. Discussion

4.1 Microstructure change of steel vessel by first use

As described in the "Results", three layers (TiFe, TiFe₂ and Ti-diffused Fe) formed on the steel surface by contacting with Ti powders, which simulate newly precipitated sponge titanium. According to the Ti-Fe binary phase diagram^[5,6] shown in Fig.9, they are the three phases in the high Fe content region and it is reasonable to think that those phases formed by interdiffusion of Fe and Ti. Here, it should be noted that the outermost surface of the Ti-diffused steel contains 3mass% Ti, which is the solubility limit of Ti in the ferrite α phase at around 1000°C.

Steel is basically composed of the α phase at room temperature and the α phase transfers to the austenite γ phase at 950°C, operating temperature of the vessel, as shown in Fig.9 and suggested by Nagesh et al^[7,8]. However, most portion of the Ti-diffused Fe should be composed of the α phase at this temperature as shown in Fig.9. High resistance against Fe elution into Mg of Fe-3mass%Ti is probably caused by the formation of the α phase by Ti inward diffusion at operating temperature of the steel vessel.

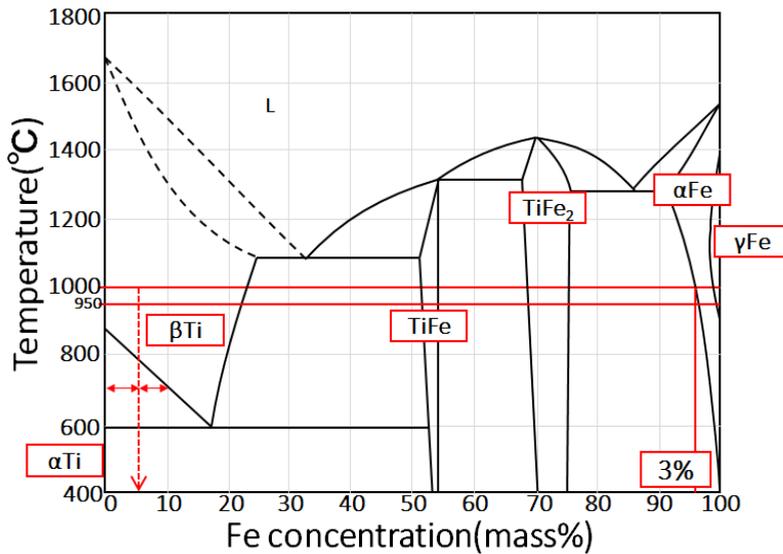


Fig.9 Phases appeared in Specimen B, which simulates the steel vessel after the first use for sponge titanium production (Ti powders were coated and heat treated at 1000°C for 10h). Phases are indicated on the binary phase diagram of Ti-Fe system ^[5,6]

4.2 Comparison of Fe elution to actual production vessel

As described in the “Introduction”, Fe content in sponge titanium is high when the vessel is used for the first time. This is consistent with the experimental result for Specimen A (Fig.8 (a)). In addition, Fe content is reduced at an opportunity of the repeated use of the vessel. This tendency is also consistent with the experimental result for Specimen B’ (Fig.8(a)). However, in the actual production mill, Fe elution reduces to 1/10-1/20 at the second use, while the experimental results indicates Fe elution from Specimen B’ simulating the second use of the vessel is 1/4 of that from Specimen A simulating the first use. The difference between the experiment and the actual mill is probably brought by the difference of the amount of the remnant on the steel surface. In the actual vessel, 3/4 of the surface area of the vessel is covered with the intermetallics, TiFe and TiFe₂, which remain on the surface without removed during the process of taking out sponge titanium from the vessel, while they are almost completely removed by a scraper in Specimen B’ because of the tiny specimen size. In fact, Fe elution of Specimen B’, which is covered with the Ti-diffused Fe, is almost the same as that of Fe-3mass%Ti, which is 1/4 of that in Specimen A.

Based on the experimental results and the above discussion, why Fe elution reduces to 1/10-1/20 in the actual mill at the second use of the vessel is discussed next using Fig.10, in which microstructure change of the surface region in the steel vessel during the first and second uses is schematically depicted.

The vessel made of unused steel is heated to around 950°C of operation temperature in the actual reduction process. At that time, the α phase transfers to the γ phase. The Ti-diffused layer forms as well as TiFe and TiFe₂ intermetallics. Here, outer portion in which high amount of Ti is contained transfers to the α phase again.

After the first operation, a lump of sponge titanium is taken out from the vessel. At that time, 1/4 of the area of the inner surface was effectively peeled out and brittle intermetallics are removed. It means that 3/4 of the area is still covered with intermetallics and Fe-3mass%Ti appears on 1/4 of the area of the total surface.

Fe elution from the steel vessel at the second use is estimated as 1/16 of that at the first use by the following calculation :

Fe elution at the second use

$$= 3/4 \text{ (area ratio of TiFe and TiFe}_2 \text{ after the first use)} \times 0 \text{ (Fe elution from TiFe, TiFe}_2)$$

$$+ 1/4 \text{ (area ratio of Fe-3\%Ti after the first use)} \times 1/4 \text{ (Fe elution ratio from Fe-3\%Ti)}$$

$$= 1/16$$

This is well consistent with the value of the actual production mill, 1/10-1/20.

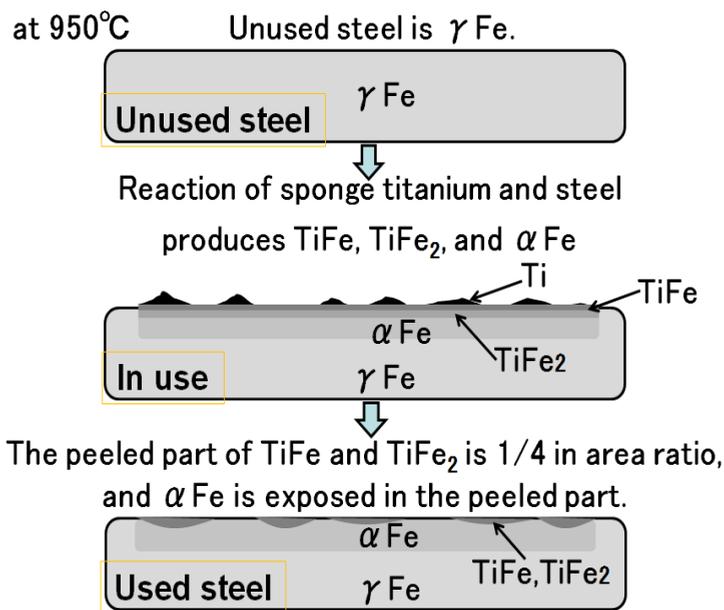


Fig.10 Schematic representation of microstructure change of the surface region in the steel vessel during the first and second uses.

5. Conclusion

Immersion experiments into molten Mg were conducted using specially designed steel based specimens which effectively simulate the first and the second uses of the steel vessel, and microstructure was closely investigated. Obtained results are as follows :

- Three layers of TiFe, TiFe₂ and Ti-diffused steel form on the surface of the steel specimen after the treatment similar to the first use of the vessel. The outermost portion of the Ti-diffused steel contains 3%Ti which is the solubility limit in Fe at 1000°C, and it should transfer to the γ phase at 950 °C, operating temperature in the actual reduction process.
- Fe elution in the specimen simulating the second use reduces considerably compared to that in the specimen simulating the first use.
- Fe elution from TiFe and TiFe₂ is almost zero, while Fe elution from Fe-3mass%Ti is 1/4 of that from the unused steel.
- By taking the information on the phases appeared on the surface in the actual vessel into account, Fe elution from the vessel at the second use is estimated as 1/16 of that at the first use. This is well consistent with the value of the actual production mill, 1/10-1/20.

6. Acknowledgements

This work was conducted as a part of the project "Research and Development on Innovative Structural Materials" by the New Energy and Industrial Technology Development Organization (NEDO).

7. References

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