

# TiC PHASE DIFFUSION LAYER FORMATION IN TITANIUM CLAD STEEL COMPOSITE HAVING AN INTERMEDIATE LAYER OF $\alpha$ -Fe<sup>①</sup>

Xia Changqing, Jin Zhanpeng

*Department of Materials Science and Engineering,  
Central South University of Technology, Changsha 410083*

**ABSTRACT** The TiC layer formed in the bond interface of the titanium clad steel composite having an intermediate layer of  $\alpha$ -Fe at 1023 K for different times was examined metallographically and analyzed using an electron microprobe technique. The mechanism of TiC phase diffusion layer formation was discussed by Fick's law assuming that stationary diffusion of carbon was established in titanium/  $\alpha$ -Fe/ steel diffusion couples.

**Key words** TiC-phase carbon activity stationary diffusion

## 1 INTRODUCTION

The titanium clad steel composite is a clad steel plate, of which the base metal is steel with 0.20% carbon and the cladding metal is titanium having excellent corrosion resistance and heat resistance, and is utilized in many engineering fields, such as in boilers for corrosive media, reactors. For producing titanium clad steel composite, in general there are an explosion bonding process which bonds materials by powder explosion in cold work<sup>[1-2]</sup> and a hot rolling process which heats and hot-rolls a slab assembly. The explosion bonding process is excellent in bonding, but the production is difficult, the cost is high, and is restricted by producible sizes. The hot rolling process is more popular for the production of stainless steel clad plates and applicable to mass production, however it is not suitable for production of titanium clad steel plate. This is because titanium very easily reacts with carbon in the steel at high temperature. Usually, the carbon is transferred to the titanium and so titanium is characterized by TiC layer on parts to be clad during carrying out hot rolling.

Romaekers *et al*<sup>[3]</sup> discussed the phase relations, diffusion paths and TiC phase thickening law in the Fe-Ti-C system at 1273 K. Ohtani *et al*<sup>[4]</sup> evaluated the isothermal section diagrams for Fe-Ti-C system at different temperatures and discussed the thermodynamic properties of TiC phase. The present authors<sup>[1-2]</sup> examined the TiC phase formation and the diffusion paths in the titanium-steel explosion weld interface. The TiC layer between titanium and steel generally has a negative influence on its performance. For producing the titanium clad steel plate *via* hot rolling, one way of decreasing the amount of carbon diffusion is to introduce an intermediate metal layer between titanium and steel with 0.20% carbon. In the present work, an intermediate layer of  $\alpha$ -Fe was introduced by hot rolling, the purpose of the paper is to examine the role of such a layer in the titanium clad steel composite.

## 2 EXPERIMENTAL PROCEDURE

The specimens used in the present work were prepared from the titanium clad steel com-

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posite having an intermediate layer of  $\alpha$ -Fe. The samples were sealed into the quartz capsules under vacuum ( $10^{-2}$  Pa) and annealed at 1023 K for different times in the GK-2B type diffusion furnace. The temperature was controlled with a thyristor regulator and was found to be within  $\pm 1^\circ\text{C}$  as measured with a calibrated Ni-Cr/Ni-Al thermocouple. After the heat treatments, these samples were water quenched by breaking the capsules. The quenched specimens were ground, polished and etched at first in an aqueous solution containing 8% hydrofluoric acid; subsequently, in an aqueous alcohol solution containing 3% nitric acid. All samples were investigated using microscopy (Neophot 21) and electron microprobe analysis (Camebax-Micro and X-650).

### 3 RESULTS AND DISCUSSION

#### 3.1 TiC Phase Diffusion Layer Formation at 1023 K

Fig. 1 shows an optical micrograph of a titanium clad steel composite having an intermediate layer of  $\alpha$ -Fe after hot-rolling at 1023 K, the strongly deformed grains were noticeable within the three layers of the composite. After 3 h annealing at 1023 K, the interface between titanium and  $\alpha$ -Fe is characterized by the existence of a reaction layer about  $0.90\text{ }\mu\text{m}$  thick. Longer

heat treatments at 1023 K caused further growth of the reaction layer and the thickness of the reaction layer was increased. Fig. 2 displays an optical micrograph of the titanium clad steel composite having an intermediate layer of  $\alpha$ -Fe after 213 h annealing at 1023 K. A thickening diffusion layer is evident in the interface of titanium/ $\alpha$ -Fe, its thickness is about  $5.4\text{ }\mu\text{m}$ . The diffusion layer was relatively uniform in thickness with smooth interphase interface. Fig. 3 shows a

**Fig. 2 Optical micrograph of the titanium clad steel composite having an intermediate layer of  $\alpha$ -Fe after 213 h annealing at 1023 K**

**Fig. 1 Optical micrograph of the titanium clad steel composite having an intermediate layer of  $\alpha$ -Fe after hot-rolling at 1023 K**

**Fig. 3 Scanning electron micrograph of the titanium-iron bond interface and distribution of each element found by EPMA after 213 h annealing at 1023 K**

scanning electron micrograph and the distributions of each element found by electron probe microanalysis (EPMA) at 1023 K for 213 h. Both transfer of the iron in titanium and diffusion of the titanium in iron were neglected and only the carbon diffusion was taken into account. The EPMA result shows that a large number of carbon was distributed and titanium peak step was appeared within the reaction layer. From quantitative electron microprobe analysis of the reaction layer, the titanium content ranges from 66.33% to 56.60% (atomic fraction) titanium, the carbon content ranges from 31.87% to 41.37% (atomic fraction) carbon and the solid solubility of iron is about 1.3% (atomic fraction) iron. Consequently, this layer corresponds to the TiC phase. The compositional analysis in the titanium close to the TiC layer did not reveal the presence of any dissolved carbon. This implies that most of the carbon diffusing into the titanium from the steel with 0.20% carbon reacts to form TiC phase consistent with the low solubility of carbon in titanium.

The intimate connection between ternary phase equilibria of the Fe-Ti-C system and diffusion layer formation was elegantly demonstrated, it was conducted to identify the TiC phase that can be formed at the interface of titanium/ $\alpha$ -Fe<sup>[1-4]</sup>. At 1023 K the composition of steel with 0.20% carbon is in the two-phase field of  $\alpha$ -Fe and  $\gamma$ -Fe. The carbon concentration difference in the  $\gamma$ -Fe phase field results in extensive carbon diffusion and the carbon diffuses from steel with 0.20% carbon to titanium. The carbon concentration profile in Fig. 3 approximately looks like the profile in Fig. 4. Fig. 4 shows that the carbon concentration is always much lower in the  $\alpha$ -Fe layer than in the  $\gamma$ -Fe and TiC parts. However, as discussed by Ågren<sup>[5-6]</sup>, the activity of carbon varies continuously over the joint of the titanium clad steel composite having an intermediate layer of  $\alpha$ -Fe. Employing the notation in Fig. 4, it yields

$$C^{\text{TiC}/\alpha} f^{\text{TiC}} = C^{\alpha/\text{TiC}} f^{\alpha} \quad (1)$$

$$C^{\gamma/\alpha} f^{\gamma} = C^{\alpha/\gamma} f^{\alpha} \quad (2)$$

where  $f^{\text{TiC}}$ ,  $f^{\gamma}$  and  $f^{\alpha}$  are respectively the activity coefficients of carbon in the different parts

of the joint. For times longer than the relaxation time for carbon diffusion in the intermediate layer of  $\alpha$ -Fe, the change of the carbon content in the  $\alpha$ -Fe layer can be neglected compared to the change in the TiC and  $\gamma$ -Fe parts and the stationary diffusion of carbon has been established. The outgoing flux of  $\gamma$ -Fe phase must equal the flux through  $\alpha$ -Fe layer and the ingoing flux in TiC phase. Employing Fick's law and the notation in Fig. 4 we obtain

$$D^{\text{TiC}} \left( \frac{C^{\text{TiC}/\alpha} - C^{\text{TiC}/\text{Ti}}}{L^{\text{TiC}}} \right) = D^{\alpha} \left( \frac{C^{\alpha/\gamma} - C^{\alpha/\text{TiC}}}{L^{\alpha}} \right) \quad (3)$$

$$D^{\gamma} \left( \frac{C^{\gamma/\alpha} - C^{\gamma/\gamma}}{L^{\gamma}} \right) = D^{\alpha} \left( \frac{C^{\alpha/\gamma} - C^{\alpha/\text{TiC}}}{L^{\alpha}} \right) \quad (4)$$

where  $D^{\text{TiC}}$ ,  $D^{\gamma}$  and  $D^{\alpha}$  are respectively the diffusivities of carbon in the TiC,  $\gamma$ -Fe and in intermediate layer of  $\alpha$ -Fe. The distances  $L^{\text{TiC}}$  and  $L^{\gamma}$  are approximated with the well-known expressions from random walk theory:

$$L^{\text{TiC}} = \sqrt{2D^{\text{TiC}}t} \quad (5)$$

$$L^{\gamma} = \sqrt{2D^{\gamma}t} \quad (6)$$

By combining Eqns. (1) ~ (6) and solving them for unknown compositions  $C^{\text{TiC}/\alpha}$ ,  $C^{\gamma/\alpha}$ , we

**Fig. 4 Piece-wise linear approximation of carbon concentration profile in Fig. 3**

obtain:

$$C^{\text{TiC}/\alpha} = \frac{C^{\text{TiC}/\text{Ti}} + \sqrt{\frac{D^{\gamma}}{D^{\text{TiC}}}} S^{\gamma}(t) C^{\gamma 0}}{1 + \frac{f^{\text{TiC}}}{f^{\gamma}} \sqrt{\frac{D^{\gamma}}{D^{\text{TiC}}}} S^{\gamma}(t)} \quad (7)$$

$$S^{\gamma}(t) = \frac{1}{\sqrt{\frac{D^{\gamma}}{D^{\alpha}}} \frac{f^{\alpha}}{f^{\gamma}} \frac{L^{\alpha}}{\sqrt{2D^{\alpha}t}} + 1} \quad (8)$$

and

$$C^{\gamma/\alpha} = \frac{C^{\gamma 0} + \sqrt{\frac{D^{\text{TiC}}}{D^{\gamma}}} S^{\text{TiC}}(t) C^{\text{TiC}/\text{Ti}}}{1 + \frac{f^{\gamma}}{f^{\text{TiC}}} \sqrt{\frac{D^{\text{TiC}}}{D^{\gamma}}} S^{\text{TiC}}(t)} \quad (9)$$

$$\text{where } S^{\text{TiC}}(t) = \frac{1}{\sqrt{\frac{D^{\text{TiC}}}{D^{\alpha}}} \frac{f^{\alpha}}{f^{\text{TiC}}} \frac{L^{\alpha}}{\sqrt{2D^{\alpha}t}} + 1} \quad (10)$$

As mentioned, the intermediate layer is usually introduced in order to decrease the concentration differences  $C^{\gamma/\alpha} - C^{\gamma 0}$  and  $C^{\text{TiC}/\alpha} - C^{\text{TiC}/\text{Ti}}$ . From Eqns. (7) ~ (10) one can deduce that this is achieved by choosing  $S^{\gamma}(t)$  and  $S^{\text{TiC}}(t)$  as small as possible. One should thus choose a material with a large  $f^{\alpha}$  and a low  $D^{\alpha}$ . However, Eqns. (7) ~ (10) also show that at long diffusion time the intermediate layer becomes gradually less important. It is known that the intermediate layer of  $\alpha$ -Fe is only slightly different from that of the steel with 0.20% carbon, it is usually not possible to increase  $f^{\alpha}$  very much. In order to obtain a strong effect, it is necessary either to use a very thick intermediate layer or to use an intermediate layer of a different metal. As an example, Cu has been reported to have a very low  $D^{\text{Cu}}$ . It also has a very low solubility of carbon<sup>[7-8]</sup> and should thus have a very high  $f^{\text{Cu}}$ .

For producing the titanium clad steel composite *via* hot rolling, a material should be interposed between a titanium and the steel in order to prevent formation of compounds at the boundary of titanium and iron. As such intermediate materials, preferable are those metals which make a perfect solid solution with titanium or iron. Ni, Mo and V have been used<sup>[9]</sup> in foil or

they have been plated or undertaken with spraying process on a cladding face.

### 3.2 Kinetics

During growth of TiC layer in Ti/  $\alpha$ -Fe/ steel diffusion couples the initially pure titanium side immediately reacts with carbon. This effect is reflected in the observed TiC layer thickness ( $d_{\text{TiC}}$ ) as a function of the square root of time, see Fig. 5. The linear nature of this graph indicates that the TiC layer grows according to the parabolic thickening law in the titanium clad steel composite having an intermediate layer of  $\alpha$ -Fe at 1 023 K. The growth rate constants of TiC layer range from  $K = 3.75 \times 10^{-13} \text{ cm}^2 \cdot \text{s}^{-1}$  to  $1.88 \times 10^{-13} \text{ cm}^2 \cdot \text{s}^{-1}$  ( $K$  is defined by  $K = d_{\text{TiC}}^2/(2t)$ , in which  $d_{\text{TiC}}$  = thickness of TiC layer,  $t$  = growth time). At 1 023 K for 2 h a strong decarburization is found near the interface between the intermediate layer of  $\alpha$ -Fe and the steel, a complete  $\alpha$ -Fe layer is formed on the steel side. The phenomenon is due to the fact that the diffusion process in the titanium clad steel having an intermediate layer of  $\alpha$ -Fe is controlled by the diffusion of the interstitial element carbon, the carbon diffusivity in the  $\alpha$ -Fe phase

**Fig. 5 Kinetics of TiC layer growth in titanium clad steel composite having an intermediate layer of  $\alpha$ -Fe at 1 023 K.**

is far greater than that in the  $\gamma$ -Fe. At the initial stage, the carbon flux through  $\alpha$ -Fe layer is larger and the TiC layer growth is faster. The mass balance is satisfied and the decarbonization occurs on the steel side. When the time is longer than the relaxation time for carbon diffusion in the  $\alpha$ -Fe layer, the carbon activity is equal at the phase boundary of  $\alpha$ -Fe/  $\gamma$ -Fe, local equilibrium is established at this phase boundary. The stationary diffusion of carbon caused by the carbon activity gradient in the  $\gamma$ -Fe is established, the outgoing flux of  $\gamma$ -Fe phase equalizes the flux through  $\alpha$ -Fe layer and the ingoing flux in TiC phase. The subsequent rate of carbon transfer to the TiC layer is governed by the carbon diffusion rate through the  $\alpha$ -Fe layer, this is one of causes of a little slowness of growth of the initially formed TiC phase, it explained the observed range of parabolic rate constants.

#### 4 CONCLUSIONS

The titanium clad steel composite having an intermediate layer of  $\alpha$ -Fe was heated at 1023 K, the TiC layer was immediately formed

along the Ti/  $\alpha$ -Fe interface. The intermediate layer of  $\alpha$ -Fe is not effective as a hindrance for the carbon diffusion. The TiC layer growth exhibited a parabolic thickening law within experimental error.

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