

Ti₃AlC₂의 800-1100°C, SO₂ 가스 분위기에서의 부식

Corrosion of Ti₃AlC₂ at 800-1100°C in SO₂ gas atmosphere

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초 록: Ti₃AlC₂ was corroded between 800 and 1100°C in an Ar-0.2% SO₂ gas atmosphere according to the equation: Ti₃AlC₂ + O₂ → rutile-TiO₂ + α-Al₂O₃ + (CO or CO₂). The scales that formed on the Ti₃AlC₂ were thin and rich in α-Al₂O₃, whose growth rate was exceedingly slow. The TiO₂ was present either as the outermost surface scale or a mixture inside the α-Al₂O₃-rich scale. In the Ti₃AlC₂, the activity and diffusivity of Ti were low, whereas those of Al were high. This was the main reason for the superior corrosion resistance of Ti₃AlC₂ over TiAl.

1. 서론

The nanolaminated ternary compound Ti₃AlC₂ has attracted enormous attention due to its superior metallic and ceramic properties. It is light, electrically and thermally conductive, easily machinable, ductile with a high stiffness-to-hardness ratio, damage tolerant, maintains strength at high temperatures, and is resistant to thermal shock and chemical attack. However, in order to utilize Ti₃AlC₂ as structural a component in a variety of corrosive environments, its corrosion characteristics require investigation.

In this study, the Ti₃AlC₂ compound was fabricated via the powder metallurgical process and corroded in an Ar-0.2%SO₂ gas atmosphere at 800-1100°C for up to 180 h. The aim of this study is to characterize the corrosion behavior of Ti₃AlC₂ in an Ar-0.2%SO₂ atmosphere, which has not adequately been explored. Pure TiAl was used as a benchmark as it is an important intermetallic compound for high-temperature structural applications. The present study would aid the comprehensive understanding of Ti₃AlC₂ under diverse corrosive environments at high temperatures.

2. 본론

Powders of TiC_x (< 45 μmØ, x = 0.6) and Al (< 45 μmØ, 99.7% purity) were weighed in a molar ratio of 3:1.1, mixed in a SPEX shaker mill in Ar for 10 min, and hot pressed at 1400°C under 25 MPa for 60 min in flowing Ar gas to synthesize 19 mmØ x 10 mm bulks. The synthesized Ti₃AlC₂ bulks were corroded at 800, 900, 1000, and 1100°C in flowing commercial-grade Ar(99.999% purity)-0.2% SO₂(99.9% purity) gas. The weight changes during corrosion were continuously monitored as a function of time using a TGA. Each sample was suspended by a platinum wire and heated in the hot zone of the furnace attached to the TGA. For comparison purposes, the hot forged monolithic Ti-50.56Al (at.%) plate from the vacuum arc melted and the HIP-treated ingot corroded in the identical Ar-0.2% SO₂ gas. The samples were investigated by means of a SEM equipped with an EDS, an XRD with Cu-Kα radiation, AES and TEM. The TEM sample was prepared by milling in a FIB system with a liquid gallium metal ion source and a maximum accelerating voltage of 30 kV. After carbon coating, the sample was examined with a 200 kV TEM equipped with a 5-nm spot size EDS.

Fig. 1 shows the SEM/XRD/TEM results of the synthesized Ti₃AlC₂. The SEM image shows the fully dense sample possessing lamellar grains with an aspect ratio as high as five (Fig. 1a). The sample density was similar with the theoretical density of Ti₃AlC₂ (4.25 g/cm³). The XRD pattern indicates that the monolithic Ti₃AlC₂ was successfully synthesized (Fig. 1b). The lamellar Ti₃AlC₂ grains consisted of nanolaminates (Fig. 1c). Their SAED is shown in Fig. 1d, where the electron beam is parallel to the [1100] direction. The hexagonal lattice parameters were derived as a=0.307 nm and c=1.85 nm, which matched those of Ti₃AlC₂.

Fig. 2 shows the TEM analytical results of Ti₃AlC₂ after corrosion at 800°C for 60 h. The scale was approximately 0.6 μm-thick (Fig. 2a). Fig. 2b displays elemental concentration profiles obtained from the EDS spot analysis. Spot 8 is the scale/matrix boundary. The carbon profile shown in Fig. 2b was suspicious, as it was notoriously difficult to quantify carbon. The scale was a (Al₂O₃, TiO₂)-mixture (Fig. 2b). Sulfur was detected only at spot 2 as 1.3%, indicating that the oxidizing tendency was much stronger than the sulfidizing tendency. In Fig. 2c, continuous nucleation of numerous, tiny oxide crystallites with round or ellipsoidal shapes occurred as opposed to epitaxial growth of oriented oxides. The corresponding elemental maps shown in Fig. 2d indicate that Al₂O₃ was intermixed with a lesser amount of TiO₂. The good corrosion resistance of Ti₃AlC₂ should be attributed to the predominant formation of the highly stoichiometric Al₂O₃. This favors formation of the protective Al₂O₃ scale on Ti₃AlC₂ in the Ar-0.2% SO₂ gas.

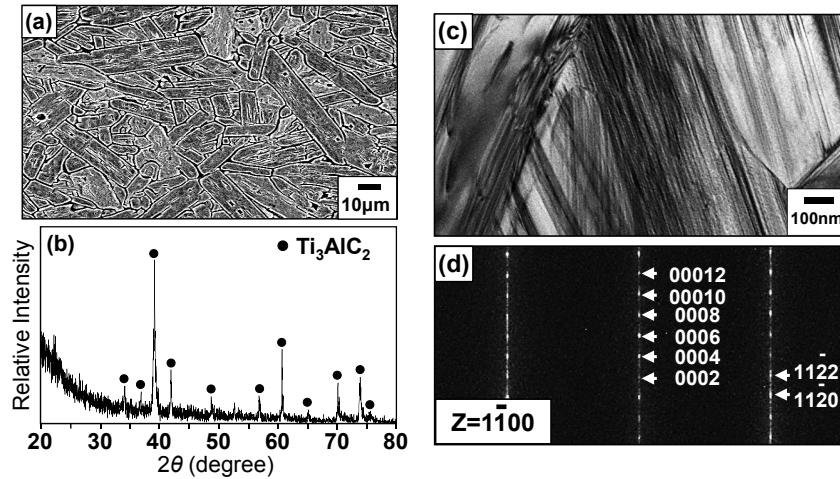


Fig. 1. Ti_3AlC_2 synthesized. (a) etched SEM image, (b) XRD pattern, (c) TEM image of the matrix grains, (d) SAED pattern of (c).

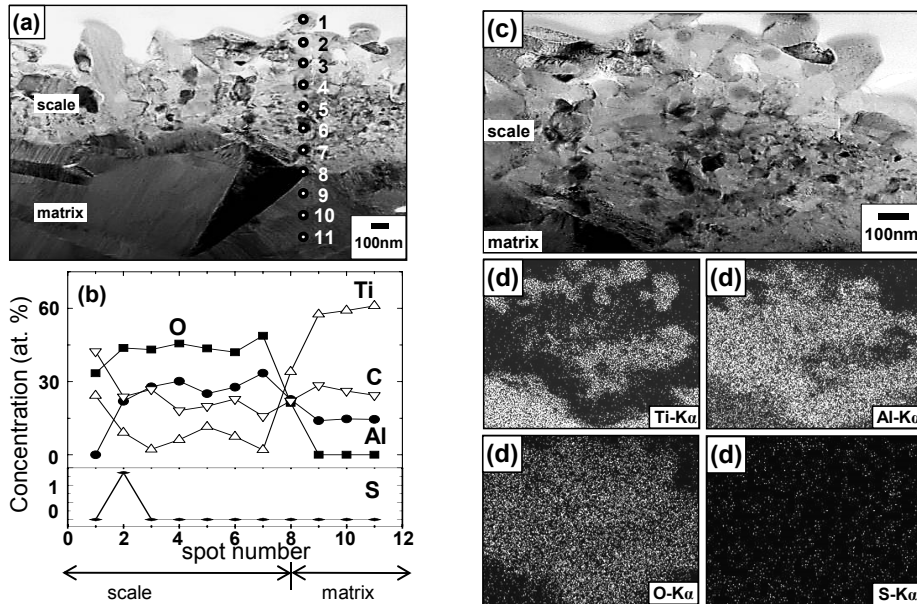


Fig. 2. Ti_3AlC_2 after corrosion at 800°C for 60 h in Ar-0.2% SO_2 gas. (a) TEM image, (b) concentration profiles of Ti, Al, C, O, and S, (c) TEM image of the scale, (d) maps of Ti, Al, O, and S.

3. 결론

Fully dense, monolithic Ti_3AlC_2 compounds were corroded at 800, 900, 1000, and 1100°C for up to 180 h under an Ar-0.2% SO_2 gas atmosphere. The formed scales were thin and consisted primarily of $\alpha\text{-Al}_2\text{O}_3$, with a much lesser amount of rutile- TiO_2 . Since the activity and diffusivity of Al were higher than those of Ti in Ti_3AlC_2 , protective $\alpha\text{-Al}_2\text{O}_3$ -rich scales formed, effectively suppressing sulfidation. Under identical corrosion conditions, the scales formed on TiAl consisted of thick, triple layers, viz. an outer TiO_2 layer containing some Al_2O_3 particles, an intermediate (Al_2O_3 , TiO_2)-mixed layer, and an inner, narrow (TiS , Ti_2S)-mixed layer. In case of TiAl, titanium in TiAl was active and diffused quickly, so as to oxidize to TiO_2 and sulfidize to TiS and TiS_2 , simultaneously. Aluminium in TiAl was inactive and did not diffuse fast. Hence, unlike Ti_3AlC_2 , TiAl could not form the $\alpha\text{-Al}_2\text{O}_3$ -rich scale.

감사의 글

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