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Enhancement in the thermal oxidation resistance of a Ni-Cr-base superalloy using ceramic coatings

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A comparative study of the thermal oxidation behavior of a Ni-Cr-base superalloy, Inconel 617, with and without a refractory ceramic coating layer has been conducted and a significant enhancement in the thermal oxidation resistance was obtained by employing the refractory ceramic coatings. 2.5-3.0 μ m thick TiAlN- or Al₂O₃-coated Inconel 617 samples showed much lower mass changes than bare Inconel 617 after annealing at 1000°C for up to 48 h by suppressing the inhomogeneous formation of Cr₂O₃ at the surface region through the reaction between oxygen and grain boundary-diffused Cr.

Key words: thermal oxidation resistance, a Ni-Cr-base superalloy, Ceramic coating, Inconel 617, surface oxidation, Cr_2O_3 formation

Introduction

It is necessary to develop very effective heat transport systems suitable for high temperature range operation (≥950°C) in order to realize advanced nuclear energy systems [1, 2]. To date two different approaches, developing either new high temperature alloys [3-5] or refractory ceramic coatings for conventional high temperature alloys [6-10], have been made to achieve a heat transport system fit for very high temperature reactors (VHTRs). In the field of nuclear technology, attention has been paid to coatings that can protect high temperature alloys against surface reactions such as carburization, oxidation, sulphidation, etc. [5-8], but not much work has been done on refractory ceramic coatings for Inconel 617, one of the promising Ni-Crbase superalloys for heat transport systems of VHTRs. In this study, TiN, TiCN, TiAlN or Al₂O₃ coating layers were deposited on Inconel 617 by an arc discharge technique and a comparative study on the structural property of each ceramic coating layers and their effect on wear and the thermal oxidation resistance of Inconel 617 has been conducted.

Experimental

A commercial Inconel 617 alloy (Ni-22Cr-12.5Co-9Mo-1Al) manufactured by High Temperature Metals Inc., USA was used in this study. 2.5-3.0 µm thick TiN, TiCN, TiAlN or Al_2O_3 coating layers were deposited on the polished Inconel 617 substrates by an arc discharge technique. During the deposition process the substrate temperature and chamber pressure were fixed at 450°C and 1.33×10^{-3} Pa (1×10⁻⁵ Torr), respectively. The structural properties of each sample terized by X-ray diffraction (XRD) were characand scanning electron microscopy (SEM) before and after annealing at 1000°C for 24 h. The wear resistance of as-deposited and annealed (1000°C for 24 h) samples was measured using a ball on disk type wear testing system under the condition of a test load 5 kg and rotation speed 100 rpm. Thermal cyclic oxidation tests were conducted at 1000°C for up to 48 h and thermal cycles were given at 12 h-intervals. After each cycle, the surface morphology, near surface composition and mass change per unit area were examined by SEM-EDS and an electronic balance.

Results and Discussion

Figure 1 shows the cross-sectional SEM micrographs of Inconel 617 coated with TiN, TiCN, TiAlN and Al_2O_3 . Please note that the cross-section of each sample was not polished to prevent delamination of the coated layer that might otherwise occur. The thickness of each coating layer is in the range of 2.5-3.0 µm with a relatively uniform thickness profile and interfacial morphology are obtained.

X-ray diffraction patterns of bare and TiN-, TiAlNor TiAlN-coated Inconel 617 samples before and after annealing at 1000°C for 24 h are shown in Fig. 2.

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Fig. 1. Cross-sectional SEM micrographs of Inconel 617 coated with TiN, TiCN, TiAlN and Al₂O₃ thin films.

 Cr_2O_3 peaks are observed from all of the samples annealed at 1000°C for 24 h indicating the presence of a surface reaction between oxygen and Cr which had diffused to the surface. In the case of the TiN-coated sample, the TiN layer starts to decompose at a temperature ~600°C and does not remain on Inconel 617 after annealing at 1000 °C, which can account for the disappearance of TiN peaks, due to its poor temperature stability. A similar trend was also observed for the TiCN-coated sample. By contrast, the TiAlN layer still exists on Inconel 617 since it has a higher temperature stability than TiN and TiCN layer even though Cr_2O_3 peaks also appeared on its surface after annealing. At a glance at the Al₂O₃-coated sample there seems to be no difference from the case of the TiN-coated sample, but the Al₂O₃ layer is thought to be still in place as a form of solid solution with Cr_2O_3 , which can be understood by a correlation with the surface morphology [11].

Figure 3 shows the surface morphology of bare and TiN-, TiAlN- or Al₂O₃-coated Inconel 617 samples after annealing at 1000°C for 24 h. It is clear that there are scales formed along the grain boundaries in the bare and the TiN-coated Inconel 617 sample. Correlating with XRD results, these scales are Cr_2O_3 layers formed by surface oxidation of grain boundary-diffused Cr and a significant volume expansion has occurred at the grain boundary regions. EDS analysis corroborates that the hill-like grain boundary regions have a much higher Cr concentration than the grain region as shown in Fig. 4. By sharp contrast, hill-like Cr_2O_3 scales along the grain boundary region were not observed for TiAlN- or Al₂O₃-coated Inconel 617 samples, indicating the homogeneously-formed Cr_2O_3 coexists with



Fig. 2. X-ray diffraction patterns of (a) Inconel 617, (b) TiN/Inconel 617, (c) TiAlN/Inconel 617 and (d) $Al_2O_3/Inconel 617$ before and after annealing at 1000°C for 24 h.



Fig. 3. SEM micrographs of (a) Inconel 617, (b) TiN/Inconel 617, (c) TiAlN/Inconel 617 and (d) $Al_2O_3/Inconel 617$ after annealing at 1000°C for 24 h.



Fig. 4. Comparison of relative Cr concentration at grain (left) and grain boundary region (right) by SEM-EDS analysis.



Fig. 5. Ware resistance of bare and TiN-, TiCN-, TiAlN- or Al_2O_3 -coated Inconel 617 (a) before and (b) after annealing at 1000°C for 24 h.

TiAlN or Al_2O_3 on the surface of Inconel 617. From this result it is suggested that a ceramic coating on Inconel 617 should have a structural stability at high temperature range (~1000°C) and physical properties superior to the spontaneously formed Cr_2O_3 layer by surface oxidation reaction of Inconel 617 in order to be applied to the heat transport system of very high temperature reactors (VHTRs).

Figure 5 shows wear test results for bare and TiN-, TiCN-, TiAlN- or Al₂O₃-coated Inconel 617 samples before and after annealing at 1000°C for 24 h. It is obvious that the as-deposited TiN/Inconel 617, TiCN/ Inconel 617, TiAlN/Inconel 617 and Al₂O₃/Inconel 617 samples show much lower wear loss than bare Inconel 617, indicating all the ceramic coating layers play a positive role as protecting layers for Inconel 617. However, there is no distinguishable improvement in wear resistance from TiN- or TiCN-coated Inconel 617 compared to bare Inconel 617 after annealing at 1000°C for 24 h since the Cr_2O_3 formed by the surface oxidation reaction plays a role as a passivation layer due to the poor temperature stability of TiN and TiCN coating layers. In both cases the TiAlN-coated Inconel 617 sample shows the best performance as a protecting layer for Inconel 617, which is consistent with the XRD and microstructural analysis presented above.



Fig. 6. Mass change curves of bare, RTP and TiN-, TiCN-, TiAlN- or Al_2O_3 -coated Inconel 617 samples tested in air at 1000°C.

Mass change curves for bare, rapid-thermally-processed (RTP) at 945°C for 30 s and TiN-, TiCN-, TiAlN- or Al₂O₃-coated Inconel 617 samples tested in air at 1000°C for up to 48 h are summarized in Fig. 6. It is clear that all samples show mass gain by the surface oxidation reaction and the mass loss caused by the spalling of coated layers, previously reported for Hastelloy XR alloy, was not observed [8]. TiN-, TiCNor Al₂O₃-coated samples produce lower mass changes than bare and RTP Inconel 617 samples and this phenomenon is thought to have a very close relationship with the structural properties of the oxide layer formed on the surface. As TiN or TiCN coating layers start to decompose at a temperature above 600°C, a denser Cr₂O₃ layer, compared to the case of bare and RTP Inconel 617, seems to be formed uniformly over the entire surface area and it may suppress further surface oxidation resulting in a lower mass change. Al₂O₃coated Inconel 617 shows the lowest mass change most likely due to the formation of solid solution with Cr₂O₃, as suggested in Figure 2, having a denser microstructure than the spontaneously-formed Cr₂O₃ layer. TiAlN-coated Inconel 617 also shows an enhanced thermal oxidation resistance compared to bare and RTP Inconel 617 samples.

Summary and Conclusions

The structural properties of four different ceramic coatings (TiN, TiCN, TiAlN and Al_2O_3) and their effect on the wear resistance and thermal oxidation resistance of Inconel 617 alloy have been studied. As-deposited TiN- or TiCN-coated samples produced an enhanced wear resistance compared to bare Inconel 617, but no significant improvement in thermal oxidation behavior was observed due to their poor temperature stability in the temperature region above 600°C. TiAlN and Al_2O_3 coatings showed lower wear loss than bare Inconel 617 and an enhanced thermal

oxidation resistance at 1000 °C by suppressing the inhomogeneous formation of Cr_2O_3 by surface oxidation of grain boundary-diffused Cr. TiAlN is thought to be a promising coating layer for Inconel 617-based heat transport systems for very high temperature reactors (VHTRs).

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References

- S. Shiozawa, S. Fujikawa, T. Iyoku, and Tachibana, Nucl. Eng. Des. 233 (2004) 11-21.
- 2. T. Takizuka, Progress Nucl. Energy 47 (2005) 283-291.
- H.M. Yun, P.J. Ennis, H. Nickel, and H. Schuster, J. Nucl. Mater. 125 (1984) 258-272.
- H.-J. Christ, U. Kunecke, K. Meyer, and H.G. Sockel, Mater. Sci. Eng. 87 (1987) 161-168.
- 5. Y. Tachibana, and T. Iyoku, Nucl. Eng. Des. 233 (2004) 261-272.
- J. Chin, W.R. Johnson, and K. Chen, Thin Solid Films 95 (1982) 85-97.
- 7. W. Thiele, and G. Lehnert, Nucl. Tech. 66 (1984) 503-507.
- 8. M. Shindo, and H. Nakajima, ISIJ Int. 29 (1989) 793-795.
- T. Takeda, K. Kunitomi, M. Ohkubo, and T. Saito, Nucl. Eng. Des. 185 (1998) 229-240.
- J.L. He, C.H. Yu, A. Leyland, and A. Matthews, Surf. Coat. Tech. 155 (2002) 67-79.
- 11. E.N. Bunting, Bur. Standards J. Res. 6 (1931) 948-949.