

Thermal oxidation behavior of TiZrN-coated Inconel 617

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Thermal oxidation behavior of $\text{Ti}_x\text{Zr}_{1-x}\text{N}$ -coated Inconel 617 ($x = 0.95, 0.82$, and 0.66) were studied at temperatures up to 1000°C . The TiZrN coating layers transformed into oxide layers after heat treatment and the composition of surface oxide layers was found to be governed by Zr content in the TiZrN coating layer. Cr_2O_3 peaks were observed in all samples and SEM-EDS analysis revealed that the Cr_2O_3 layer is formed beneath the surface oxide layer by the reaction between Cr in the Inconel 617 substrate and oxygen infiltrated through the surface pores. The microstructure of heat-treated TiZrN-coated Inconel 617 samples evolved from a very porous to a dense grain structure as the Zr content in the TiZrN coating layer increases. The $\text{Ti}_{0.66}\text{Zr}_{0.34}\text{N}$ -coated Inconel 617 showed a significantly enhanced wear resistance over bare Inconel 617 after thermal oxidation.

Key words: Thermal oxidation behavior, TiZrN coating, Inconel 617, Microstructure, Wear resistance.

Introduction

Inconel 617 is a solid-solution, strengthened, nickel-chromium-cobalt-molybdenum alloy, and the combination of high strength, high temperature stability and excellent resistance to a wide range of corrosive environments makes this alloy a very attractive material for heat exchangers and gas turbines [1-3]. In the field of nuclear technology, Inconel 617 is recognized as one of the most promising materials for heat transport systems of the very high temperature reactors (VHTRs) which are expected to operate at temperatures between 900 and 1000 [4-6]. At these temperatures, the metallic components of heat transport systems are subjected to combined effects of corrosion, mechanical and thermal stresses during long term operation. In particular, the instability of chromium oxide scale formed on the Inconel 617 alloy surface by an accelerated inter-diffusion reaction at high temperatures (> 900) is one of the major life-limiting factors [7-9]. Therefore, high temperature stability of Inconel 617 depends directly upon inhibiting the formation of brittle and unstable chromium oxide scale on the alloy surface region. This has triggered extensive research effort to find solutions that can offer strengthened high temperature stability to Inconel 617.

Hard coatings of ternary nitrides such as TiAlN ,

TiBN , TiHfN , TiCrN and TiZrN have attracted much attention as substitutes for binary nitrides since they can provide a wide range of structures with ability to control mechanical and electrical properties.[10-14] Recently, it has been reported that the overlay coatings of ternary nitrides can also offer metal alloys improved high temperature stability against corrosion and wear due to their exceptional nature of chemical inertness and mechanical hardness [15-19]. Although much research work has been done on the microstructure, phase composition and mechanical properties of TiZrN coatings deposited by various physical vapor deposition (PVD) techniques, but the information on the thermal oxidation behavior of the TiZrN-coated metal alloys is very limited [20-24].

In this work, $\text{Ti}_x\text{Zr}_{1-x}\text{N}$ coating layers with different composition ($x = 0.95, 0.82$, and 0.66) were applied to Inconel 617, a Ni-Cr-base superalloy, by a reactive sputtering technique and a comparative study on thermal oxidation behavior of the TiZrN-coated Inconel 617 was carried out.

Experimental

The TiZrN coatings were deposited on the polished Inconel 617 (Ni-22Cr-12.5Co-9Mo-1Al) substrates (High Temperature Metals Inc., USA) by reactive sputtering technique using TiZr targets with three different compositions (Ti : Zr = 95 : 5, 82 : 18, and 66 : 34 at%, respectively). During the deposition process, the mixture of argon and nitrogen (Ar/N_2 : 3 : 5 : 1) was used as sputtering gas, and the substrate

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temperature, working pressure, and rf power were fixed at 450, 1×10^{-2} Torr, and 200 W, respectively. The thicknesses of TiZrN coatings were controlled 2.5–3 μm . Thermal oxidation behavior of each sample was examined by thermal cyclic oxidation test at 1000 for up to 48 h and thermal cycle was given at 12 h intervals. The morphological, structural and compositional properties of each sample were characterized by X-ray diffraction (XRD, Cu-K α), scanning electron microscopy (SEM), and energy dispersive spectroscopy (EDS) before and after heat treatment. Especially for the cross-sectional near surface compositions, a combined SEM and EDS technique was applied. The wear resistance of as-deposited and heat-treated 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.

Results and Discussion

Fig. 1 shows narrow X-ray diffraction patterns of as-deposited TiZrN-coated Inconel 617 samples prepared with variation of Ti/Zr ratio. In all samples, the TiZrN layers were identified as the face-centered cubic phase

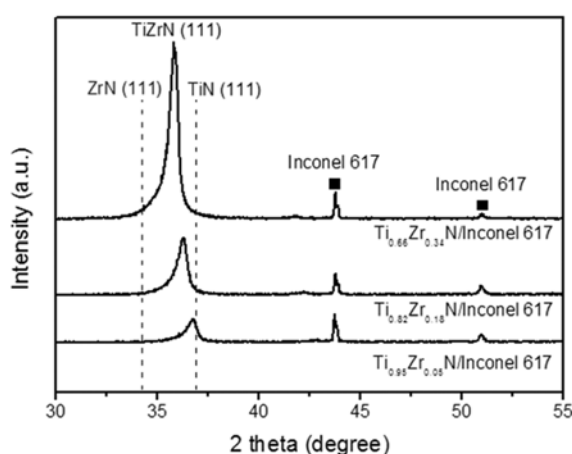


Fig. 1. X-ray diffraction patterns of as-deposited TiZrN-coated Inconel 617.

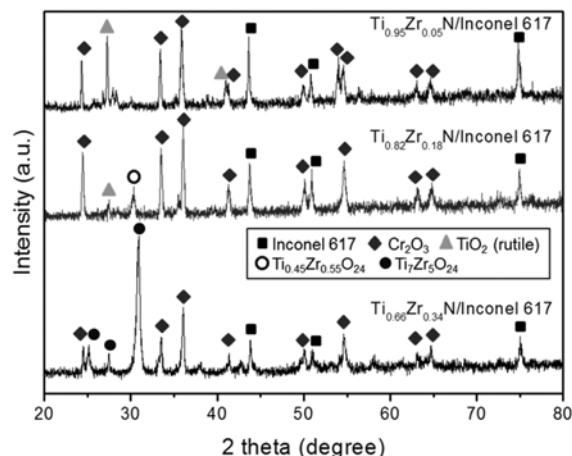


Fig. 2. X-ray diffraction patterns of TiZrN-coated Inconel 617 after heat treatment at 1000 °C in air for 24 h.

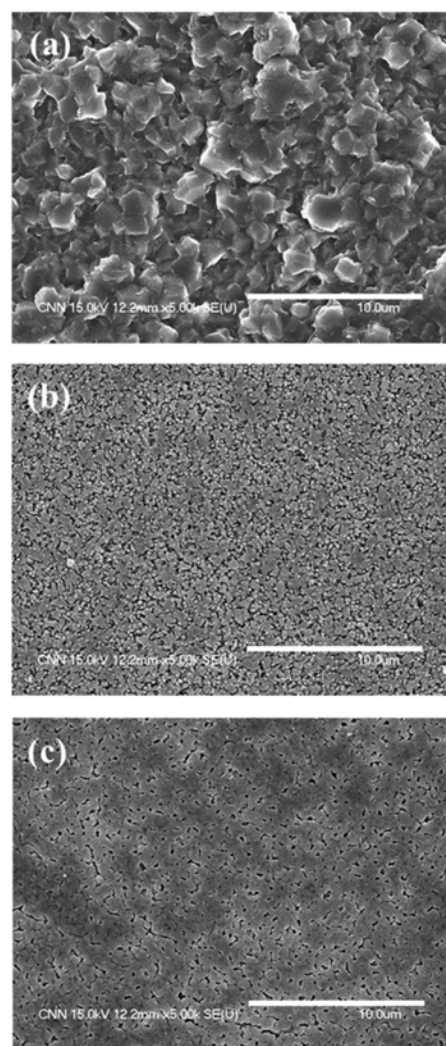


Fig. 3. SEM micrographs of the surface morphologies of Inconel 617 coated with (a) $\text{Ti}_{0.95}\text{Zr}_{0.05}\text{N}$, (b) $\text{Ti}_{0.82}\text{Zr}_{0.18}\text{N}$, and (c) $\text{Ti}_{0.66}\text{Zr}_{0.34}\text{N}$ layer after heat treatment at 1000 °C in air for 24 h.

mainly consisted of (111) and (220) peaks, and no signals of a secondary phase were observed while diffraction peaks of the Inconel 617 substrate were detected. The reflection line of TiZrN (111) peak which is known as the hardest orientation in transition metal nitrides is observed between the ZrN (111) peak and the TiN (111) peak, as reported previously by other researchers [23–25]. It is noticeable that the TiZrN (111) peak position shifts from the TiN (111) toward the ZrN (111) as Zr content in the TiZrN layers increases, indicating the increase in the lattice parameter of the TiZrN layer due to the formation of substitutional solid solution. The (111) peak showed much higher intensity compared to other peaks, which indicates that the TiZrN layers were grown along the preferred orientation of $\langle 111 \rangle$.

X-ray diffraction patterns of the TiZrN-coated Inconel 617 samples after heat treatment at 1000 °C, in air for 24 h are presented in Fig. 2. It is found that the composition of oxide layers formed on the surface after

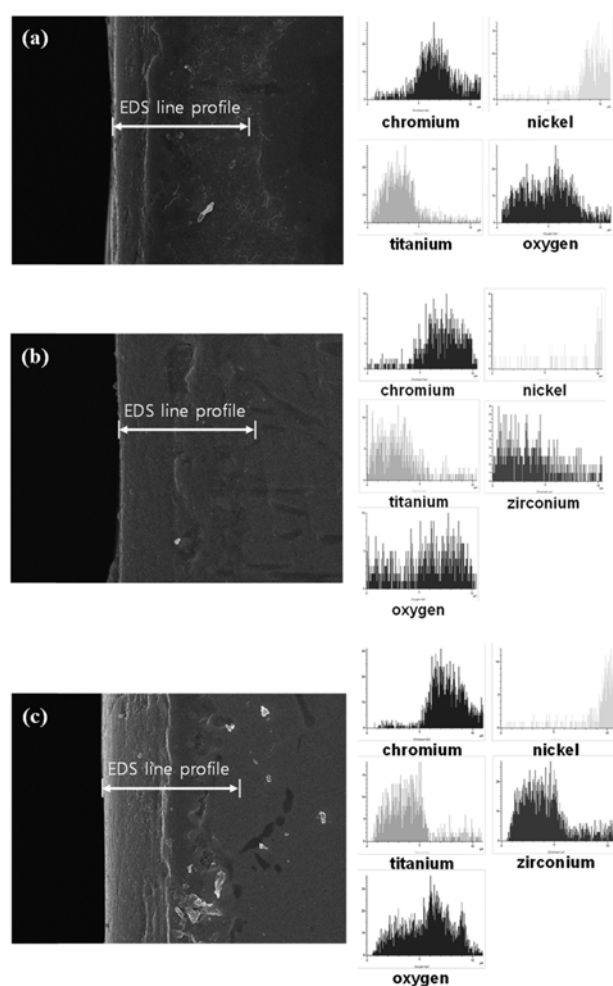


Fig. 4. SEM cross-sectional images and elemental distribution profiles of Inconel 617 coated with (a) $\text{Ti}_{0.95}\text{Zr}_{0.05}\text{N}$, (b) $\text{Ti}_{0.82}\text{Zr}_{0.18}\text{N}$, and (c) $\text{Ti}_{0.66}\text{Zr}_{0.34}\text{N}$ layers after heat treatment at 1000 °C in air for 24 h.

thermal oxidation is governed by Zr content in the TiZrN coating layer. Cr_2O_3 peaks are observed from all of the samples and this is attributed to the reaction between oxygen and Cr which is one of the major components of Inconel 617. In the $\text{Ti}_{0.95}\text{Zr}_{0.05}\text{N}$ -coated sample, peaks of rutile phase TiO_2 and Cr_2O_3 appeared at the surface region after heat treatment. As temperature increases, the $\text{Ti}_{0.95}\text{Zr}_{0.05}\text{N}$ coating layer transformed into TiO_2 layer through thermal decomposition and subsequent thermal oxidation, and transition of TiO_2 from anatase to rutile phase was observed at temperature between 800–900 °C. Since the coating layer has a Ti-rich composition, reflection lines of Zr-containing oxides were not detected. In the case of $\text{Ti}_{0.82}\text{Zr}_{0.18}\text{N}$ -coated Inconel 617, the heat treatment has made the nitride coating layer decomposed and oxidized, resulting in the formation of binary TiO_2 (rutile) and ternary oxide identified as Ti-Zr-O due to the increased Zr content in the coating layer compared to the $\text{Ti}_{0.95}\text{Zr}_{0.05}\text{N}$ coating layer. At the surface region of the $\text{Ti}_{0.66}\text{Zr}_{0.34}\text{N}$ -coated Inconel 617, ternary Ti-Zr-O is found to be formed and exist with Cr_2O_3 after thermal

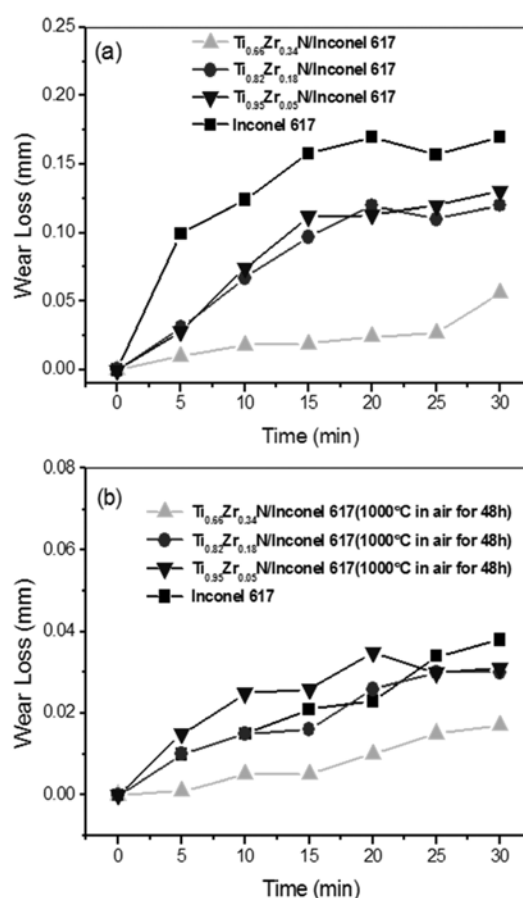


Fig. 5. Comparison of wear loss of uncoated and TiZrN-coated Inconel 617 samples (a) as-deposited and (b) after heat treatment 1000 °C in air for 48 h.

oxidation, and no evident peaks of TiO_2 were observed.

Fig. 3 and Fig. 4 show the surface microstructure and cross-sectional SEM images along with elemental distribution profiles of the TiZrN-coated Inconel 617 after heat treatment at 1000 °C in air for 24 h. In Fig. 3, it is clearly shown that the surface microstructure of the heat-treated TiZrN-coated Inconel 617 samples evolves from a very porous to a dense grain structure as the Zr content in the TiZrN layers increases. The $\text{Ti}_{0.95}\text{Zr}_{0.05}\text{N}$ -coated Inconel 617 exhibits a very porous microstructure made up of coarse grains and SEM-EDS analysis shows that the outmost surface layer with coarse grains is mainly composed of Ti and oxygen. Beneath this Ti-rich surface layer, Cr and oxygen coexist. In the light of the XRD results combined with the cross-sectional EDS analysis, the surface layer is confirmed as a rutile phase TiO_2 and Cr_2O_3 layer is formed on top side of Inconel 617 substrate. When the $\text{Ti}_{0.95}\text{Zr}_{0.05}\text{N}$ coating layer exposed to a high temperature environment, the nitride layer starts to decompose and the porous TiO_2 layer is formed on the surface by the reaction between Ti and oxygen. Once this porous TiO_2 surface layer is formed, oxygen penetrates into the Inconel 617 substrate through the pores in the surface oxide layer and reacts with Cr contained in the Inconel 617, which results in

the formation of the Cr_2O_3 subsurface layer. As Zr participates in the surface oxidation reaction due to the increased Zr content in the TiZrN coating layer (Fig. 4 (b) and (c)), the formation of ternary Ti-Zr-O occurs and this leads to a remarkable densification of surface oxide layer, as shown in Fig. 3 (b) and 3 (c). The $\text{Ti}_{0.66}\text{Zr}_{0.34}\text{N}$ -coated Inconel 617 shows the microstructure with the lowest porosity among the three compositions and the formation of the Cr_2O_3 subsurface layer seems to be suppressed to some extent comparing the intensity of Cr_2O_3 peaks in Fig. 2.

Fig. 5 shows wear test results of bare and TiZrN-coated Inconel 617 before and after heat treatment at 1000°C in air for 48 h. It is obvious that the as-deposited TiZrN-coated Inconel 617 samples show much lower wear loss than the bare Inconel 617, which indicates all the three compositions of TiZrN coating layer play a positive role as protecting layers for the Inconel 617. The lowest wear loss values were obtained for $\text{Ti}_{0.66}\text{Zr}_{0.34}\text{N}$ -coated Inconel 617. However, after treatment, a significant enhancement in wear resistance over the bare Inconel 617 was observed only for the $\text{Ti}_{0.66}\text{Zr}_{0.34}\text{N}$ -coated Inconel 617 and this can be readily explained by taking into account of the composition and microstructure of the oxide layer formed on the surface after heat treatment. By thermal oxidation, the $\text{Ti}_{0.95}\text{Zr}_{0.05}\text{N}$ and $\text{Ti}_{0.82}\text{Zr}_{0.18}\text{N}$ coating layers were found to be transformed into a very porous oxide layer mostly consisted of TiO_2 and a less porous surface layer in which TiO_2 exists with Ti-Zr-O, respectively while the $\text{Ti}_{0.66}\text{Zr}_{0.34}\text{N}$ layer turned into a dense Ti-Zr-O layer. From this result, the presence of TiO_2 in the surface layer is considered to lead to a porous microstructure which produces a degraded wear resistance.

Conclusions

$\text{Ti}_x\text{Zr}_{1-x}\text{N}$ coating layers ($x = 0.95, 0.82$, and 0.66) were applied to the Inconel 617 by a reactive sputtering technique and thermal oxidation behavior of the TiZrN-coated Inconel 617 was studied by comparison of morphological, structural and compositional properties. The TiZrN layers were grown along the preferred orientation of $\langle 111 \rangle$ and the TiZrN (111) peak shift from the TiN (111) toward the ZrN (111) as the Zr content in the TiZrN layers increase, indicating the increase in the lattice parameter due to the formation of substitutional solid solution. After heat treatment at temperatures up to 1000°C in air, the $\text{Ti}_x\text{Zr}_{1-x}\text{N}$ coating layers were decomposed and turned into oxide layers consisted of TiO_2 ($\text{Ti}_{0.95}\text{Zr}_{0.05}\text{N}$), TiO_2 and Ti-Zr-O ($\text{Ti}_{0.82}\text{Zr}_{0.18}\text{N}$), and Ti-Zr-O ($\text{Ti}_{0.66}\text{Zr}_{0.34}\text{N}$). Cr_2O_3 layer was found to be formed beneath these surface oxide layers by the reaction of Cr contained in the Inconel 617 substrate with oxygen infiltrated through the surface pores. A remarkable densification of the surface oxide layer was observed as Zr participates in thermal oxidation reaction

due to the increased Zr content in the TiZrN coating layer. A distinguished enhancement in wear resistance was obtained for the $\text{Ti}_{0.66}\text{Zr}_{0.34}\text{N}$ -coated Inconel 617 compared to bare Inconel 617 after thermal oxidation since the Ti-Zr-O layer with dense microstructure was formed on the surface and plays a positive role as a protecting layer.

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