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This report describes the synthesis and thermal stability of nanocrystalline oxide composites for thermal barrier coating applications. Nanocomposite powders were coated onto nickel-based substrates using alumina gel both as an interlayer and as an adhesive additive in subsequent Al2O3-Y2O3-ZrO2 coatings. Prior to coating of the nanocomposite powders, bond coats were applied to the nickel substrates by plasma spraying. The effects of alumina content and pretreatment conditions on the thermal stability of the coatings were investigated. Thermal gravimeric analysis and optical microscopy experiments were performed to better understand the mechanism of failure in the thermal barrier coatings and determine the optimal coating composition and pretreatment conditions.

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Processing and Deposition of Nanocrystalline Oxide Composites for Thermal Barrier Coatings

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1. Introduction

Previous studies have demonstrated bond coat oxidation is the dominant degradation mechanism responsible for thermal barrier coating (TBC) failure.[1-7] Recent efforts to improve bond coat oxidation resistance have focused on modifying bond coat composition and bond coat pretreatment conditions. [8-15] The goal was to form a protective alumina scale on the bond coat surface prior to depositing the Y_2O_3-ZrO_2-based TBC. The alumina scale acts as an oxidation barrier, as well as to potentially improve the bond coat-TBC adhesion necessary for increased cyclic oxidation life. [16-17] Sun *et al.* utilized chemical vapor deposition to introduce an alumina interlayer between the bond coat and Y_2O_3-ZrO_2. The alumina interlayer greatly improved the performance of the TBC, increasing the cyclic life from 9 to 30 hr, when cycled between 25 °C and 1150 °C. [1]

In our approach, an Al_2O_3 interlayer was incorporated using wet-chemical processing, a less expensive and more flexible deposition route. An Al_2O_3 gel was paintbrush-coated onto a plasma-sprayed bond coat, followed by deposition of a nanocomposite Al_2O_3-Y_2O_3-ZrO_2 top coat. The effects of the Al_2O_3 interlayer and the Al_2O_3 content in the top coat on the thermal stability of the coatings were examined.

2. Synthesis of Al_2O_3 Gel and Al_2O_3-Y_2O_3-ZrO_2 Nanocomposites

Al_2O_3 gel was synthesized using chemical precipitation. $Al(NO_3)_6 \cdot 9H_2O$ was first dissolved in distilled H_2O at a concentration of 0.2 M. Ammonium hydroxide (NH_4OH) was added dropwise to the solution until the $pH = 10$, inducing aluminum hydroxide precipitation. The slurry was aged for 3 hr, vacuum filtrated, and washed 3 times with distilled water to remove salts or other impurities. The density of the alumina gel was measured to be 0.05 g Al_2O_3/ml gel.

The Al_2O_3 gel was used as both an interlayer coating and an adhesive additive to the Al_2O_3-Y_2O_3-ZrO_2 materials used in the top layer. Compositions and synthesis of the Al_2O_3-Y_2O_3-ZrO_2 powders were similar to those used in our previous reports.[18] The nanocomposite powders were calcined at 650 °C and 1300 °C for 6 hr prior to coating. When applied as an interlayer, the gel was coated directly onto the substrate using a paintbrush. As an adhesive, the Al_2O_3 gel was mixed with the nanocomposite Al_2O_3-Y_2O_3-ZrO_2 powders, forming a viscous slurry. The Al_2O_3 gel acted as a cement, increasing the mechanical stability of the nanocomposite powders when coated onto the Al_2O_3 interlayer. A slurry consisting of 10 g of nanocomposite powder with 10 ml of Al_2O_3 gel was used as the coating mixture. Prior to coating, the slurry was ball milled for 30 min.

3. Coating of Ni Substrates with Al_2O_3 Interlayer and Al_2O_3-Y_2O_3-ZrO_2 TBC

Metal substrates with and without plasma-sprayed bond coats were used to examine the thermal stability of the TBC systems containing the Al_2O_3 gel interlayer. Initial studies without a bond coat determined the optimum treatment temperature for the Al_2O_3 interlayer. Al_2O_3 gel was paintbrush-coated onto the Ni substrates and dried at 110 °C for 2 hr followed by heat treatment at 700-1000 °C for 1 hr in air. Following the heat treatment, a coating solution consisting of 5 wt% Al_2O_3-1.7 wt% Y_2O_3-93.3 wt% ZrO_2 was deposited and dried at 110 °C for 2 hr. One Ni substrate was coated with only the Al_2O_3-Y_2O_3-ZrO_2 nanocomposite without the Al_2O_3 interlayer. The system with Al_2O_3 interlayer and Al_2O_3-Y_2O_3-ZrO_2 TBC was heat treated at 1150 °C in argon for 1 hr, followed by heat treatment at 1150 °C in air for 1 hr.

The optimum pretreatment temperature for the Al_2O_3 interlayer was evaluated by optical microscopy (see Figure 1). When an Al_2O_3 interlayer was not used, the Al_2O_3-Y_2O_3-ZrO_2 top coat suffered from cracking, as the Ni substrate was visibly exposed in Figure 1(a). Uniform Ni substrate coverage was maintained when the Al_2O_3 interlayer was utilized and pretreated at 700-800 °C (Figures 1(b) and 1(c)). No cracking or flaking of the coatings was observed, indicating good thermal stability. When the Al_2O_3 interlayer was pretreated $\geq$ 900 °C, the coating suffered from slight loss in thermal stability, as cracking of the coatings was present, exposing the underlying Ni substrate (Figures 1(d)-(e)). In further studies, 800 °C was used as the optimal pretreatment temperature for the Al_2O_3 interlayer.

4. Thermal Stability of the Ni-based Substrates with Plasma-Sprayed Bond Coat, Al_2O_3 Interlayer and Al_2O_3-Y_2O_3-ZrO_2 TBC

Following optimization of the pretreatment conditions for the Al_2O_3 interlayer, coatings were applied to Ni-based substrates with plasma-sprayed NiCrAlY-based bond coats. Prior studies indicated that plasma-sprayed NiCrAlY bond coats were the most thermally stable, so they were used as the platform for studying the Al_2O_3 interlayers.[18] Prior to deposition of the top coat, Al_2O_3 interlayers were coated and pretreated at 800 °C for 1 hr. Effects of Al_2O_3 content (5-15 wt%) and calcination temperature (500-1300 °C) on the nanocomposite top coat were examined.

Top coats of nanocomposite powders calcined at 650 °C suffered from cracking and agglomeration due to sintering when heat treated at 1150 °C in argon for 1 hr (Figure 2(a)). In contrast, top coats of nanocomposite powders calcined at 1300 °C were uniform in coating coverage and crackfree (Figure 2(b)). Calcining top coat powders at temperatures equal to or greater than the coating heat treatment temperatures was necessary to ensure good thermal stability of the nanostructured coatings.

Top coats containing 5 wt% and 10 wt% of Al_2O_3 possessed the highest thermal stability, as uniform coatings were maintained following heat treatment at 1150 °C in argon for 1 hr (Figures 2(b)-(c)). When the top coat Al_2O_3 composition was increased to 15 wt%, the mechanical stability of the coating decreased, as evidenced by cracking present in Figure 2(d). The difference in thermal expansion coefficient between Al_2O_3 and ZrO_2 could have resulted in cracking of coating. Intermediate levels of Al_2O_3 (5-10 wt%) potentially improved the oxidation resistance of the top coat without loss in mechanical stability.

All of the tested coatings displayed some loss in coating coverage following extended heat treatments in air at 1150 °C for 10 hr (Figure 3). Top coat containing 5 wt% Al_2O_3 displayed only a slight loss in coating coverage after 10 hr of heat treatment (Figure 3(b)). Compositions containing > 5 wt% Al_2O_3 suffered significant loss in coating coverage after the 10-hr treatment (Figures 3(c) and (d)). Following extended heat treatment (50 hr) in air at 1150 °C, all top coat compositions displayed significant coating spallation due to oxidation of the underlying bond coat and substrate (Figure 4).

5. Oxidation Behavior of Ni Substrates with Al_2O_3 Interlayer and Al_2O_3-Y_2O_3-ZrO_2 TBC

A Perkin Elmer TAC 7/DX thermal analyzer measured weight gain due to oxidation of the coated substrates. Ni substrates were coated with the nanocomposite Al_2O_3-Y_2O_3-ZrO_2 top coat with and without the Al_2O_3 interlayer. The TBC-coated samples were placed in a platinum sample pan and heated to an initial temperature of 600 °C. Samples were then heated from 600 °C to 1100 °C (ramp = 10 °C/min), soaking at 1000 °C for 4 hr, at 1050 °C for 4 hr, and at 1100 °C for 2 hr. Weight gain due to oxidation of the underlying Ni substrates was recorded (Figure 5).

The Al_2O_3 interlayer and nanocomposite top coat provided significant oxidation resistance relative to the uncoated Ni substrate (Table 1). Following the heat treatment at 1100 °C, uncoated Ni substrate had a weight gain of 1.3 wt%. Coated substrate containing the Al_2O_3 interlayer had smaller weight gains. Weight gains for systems with 5 wt%Al_2O_3-1.7%Y_2O_3-93.3% ZrO_2 were 0.77 wt% and 0.87 wt% after heat treatment at 1100 °C in the presence and absence of an Al_2O_3 interlayer.

Al_2O_3 content in the top coat had a negligible influence on the oxidation behavior of the TBC, as several top coat compositions possessed similar weight gains following heat treatment (Table 1). The optimum composition for the nanocomposite top coat was 5 wt%Al_2O_3-1.7%Y_2O_3-93.3% ZrO_2, which displayed superior thermal and mechanical stability when applied onto a Ni-based substrate with a plasma-sprayed NiCrAlY bond coat and an Al_2O_3 interlayer.

6. Conclusions

The TGA results and heat treatment studies demonstrated that the Al_2O_3 interlayer suppressed oxidation of the underlying substrate and enhanced thermal stability of the nanostructured Al_2O_3-Y_2O_3-ZrO_2 TBC. Utilizing Al_2O_3 as an interlayer and an adhesive cement in the top coat provided for an inexpensive and flexible route for the processing of TBC. By utilizing a wet-chemical processing approach for depositing the interlayer and the top coat, the microstructure of the TBC was retained. Such nanocomposite coatings could prove advantageous in TBC applications.

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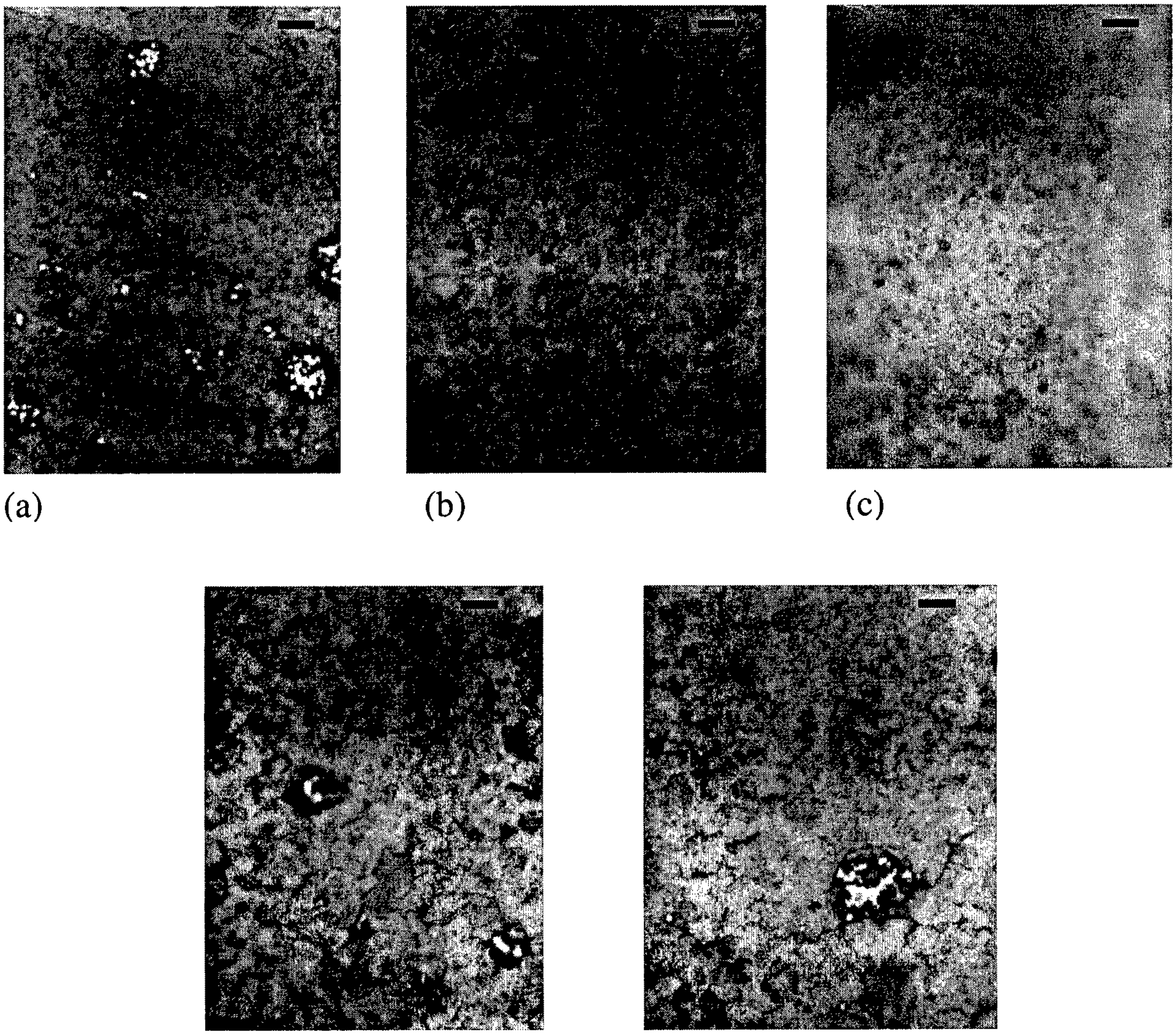
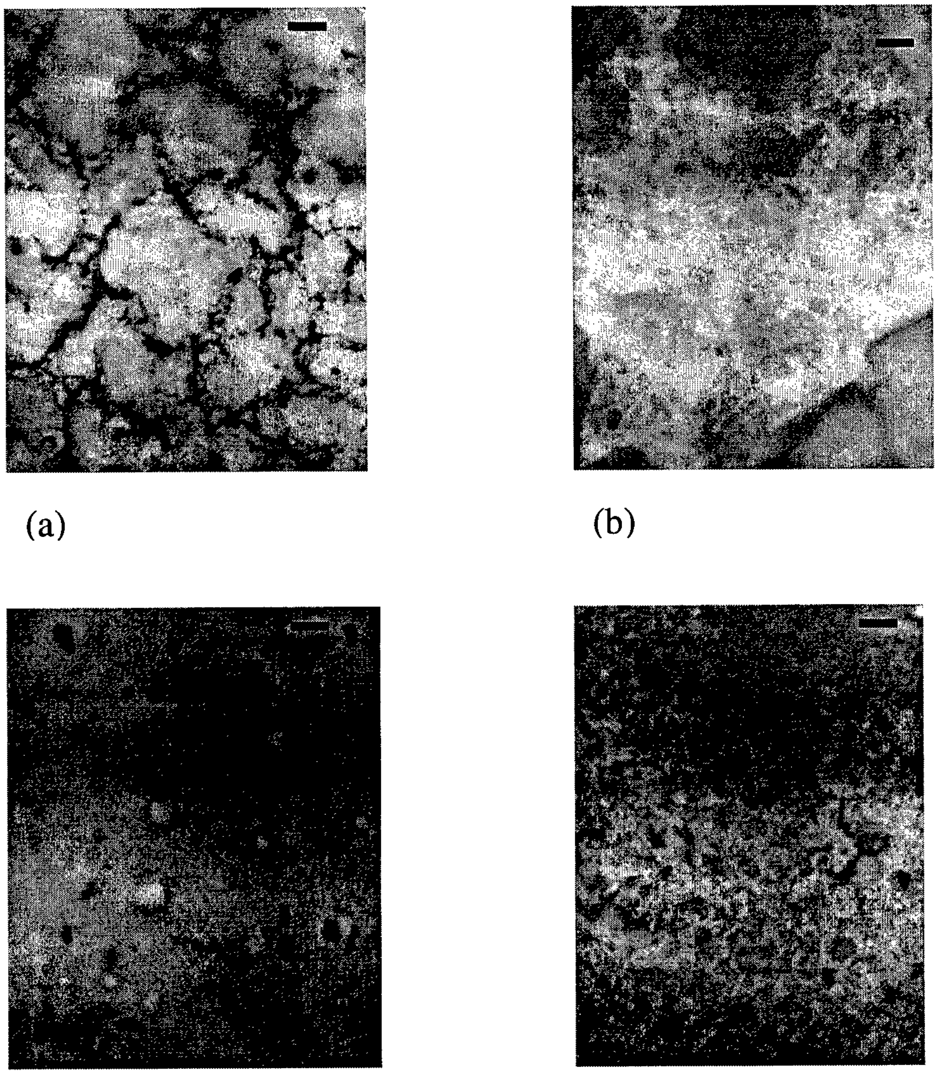


(a) (b) (c)

(d) (e)

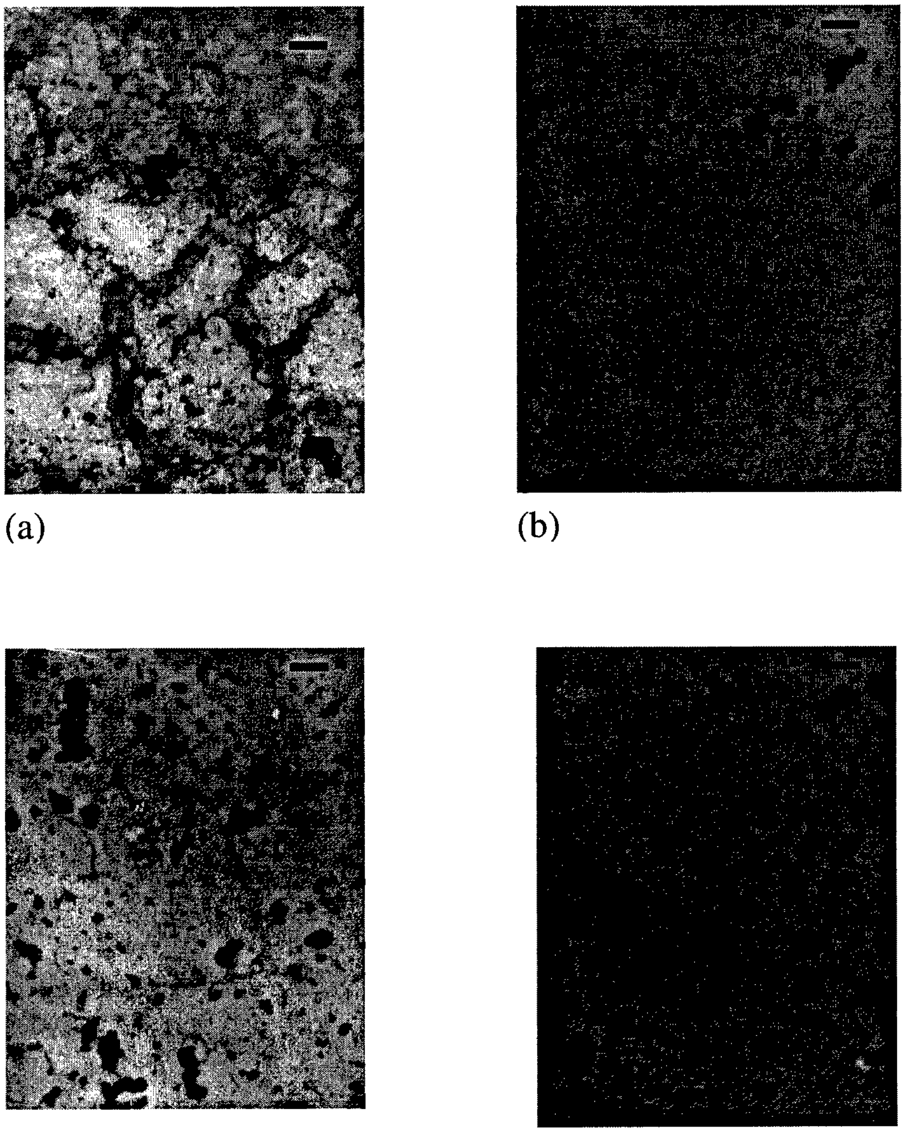
Figure 1. Optical micrographs of Ni substrates coated with (a) no interlayer and (b-e) Al_2O_3 interlayer, and 5% Al_2O_3-1.7% Y_2O_3-93.3% ZrO_2 TBC following heat treatment at 1150 °C in air for 1 hr. The Al_2O_3 interlayer was pretreated at (b) 700 °C, (c) 800 °C, (d) 900 °C and (e) 1000 °C. Scale bar shown is 100 μm.



(a) (b)

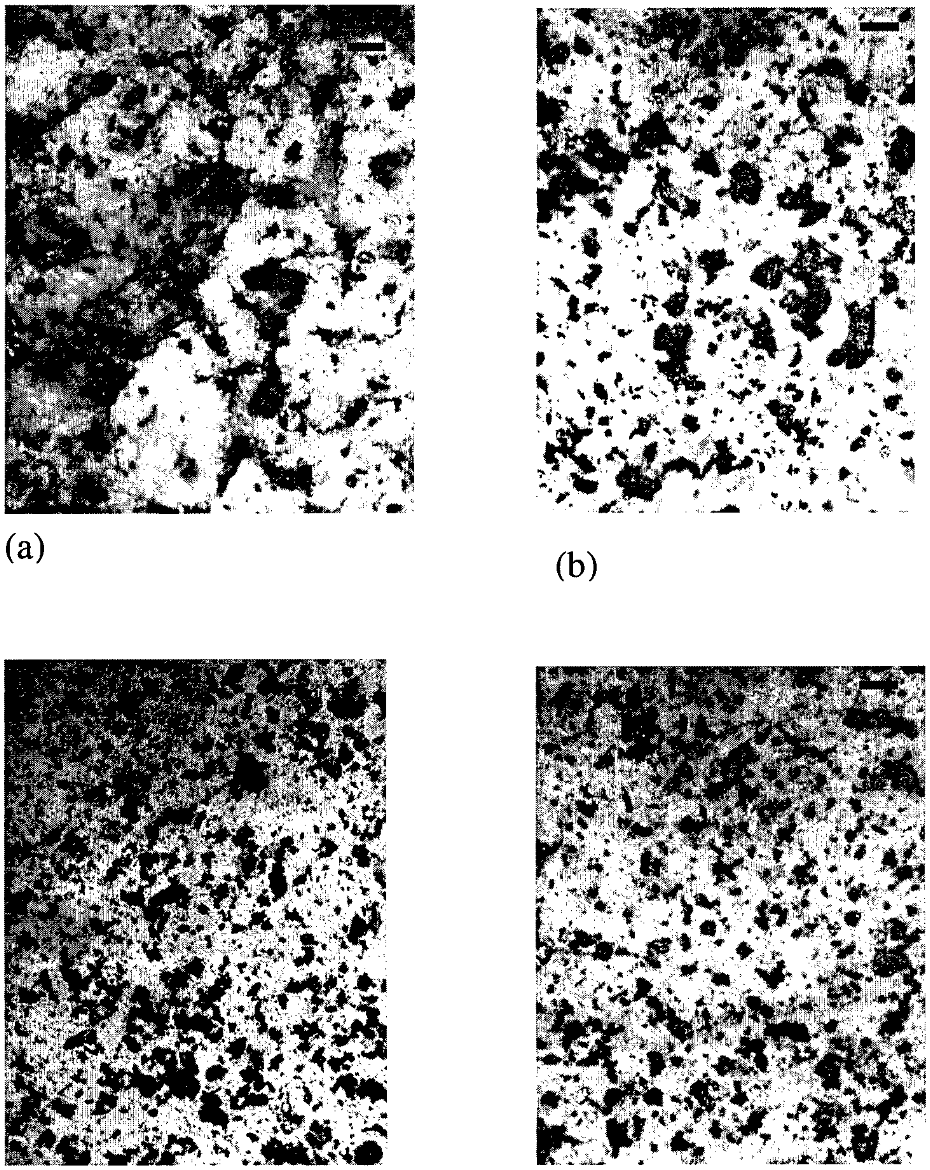
(c) (d)

Figure 2. Optical micrographs of Ni-based substrates with a plasma-sprayed bond coat, an Al_2O_3 interlayer, and a top coat consisting of (a) 5.0% Al_2O_3-1.6% Y_2O_3-93.4% ZrO_2, (b) 5.0% Al_2O_3-1.7% Y_2O_3-93.3% ZrO_2, (c) 10% Al_2O_3-1.5% Y_2O_3-88.5% ZrO_2, and (d) 15% Al_2O_3-1.4% Y_2O_3-83.6% ZrO_2. Top coat powders were calcined at 650 °C in (a) and 1300 °C in (b), (c) and (d). The coated substrates were heated to 1150 °C in argon for 1 hr. Scale bar shown is 100 μm.



(a) (b) (c) (d)

Figure 3. Optical micrographs of samples described in Figure 2. The coated substrates were heated to 1150 °C in air for 10 hr. Scale bar shown is 100 μm.



(a) (b)

(c) (d)

Figure 4. Optical micrographs of samples described in Figure 2. The coated substrates were heated to 1150 °C in air for 50 hr. Scale bar shown is 100 μm.

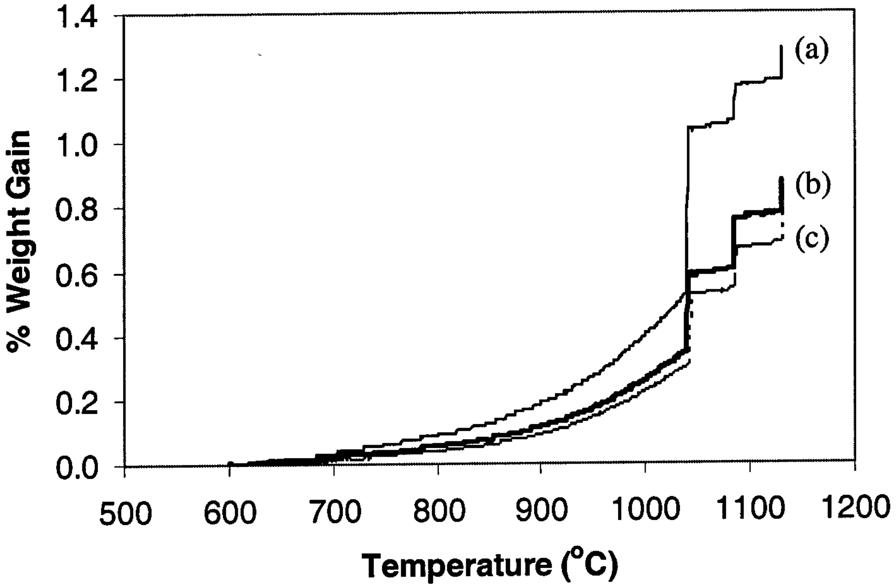


Figure 5. Weight gain as a function of temperature for (a) uncoated Ni substrate, (b) Ni substrate coated with 5% Al_2O_3-1.7% Y_2O_3-93.3% ZrO_2, and (c) Ni substrate coated with Al_2O_3 interlayer and 5% Al_2O_3-1.7% Y_2O_3-93.3% ZrO_2.