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## PREDICTING COATING DEGRADATION UNDER VARIABLE PEAK TEMPERATURES

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### ABSTRACT

The cyclic oxidation behavior of a CoCrAlY coating on a GTD-111 substrate was characterized by thermal cycling between ambient temperature and a variable peak temperature. The initial peak temperature of the thermal cycle was 954°C (1750°F) and tested for  $n_1$  cycles. The peak temperature was then increased to 1010°C (1850°F) for  $n_2$  cycles. Finally, the peak temperature was raised again to 1066°C (1950°F) for  $n_3$  cycles, where  $n_1$ ,  $n_2$ , and  $n_3$  are in the range of a few hundred to a few thousand cycles. In all three cases, thermal cycles consisting of 55 minutes at the peak temperature and 5 minutes heating/cooling were used. Weight change of the test specimens was measured as a function of thermal cycle. The results were compared against a coating life model that treats coating degradation mechanisms including oxidation, spallation, and aluminum loss due to both inward and outward diffusion. Using this model, the influence of the variable peak temperature on coating life was predicted in accordance with experimental results.

### INTRODUCTION

A life prediction methodology has been developed by the present authors for combustion turbine coatings (Chan, 1997; Chan et al., 1997, 1998). This methodology is based on a computer model that treats coating degradation mechanisms such as oxidation, spallation, and diffusion. Lifetime estimation is made based on the amounts of Al content and the volume fraction of the  $\beta$  phase in the coating. The computer model, named COATLIFE, has been evaluated against laboratory data of MCrAlY, aluminide, and PtAl-modified aluminide coatings with promising results. Agreement between model predictions and field data of PtAl coating is also very encouraging (Chan et al., 1997, 1998).

Most of the coating life predictions so far have involved thermal cycling between a set of maximum and minimum temperatures. During service, the coating is expected to experience complex thermal histories including variable temperatures. It is, therefore, important to examine the coating life model under variable temperature conditions to assess its range of capability.

This paper presents the results of an investigation whose aim was to evaluate the applicability of COATLIFE for variable temperature conditions. The cyclic oxidation behavior of a CoCrAlY coating under variable temperature conditions has been characterized by performing multi-step temperature cyclic oxidation tests at peak temperatures of 954°C, 1010°C, and 1066°C (1750°F, 1850°F, and 1950°F). The multi-step temperature cyclic oxidation data are used in conjunction with single-step

temperature cycling data obtained in previous investigations (Chan et al., 1997, 1998) to evaluate the coating life model. In particular, the COATLIFE model is used to predict the response of the coating under both single and multi-step temperature conditions. Comparison of the model calculation and experimental data indicates that the proposed life prediction methodology is applicable for thermal cycling involving variable temperatures.

### EXPERIMENTAL PROCEDURES

For cyclic oxidation testing, flat rectangular test specimens (1.19-inch  $\times$  0.63-inch  $\times$  0.06-inch) were machined from the shank sections of a fully heat-treated GTD-111 blade by using an Electro Discharge Machining (EDM) process. The nominal composition of the alloy (Embley and Kallianpur, 1985) is given in Table 1. The specimens were applied a CoCrAlY coating using Electron Beam Physical Vapor Deposition (EB-PVD) process. Following application of the coating, the specimens were given a partial solution heat treatment at 1121°C (2050°F) and an aging treatment at 843°C (1550°F). The chemical composition of the coating, as determined by the Energy Dispersive Spectroscopy (EDS), in the as-deposited and heat treated condition was Al 9.9%, Cr 24.5%, Ni 2.5%, and Co 60.3%, and Y 0.3% by weight. The initial thickness of the coating was about 250  $\mu$ m (10 mil).

Table 1. Nominal Chemical Composition of GTD-111 Alloy

C	Cr	W	Co	Mo	Al	Ti	Ta	Zr	B	P (max)	S (max)
0.10	0.14	3.8	9.5	1.5	3.0	4.9	2.8	0.03	0.01	0.015	0.008

Cyclic oxidation tests were conducted using a facility designed and fabricated at Southwest Research Institute (SwRI). The test facility consists of a furnace, a forced air cooling system, a coated superalloy frame for suspending specimens, and a computer controlled moving arm that transfers specimens in and out of the furnace and to the cooling system. For cyclic oxidation testing, the specimens were inserted into the furnace, which was maintained at a peak temperature and held at that temperature for 55 minutes prior to moving them into the cooling system. The specimens were air cooled for five minutes and then reinserted back into the furnace. The cyclic oxidation tests were performed at variable peak temperatures in two multi-step thermal cycles, which are summarized in Table 2. The CoCrAlY coated GTD-111 specimens were tested first at a peak temperature of 1750°F (954°C) for 300 or 900 thermal cycles, followed by testing at a peak

temperature of 1010°C (1850°F) for 1700 thermal cycles and then at 1066°C (1950°F) for 500 cycles. The tests at each peak temperature were interrupted at predetermined intervals to weigh the specimens. Following testing, the specimens were sectioned and examined by optical and Scanning Electron Microscopy (SEM). The composition of the phases in the coating was determined using the EDS, while quantitative metallography was then used to determine the amount of  $\beta$ -phase (CoAl) remaining in the coating.

**Table 2. Temperature and Cycle Conditions of Multi-Step Thermal Cycles**

Cycle	Thermal History
A	900 Cycles at 954°C (1750°F)/1700 cycles at 1010°C (1850°F)/500 cycles at 1066°C (1950°F)
B	300 cycles at 954°C (1750°F)/1700 cycles at 1010°C (1850°F)/500 cycles at 1066°C (1950°F)

### COATING LIFE MODEL

The cyclic oxidation model developed by Chan (1997) was used for predicting the life of combustion turbine coatings. The computer code developed for this application has been referred to as COATLIFE, which has been used as a life-prediction tool for various combustion turbine coatings. Figure 1(a) and (b) show, respectively, a schematic of the cyclic oxidation model and the corresponding methodology for predicting the usable life of a coating. The main features of the coating life model are: (1) oxidation kinetics, (2) spallation kinetics of oxides formed on the coating, (3) outward and inward diffusion, (4) overall kinetics of Al loss from the coating due to oxidation, spallation, and inward diffusion, and (5) a life prediction scheme based on a critical value of Al content that corresponds to the complete depletion of  $\beta$  in the microstructure. Since the coating life model has been published, the details of the model will not be repeated here but they are available in earlier publications (Chan, 1997; Chan et al., 1997, 1998).

The remaining life, RL is defined based on the assumption that the useful life of the coating is zero when the volume fraction of the  $\beta$  phase is zero, leading to (Chan et al., 1997, 1998)

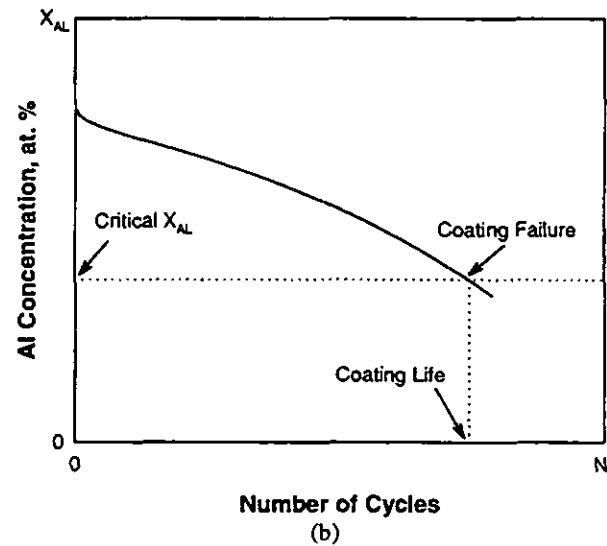
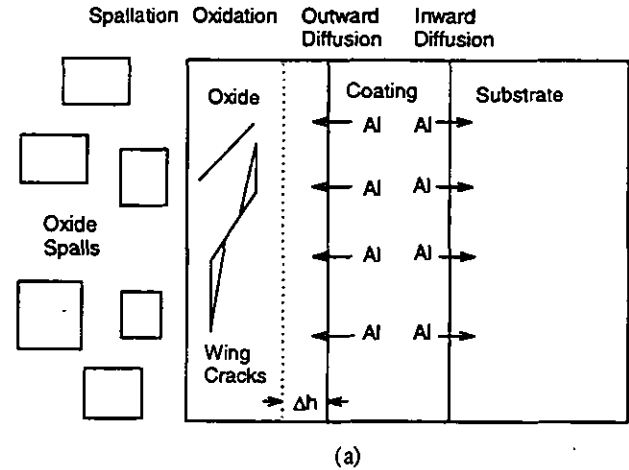
$$RL = \frac{X_{Al}(n) - X_{Al}^*}{X_{Al}(0) - X_{Al}^*} \text{ for } X_{Al}^\beta \geq X_{Al}(n) \geq X_{Al}^* \quad (1)$$

which gives a remaining life of unity when  $X_{Al}(n) = X_{Al}(0)$  but a zero remaining life when  $X_{Al}(n) \leq X_{Al}^*$ . In Eq. (1)  $X_{Al}^\beta$  is the aluminum content in the  $\beta$  phase and  $X_{Al}^*$  is the aluminum content in the  $\gamma$  or  $\gamma$  phase at the appropriate phase boundary in equilibrium with the  $\beta$  phase. The volume fraction of the  $\beta$  phase,  $V_\beta(n)$ , in the coating at the  $n^{\text{th}}$  cycle is calculated using the lever rule and is given by (Chan et al., 1997, 1998)

$$V_\beta = 1 \text{ for } X_{Al} \geq X_{Al}^\beta \quad (2)$$

and

$$V_\beta(n) = \frac{X_{Al}(n) - X_{Al}^*}{X_{Al}^\beta - X_{Al}^*} \text{ for } X_{Al}^\beta \geq X_{Al}(n) \geq X_{Al}^* \quad (3)$$



**Figure 1. Schematics of the coating life model (Chan et al., 1997, 1998): (a) degradation mechanisms treated in the model, and (b) life prediction scheme based on a critical Al content.**

The material constants in the coating life model include those in the oxidation kinetics, spallation kinetics, and diffusion equations. The constants in the oxidation and spallation kinetics equations were evaluated from the weight change curves obtained for cyclic oxidation tests with a constant maximum temperature of 954°C, 1010°C, and 1066°C (1750°F, 1850°F or 1950°F). The same set of material constants was then used in the multi-step temperature cyclic oxidation calculations. Both the single-step and multi-step thermal cycling calculations were performed by following the experimental thermal histories on a cycle by cycle basis until coating failure.

### RESULTS

#### Single-Step Thermal Cycling

The cyclic oxidation results of the CoCrAlY coating subjected to single-step thermal cycling between ambient temperature and a constant

peak temperature are presented in Figure 2, which shows the weight change data for peak temperatures of 954°C, 1010°C, and 1066°C. In all cases, weight gain occurred initially but weight loss set in when the number of thermal cycles increased. Weight loss was significant at 1066°C (1950°F) after a few hundred (e.g., 500) cycles, but it was minimal at 954°C (1750°F). At 1010°C (1850°F), the weight change data showed a large scatter. This set of weight change data was used to determine the oxidation and spallation constants in the coating life model. The calculated weight change curves are compared with experimental data in Figure 2. The comparison indicated that the model reproduced the oxidation behavior of the coating very well.

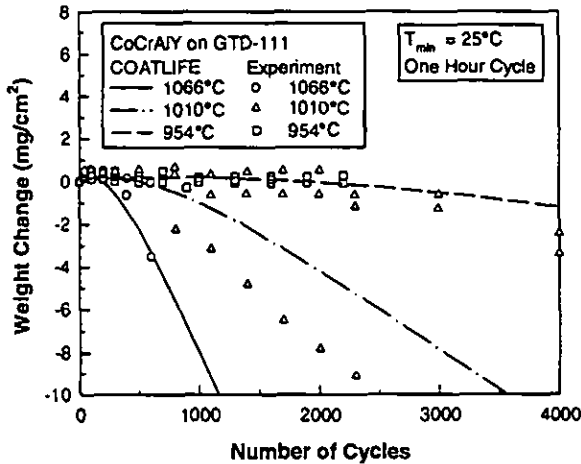


Figure 2. Experimental and calculated weight change curves of CoCrAlY for three maximum temperatures.

Experimental values of the Al content in the CoCrAlY coating after thermal cycling are shown in Figure 3. The corresponding values of the volume fraction of  $\beta$  are shown in Figure 4. Both the Al content and the volume fraction of  $\beta$  decrease with increasing thermal cycles. The rates of Al and  $\beta$  depletion increase with the peak temperature in the thermal cycle. For example, the largest amounts of Al and  $\beta$  depletion occurred at 1066°C, followed by 1010°C, and 954°C.

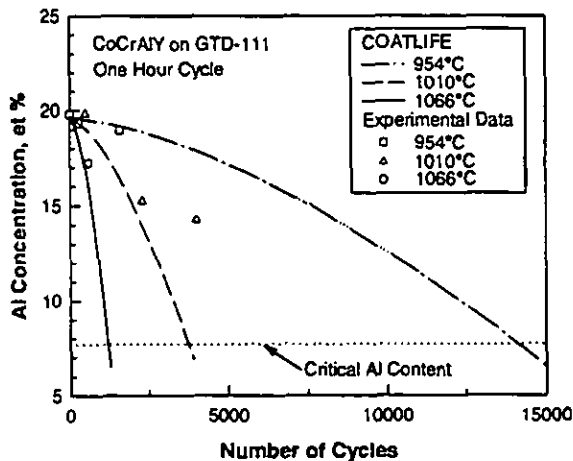


Figure 3. Measured values of the Al content in the coating compared against model calculations

For both Al content and volume fraction of  $\beta$ , model calculations are in good agreement with the experimental data. The model tends to be conservative and underpredicts the Al content and the volume fraction of  $\beta$  in specimens tested at 1010°C due to experimental scatter. Based on a critical Al content of 7.7%, the predicted coating lives for CoCrAlY on GTD-111 are 1200, 3750, and 14100 cycles for one-hour thermal cycle at peak temperatures of 1066°C, 1010°C, and 954°C; respectively. At this critical level of the Al content, the volume fraction of  $\beta$  is zero.

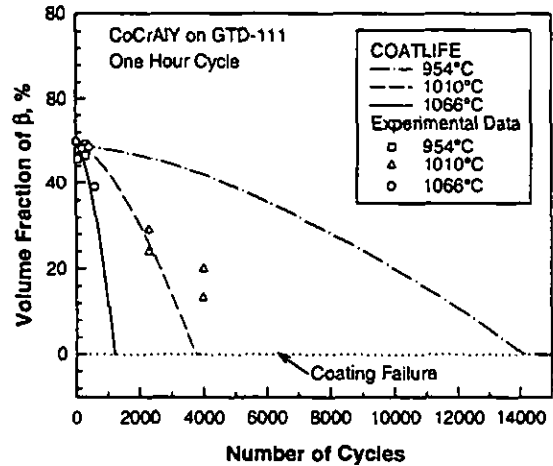


Figure 4. Measured values of the volume fraction of  $\beta$  in the coating compared against model calculations.

### Multi-Step Thermal Cycling

The cyclic oxidation behavior of CoCrAlY subjected to Cycle A is presented in Figures 5 (a), (b), and (c), which show, respectively, the experimental results of weight change, Al content, and volume fraction of  $\beta$ , compared against model calculations. The experimental weight change data indicated that weight loss commenced after 500 cycles at 954°C (1750°C), continued during the 1700 cycles at 1010°C (1850°F), and accelerated at 1066°C (1950°F). This behavior was accurately predicted by the model, as shown in Figure 5(a). The calculated Al content and volume fraction of  $\beta$  for Cycle A are shown in Figures 5(b) and (c). The corresponding experimental values of Al content and volume fraction of  $\beta$  are, respectively, 9% and 4%, which are in excellent agreement with model predictions.

Cyclic oxidation results for Cycle B are compared against model predictions in Figure 6. In this case, weight gain occurred during the 300 cycles at 954°C (1750°F) and weight loss did not commence until after 700 cycles at 1010°C (1850°F). Again, weight loss accelerated when the peak temperature was raised to 1066°C (1950°F). The overall oxidation behavior was accurately predicted by the model, Figure 6(a). The largest discrepancy between model and experiment occurred at the end of the thermal cycle. The calculated values of the Al content and volume fraction of  $\beta$  are compared against experimental results in Figures 6 (b) and (c), respectively. In both cases, Al and  $\beta$  depletion occurred at very slow rates at 954°C (1750°F). As expected, the depletion rates increased when the temperature increased to 1010°C (1850°F) and they accelerated further at 1066°C (1950°F). At the end of Cycle B, the Al content and volume fraction of  $\beta$  were 9% and 3%, respectively. The model predictions are in good agreement with the experimental data, as shown in Figures 6(b) and (c).

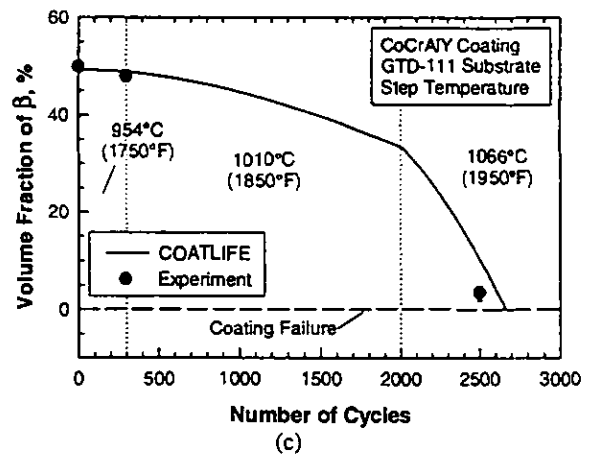
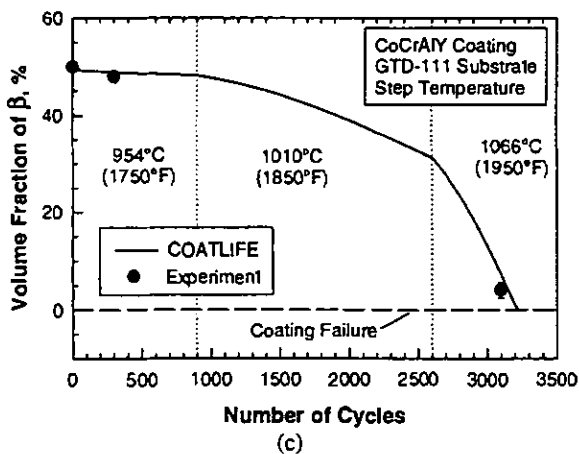
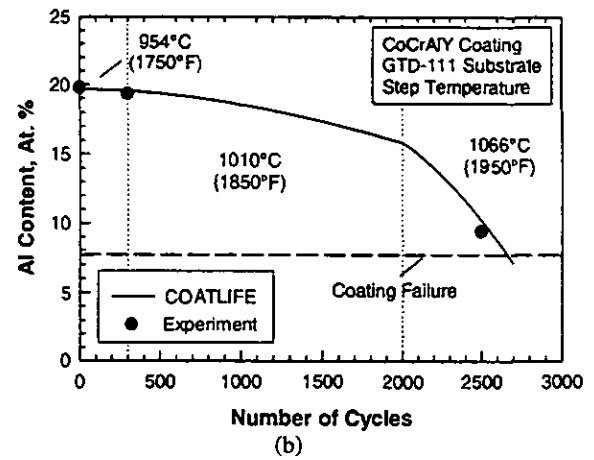
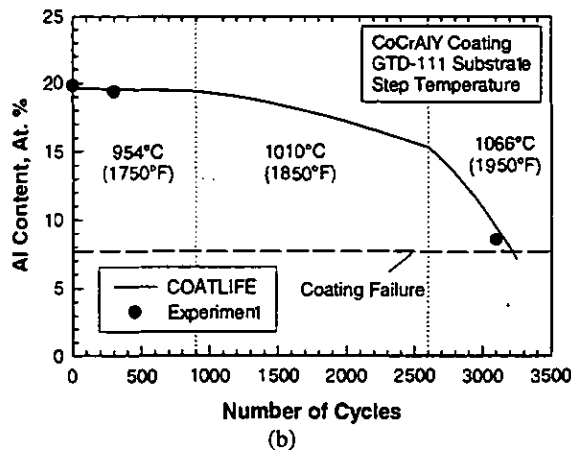
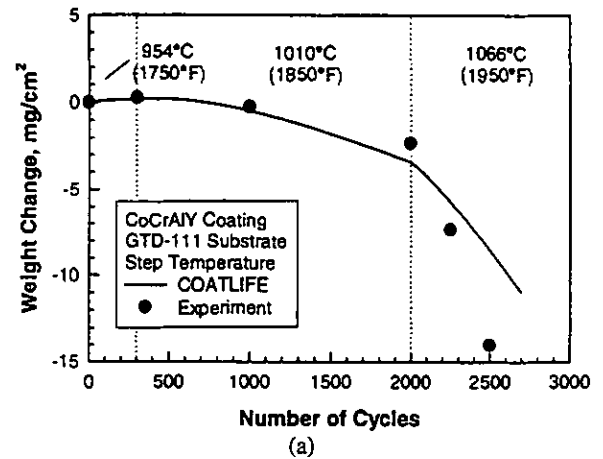
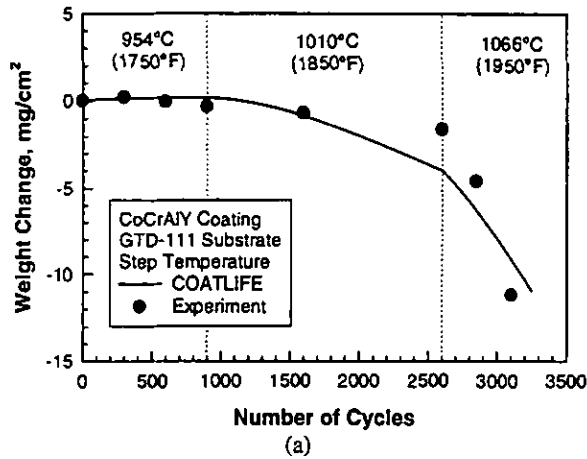


Figure 5. Cyclic oxidation results compared against model predictions for multi-step temperature cycling using Cycle A [900 cycles at 954°C (1750°F)/1700 cycles at 1010°C (1850°F)/500 cycles at 1066°C (1950°F)]: (a) weight change, (b) Al content, and (c) volume fraction of  $\beta$ .

Figure 6. Measured and calculated cyclic oxidation results for multi-step temperature cycling using Cycle B [300 cycles at 954°C (1750°F)/1700 cycles at 1010°C (1850°F)/500 cycles at 1055°C (1950°F)]: (a) weight change, (b) Al content, and (c) volume fraction of  $\beta$ .

Figure 7 shows the microstructure of the CoCrAlY coating after multi-step thermal cycling. The initial volume fraction of  $\beta$  in the coating was about 50%. After thermal cycling, most the  $\beta$  phase transformed into  $\gamma$  as a result of Al loss. The amount of the remaining  $\beta$  phase varied with location in the coating, ranging from 2% to 5% with an average of 3% based on five measurements. Figure 7 also shows that the presence of oxide particles on the original coating substrate boundary. The interdiffusion zone contains large  $\beta$  particles in a  $\gamma$  matrix. The microstructure of the GTD-111 substrate is  $\gamma + \gamma'$ , which remains relatively unchanged after thermal cycling, Figure 7.

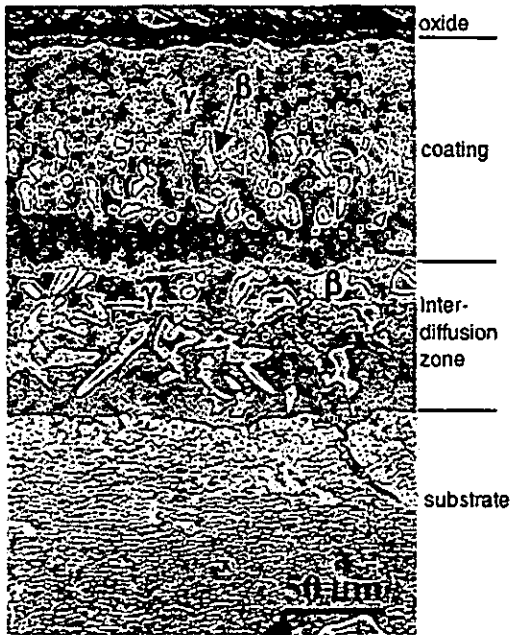


Figure 7. Microstructure of CoCrAlY after multi-step thermal cycling (Cycle B). The volume fraction of  $\beta$  remaining in the coating was about 3.5%.

One of the key assumptions of the coating life model is the formation and propagation of shear cracks with wing-tips in the oxide. The experimental support for the winged shear crack is presented in Figure 8, which shows a shear crack (S) with two wing tips; one of the wing tips propagated in the oxide ( $W_1$ ) and the other ( $W_2$ ) propagated along the oxide/coating interface.

## DISCUSSION

The cyclic oxidation behavior of CoCrAlY exhibited a fairly large scatter at 1010°C. The experimental scatter is most prominent in the weight change data. Figure 2. At the present time, the cause of the large scatter in the weight change data has not been identified, but similarly scatter have been observed in other coatings. Because of the large variation, the use of weight change data as a measure of oxidation resistance or the basis for deducing material constants should be done cautiously and judiciously. Supporting results such as Al content and the volume fraction of the  $\beta$  phase must also be used to confirm any deduction based on the weight change data. Interpretation of weight change data can be difficult when the weight change is zero. Under this circumstance, it is difficult to delineate whether oxidation is negligible or oxidation and spallation occur at identical rates.

The accuracy of the Al content by the EDAX technique is  $\pm 2\%$ . The accuracy of the volume fraction of the  $\beta$  phase is also on the order of  $\pm 2\%$ . Overall, the model predictions of weight change, the Al content, the volume fraction of the  $\beta$  phase, and the coating life are quite remarkable, considering the experimental variations. Experimental data of Al content and the volume fraction of the  $\beta$  phase are not currently available for thermal cycling at the intermediate temperature (1010°C) between 500 to 2000 cycles, but they are to be generated in future work.

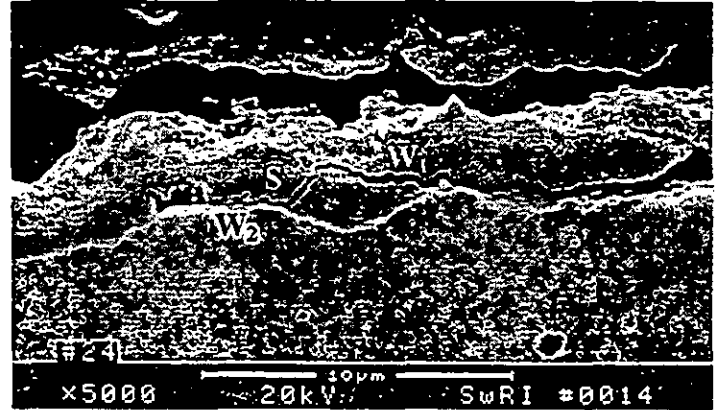


Figure 8. Micrograph shows a winged shear crack (S) with one tip ( $W_1$ ) propagating in the oxide and one tip ( $W_2$ ) propagating along the oxide/coating interface.

## SUMMARY

The cyclic oxidation behavior of a CoCrAlY coating on the GTD-111 substrate was characterized by thermal cycling under a constant or variable peak temperature. Weight change, Al content, and volume fraction of  $\beta$  were measured. The experimental results were used to evaluate an existing coating life model, called COATLIFE, to examine its range of applicability. The evaluation indicated that the coating life model is capable of predicting the useful life of CoCrAlY on GTD-111 for thermal cycling involving a constant peak temperature or variable peak temperatures. The results demonstrate the capability of COATLIFE as a life-prediction tool for combustion turbine coatings.

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