

Temperature dependence of dynamic Young's modulus and internal friction in LPPS NiCrAlY

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The piezoelectric ultrasonic composite oscillator technique (PUCOT), operating near 80 kHz, was used to measure the temperature dependence, in the range 23–1000 °C, of dynamic Young's modulus, E , and internal friction, Q^{-1} , in three compositions of low-pressure plasma-sprayed NiCrAlY: Ni–15.6Cr–5.2Al–0.20Y (16–5), Ni–17.2Cr–11.6Al–0.98Y (17–12), and Ni–33Cr–6.2Al–0.95Y (33–6). Ambient temperature (23 °C) dynamic Young's moduli for the three alloys were 205.0, 199.8, and 231.0 GPa, respectively. In each case, dE/dT was found to be $-0.06 \text{ GPa } ^\circ\text{C}^{-1}$ over temperature ranges 23–800, 23–400 and 600–900, and 23–700 °C, respectively. Internal friction was essentially independent of temperature to about 600 °C (700 °C for the 16–5 alloy), at which point a temperature dependence of the form $Q^{-1} = A \exp(-C/RT)$ was observed. The constant A for the three alloys was determined to be 62.7, 555, and 2.01×10^6 , respectively. The constant C for the three alloys was determined to be 82.8, 111, and 170 kJ/mol^{-1} , respectively. While the physical mechanism is not fully understood, both the pre-exponential constant A and the activation energy C correlate with durability in thermal barrier coatings (TBCs) wherein these alloys are used as bond coats.

1. Introduction

Low-pressure plasma-sprayed (LPPS) NiCrAlY is often employed as the "bond coat", intermediate between the thermally insulating "top coat" and the protected structural member, in thermal barrier coatings (TBCs) [1]. The function of the bond coat is to increase TBC durability (length of time to failure) by protecting the structural member from oxidation and promoting adherence of the top coat. A TBC fails when sections of the top coat separate from the bond coat in single layers. This spalling process is due to cracking in the neighbourhood of the interface between the top coat and the bond coat. The cracking is driven by stresses attributed to oxidation of the bond coat and cyclic thermal expansion mismatch (thermal fatigue).

Intuition suggests that TBC durability should be increased by using bond coats with greater oxidation resistance. Nevertheless, Stecura [2] and Brindley and Miller [3] have reported that the use of some bond-coat compositions with lower oxidation resistance will result in longer top-coat life. For example, high-chromium (35 wt %), low-aluminum (6 wt %) NiCrAlY bond coats provide significantly better TBC durability than the NiCrAlY compositions typically used for overlay coatings (15–22 wt % Cr and $> 6 \text{ wt } \% \text{ Al}$), even though the oxidation resistance of the high-chromium coatings is not as good as that

provided by overlay coatings. Proposed reasons for this finding are that bond-coat elastic modulus, coefficient of thermal expansion, strength, or compositional effects on adhesion may be important factors in TBC durability [1]. Evaluation of the effect of bond-coat elastic modulus on TBC durability (and TBC durability modelling, in general) requires that the elastic moduli of various bond-coat compositions be measured over the range of anticipated service temperatures.

Siemers and Hillig [4] used an ultrasonic pulse-echo technique to measure dynamic Young's modulus of LPPS Ni–16Cr–6Al–0.5Y at ambient temperature; a value of 164 GPa was reported. They also used the same technique to determine the temperature dependence of dynamic Young's modulus in LPPS Ni–22Cr–10Al–1Y where values ranged from 198 GPa at ambient temperature to about 150 GPa at 600 °C. An inflection in the modulus–temperature curve, attributed to the formation of CrNi_3 , was observed near 600 °C. Hillery *et al.* [5] determined the temperature dependence of Young's modulus in LPPS Ni–22Cr–10Al–0.3Y by means of both quasistatic and dynamic tests. The quasistatic tests yielded Young's modulus values of 206 GPa at 20 °C, 180 GPa at 538 °C, and 101 GPa at 760 °C. Data obtained at 982 and 1093 °C were deemed unusable

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because no perceptible elastic range was observed on the stress–strain curve. Dynamic testing yielded dynamic Young’s modulus values which varied in a linear fashion from 200 GPa at 20 °C to 170 GPa at 600 °C. Beyond the linear range, dynamic Young’s modulus values dropped rapidly and decreased to 120 GPa at 1075 °C. All of the compositions tested by Siemers and Hillig [4] and Hillery *et al.* [5] are considered typical of those used for overlay coatings.

This paper reports the results of an experimental study in which the piezoelectric ultrasonic composite oscillator technique (PUCOT), operating near 80 kHz, was used to measure the temperature dependence, from 23–1000 °C, of dynamic Young’s modulus in three compositions of LPPS NiCrAlY: Ni–15.6Cr–5.2Al–0.20Y, Ni–17.2Cr–11.6Al–0.98Y and Ni–33.0Cr–6.2Al–0.95Y (for the sake of brevity, the compositions are hereafter referred to in terms of their approximate chromium and aluminium contents i.e. 16–5, 17–12, and 33–6, respectively). The first two compositions are considered typical of those used for overlay coatings, while the last composition is considered to be a “high-chromium” coating in the sense used elsewhere [2, 3]. The PUCOT is capable of measuring internal friction simultaneously with dynamic Young’s modulus. Because internal friction and dynamic Young’s modulus are complementary material properties, the internal friction results obtained in this study are reported as well.

2. Experimental procedure

2.1. LPPS NiCrAlY

Specimens were prepared by the plasma-spray process [6] in a partial vacuum of approximately 5.3 kPa. The NiCrAlY was sprayed on to a stainless steel pipe (50.8 mm diameter, 3.175 mm wall thickness) cooled internally by argon gas at 276 kPa. NiCrAlY deposits ranged in thickness from 9.5–12.7 mm. The plasma-spray parameters were 75 kW gun power, 450 mm standoff distance, 68 g min⁻¹ powder feed rate, 11 standard l min⁻¹ argon powder gas, 50 standard l min⁻¹ argon arc gas, and 14.2 standard l min⁻¹ argon–3.75% hydrogen auxiliary gas.

The coated pipes were annealed in air for 4 h at 1080 °C, followed by 32 h at 872 °C, to relieve stress and aid in homogenization. The annealed cylinders were examined metallographically to ensure that any region depleted of solute by oxidation or by interdiffusion with the substrate was not included in the dynamic Young’s modulus test specimens. Freestanding cylindrical NiCrAlY specimens were cut from the NiCrAlY deposits by wire electrical discharge machining (EDM). The specimens were cut so that their cylindrical axis was parallel to that of the stainless steel pipe and perpendicular to the spray direction. The freestanding specimens were then centreless ground to final dimensions of approximately 3.175 mm diameter and 60 mm length.

The microstructure of the specimens was characterized by X-ray diffraction (XRD) and by optical and scanning electron microscopy. Specimens of the 16–5 alloy were observed to possess a two-phase micro-

structure consisting of γ (face centred cubic (fcc) Ni–Cr–Al solid solution) and γ' (fcc-ordered Ni₃Al). Specimens of the 17–12 and 33–6 alloys were observed to possess a three-phase microstructure consisting of γ , γ' , and α (body centred cubic chromium).

2.2. The PUCOT

The PUCOT [7] was used to measure dynamic Young’s modulus and internal friction as functions of temperature. With respect to dynamic elastic modulus testing techniques, the PUCOT is classified as a resonance method, i.e. dynamic Young’s modulus is measured at a single frequency, in this case, the frequency of the specimen’s first axial mode. Resonance is attained by joining the specimen to two frequency-matched quartz crystals, thus forming a composite oscillator. An alternating voltage is applied to parallel faces of one crystal (the drive); the piezoelectric effect results in vibrations being excited in the composite oscillator. The inverse piezoelectric effect results in the appearance of an alternating voltage across parallel faces of the second crystal (the gauge). A closed-loop crystal oscillator is used to obtain the drive voltage required to produce a preselected gauge voltage. The oscillator is tuned so that the drive voltage is a minimum, thus indicating resonance. Experimental variables recorded are specimen length and density, l_s and ρ_s , respectively, masses of the specimen, drive and gauge crystals, and three component oscillator, m_s , m_{DG} , and m_{DGS} , respectively, period of the drive and gauge crystals alone, τ_{DG} , and period of the three component oscillator, τ_{DGS} , drive and gauge voltage, V_D and V_G , respectively. The resonant period of the specimen, τ_s , is extracted from the resonant period of the three-component oscillator using

$$\tau_s = (m_s)^{1/2} \left[\frac{\tau_{DG}\tau_{DGS}}{(\tau_{DG}^2 m_{DGS} - \tau_{DGS}^2 m_{DG})^{1/2}} \right] \quad (1)$$

Dynamic Young’s modulus, E , is given by

$$E = 4\rho_s l_s^2 / \tau_s^2 \quad (2)$$

Internal friction, Q^{-1} , is given by

$$Q^{-1} = \frac{2}{m_s C_m} \left(\frac{N\tau_s}{\pi} \right)^2 \frac{V_D}{V_G} \quad (3)$$

where N is the ideal electromechanical transformer ratio and C_m is the capacitance of the gauge voltage measuring circuit.

Measurements using the three-component oscillator are limited by the α to β transformation in quartz, which occurs at 577 °C. This limitation is overcome by inserting a frequency-matched fused-quartz spacer rod between the quartz crystals and the specimen, thus forming a four-component oscillator. The spacer rod and specimen can be lowered into the furnace, while the quartz crystals remain outside at ambient temperature. In this experiment, fused-quartz spacer rods were used for all temperatures except 23 °C. Specimens were allowed to stabilize at temperature for 15 min. An argon gas environment was provided for temperatures of 500 °C and greater.

TABLE I Temperature dependence of E and Q^{-1} at 80 kHz

| Temp. (°C) | Ni-15.6Cr-5.2Al-0.20Y | | Ni-17.2Cr-11.6Al-0.98Y | | Ni-33Cr-6.2Al-0.95Y | |
|---------------|-----------------------|---------------------------|------------------------|---------------------------|---------------------|---------------------------|
| | E (GPa) | Q^{-1} (10^{-6}) | E (GPa) | Q^{-1} (10^{-6}) | E (GPa) | Q^{-1} (10^{-6}) |
| 23 | 205.0 | 20.4 | 199.8 | 24.7 | 231.0 | 31.1 |
| 100 | 199.0 | 38.3 | 195.5 | 33.2 | 225.8 | 204 |
| 200 | 194.0 | 40.1 | 189.0 | 32.2 | 219.7 | 68.5 |
| 300 | 185.0 | 99.7 | 187.1 | 30.1 | 215.0 | 29.8 |
| 400 | 181.2 | 53.1 | 177.1 | 75.1 | 208.5 | 64.0 |
| 500 | 176.4 | 43.7 | 176.9 | 36.0 | 201.4 | 479 |
| 600 | 168.2 | 51.4 | 174.6 | 122 | 196.6 | 154 |
| 700 | 162.7 | 2310 | 167.4 | 712 | 191.5 | 1590 |
| 800 | 154.4 | 5511 | 162.0 | 2240 | 180.6 | 7480 |
| 900 | 137.0 | 13300 | 154.6 | 6210 | — | — |
| 1000 | — | — | — | — | 131.8 | 262000 |

3. Results

Dynamic Young's modulus and internal friction were determined for each of the three alloys at 23 °C, and from 100–1000 °C in 100 °C increments, with the following exceptions: measurements could not be obtained for the 16–5 and 17–12 alloys at 1000 °C because of thermal expansion mismatch-induced cracking of the ceramic cement at the joint between the specimen and the spacer rod; measurements were not obtained for the 33–6 alloy at 900 °C because of limited availability of specimens of the required size. The results are presented in Table I.

4. Discussion

4.1. Dynamic Young's modulus

In the absence of anelastic relaxation, the variation with temperature of dynamic Young's modulus in metals and alloys is linear from below the Debye temperature to near the melting temperature [8]. For the purpose of this study, an alloy is considered to exhibit elastic behaviour over a temperature range wherein such a linear relationship can be demonstrated within the limits of experimental uncertainty. The experimental uncertainty in the calculated values of dynamic Young's modulus can be related to the uncertainty of the experimentally determined parameters used in the calculation through use of the procedure of Kline and McClintock [9]. Based upon their procedure [9], Cook *et al.* [10] reported an experimental uncertainty of 0.5% (at a confidence level of 68%) for dynamic Young's modulus measurements made with the PUCOT. For the present study, it was desired to use a more conservative confidence level of 95%, thus the corresponding experimental uncertainty of 1.0% will be used. The data and least squares fitted lines are plotted for points meeting the criterion for elastic behaviour (Figs 1–3). The error bars indicate the $\pm 1\%$ uncertainty on the calculated values.

For the 16–5 alloy, the linear range extended from 23–800 °C. The fitted line (Fig. 1) was $E = 206.0 - 0.063T$, with $R = 0.998$, where R is the coefficient of correlation. Above 800 °C, the deviation from linearity can probably be attributed to re-resolution of γ' , because the 850 °C isothermal section of the

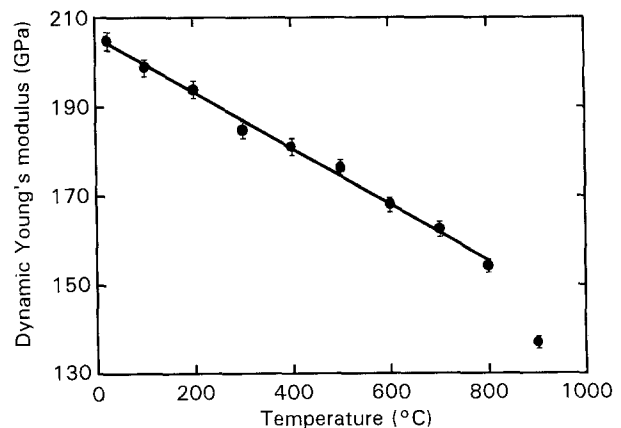


Figure 1 Temperature dependence of dynamic Young's modulus in LPPS Ni-15.6Cr-5.2Al-0.20Y.

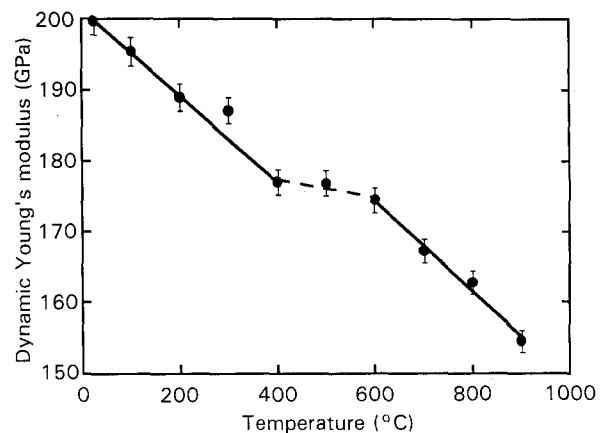


Figure 2 Temperature dependence of dynamic Young's modulus in LPPS Ni-17.2Cr-11.6Al-0.98Y.

Ni-Cr-Al ternary phase diagram [11] predicts a $\gamma + \gamma'$ microstructure, while the 1000 °C isothermal section predicts the existence of γ only.

For the 17–12 alloy, a bilinear relationship was observed. From 23–400 °C, the fitted line (Fig. 2) was $E = 201.3 - 0.061T$, with $R = 0.999$. From 400–600 °C, dynamic Young's modulus remained essentially constant. From 600–900 °C, the fitted line (Fig. 2), was

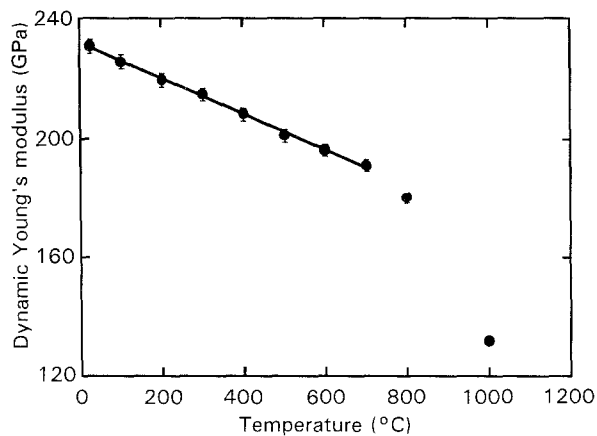


Figure 3 Temperature dependence of dynamic Young's modulus in LPPS Ni-33Cr-6.2Al-0.95Y.

$E = 213.7 - 0.065T$, with $R = 0.994$. If a single line is fitted to the data, three of the ten data points are not fit by the model, while the bilinear approach leaves only the 300 °C data point in non-conformity with the model (possibly experimental error). Two additional features support the bilinear model: first, the atomic bonding in these alloys is similar, and because the dynamic Young's modulus is a measure of atomic bond strength, dE/dT values should be similar. If a single-line model is used, a dE/dT value about 20% smaller than that of the other two alloys is obtained. For the bilinear model, dE/dT values for the upper- and lower-temperature branches are roughly equal to each other and to that of the other two alloys. Second, at 400 °C (the beginning of the discontinuity), there is a small rise in internal friction which is indicative of anelastic behaviour. The discontinuity in the modulus-temperature curve is believed to be due to an order-disorder reaction involving CrNi_3 [4].

For the 33-6 alloy, the linear range extended from 23-700 °C. The fitted line (Fig. 3) was $E = 231.9 - 0.059T$, with $R = 0.999$. Above 700 °C, the deviation from linearity is likely due to re-resolution of γ' in the light of phase-diagram evidence similar to that given for the case of the 16-5 alloy.

It is thus observed that the high-chromium composition has a dynamic Young's modulus roughly 15% higher than that of the two overlay compositions, while dE/dT for all three compositions is basically the same ($-0.06 \text{ GPa } ^\circ\text{C}^{-1}$) within the previously stated temperature ranges. However, the elastic modulus of each of the LPPS NiCrAlY alloys is higher, at all temperatures examined, than that of the plasma-sprayed zirconia (20-60 GPa) typically used in TBC top coats. Because the elastic modulus of the less-stiff material controls the stress level near the interface between the bond coat and top coat, it is doubtful that the differences among bond-coat moduli account for the TBC durability differences observed elsewhere [2, 3].

4.2. Internal friction

In the absence of significant anelastic relaxation, internal friction is relatively insensitive to temperature.

Above about $0.5T_m$, where T_m is the melting temperature, internal friction tends to rise continuously to large values. This effect is known as the "high-temperature background", and is known to be highly structure-sensitive [12]. In this temperature range, internal friction can usually be described by an expression of the form

$$Q^{-1} = A \exp(-C/RT) \quad (4)$$

where R is the gas constant and A and C are empirical parameters whose values are found from the intercept and slope, respectively, of a semilogarithmic plot of Q^{-1} against $1/T$. There is no universally-accepted theory of the high-temperature background, but it is generally agreed that a mechanism involving interactions among dislocations and point defects is involved. The constant A is, therefore, usually considered to be related to dislocation parameters, while the constant C is interpreted as an activation energy.

Based upon the internal friction data in Table I, the high-temperature background apparently begins at about 600 °C (700 °C for the 16-5 alloy). Therefore, the higher temperature data were fitted to Equation 4 and are presented graphically in Fig. 4. For the 16-5 alloy, $A = 62.7$ and $C = 82.8 \text{ kJ mol}^{-1}$ were obtained with $R = 0.998$. For the 17-12 alloy, $A = 555$ and $C = 111 \text{ kJ mol}^{-1}$ were obtained with $R = 0.999$. For the 33-6 alloy, $A = 2.01 \times 10^6$ and $C = 170 \text{ kJ mol}^{-1}$ were obtained with $R = 0.997$.

The most striking feature of these data is the factor of 10000 difference between values of A for the high-chromium composition and the other compositions. Differences in C between the two types of coating alloy are not so dramatic, but exist nonetheless. It is unfortunate that a quantitative theory of the high-temperature background does not yet exist, because both A and C correlate with TBC durability. The activation energies do not correspond to any diffusion process expected to occur in these alloys, but this is not surprising given the frequency of measurement. Conversely, internal friction measurements at lower frequencies might prove useful for future coating alloy development.

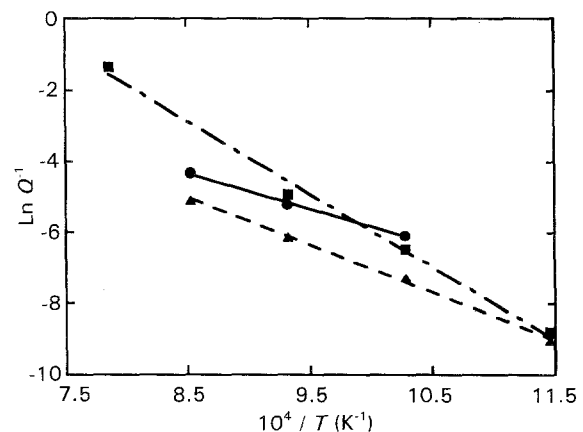


Figure 4 Thermal activation of internal friction in three NiCrAlY alloys: (●) 16-5, (▲) 17-12, (■) 33-6.

5. Conclusion

The temperature dependence of dynamic Young's modulus and internal friction was measured for three LPPS NiCrAlY coating alloys in the temperature range 23–1000 °C. The alloy considered to be "high chromium" in the sense given elsewhere [2, 3] possessed a dynamic Young's modulus 15 % higher than that of the two alloys considered to be typical of those used for overlay coatings. However, the elastic modulus of each of the LPPS NiCrAlY alloys is higher, at all temperatures examined, than that of the plasma-sprayed zirconia typically used as a TBC top coat. Because the elastic modulus of the less-stiff material controls the stress level near the interface between the bond coat and top coat, this study indicates that the differences among bond-coat moduli do not account for the TBC durability differences observed by Stecura [2] and Brindley and Miller [3]. In contrast, the high-chromium alloy possessed internal friction characteristics markedly different from those of the two overlay coatings. Although the nature of the physical mechanism is not clear at this time, it is noteworthy that both internal friction parameters *A* and *C* correlate with TBC durability.

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