

Strength and Modulus of a Molybdenum-Coated Ti-25Al-10Nb-3V-1Mo Intermetallic

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The three-point bend strength, Young's modulus, and vibrational damping of a plasma-sprayed molybdenum-coated Ti-25Al-10Nb-3V-1Mo intermetallic were measured. The bend strength of the intermetallic samples was significantly reduced as a result of the molybdenum coating. This decrease in the strength was attributed to cracks formed in the molybdenum coating during the plasma spraying process. Experimental measurements done using the piezoelectric ultrasonic composite technique (PUCOT) indicated that the modulus and vibrational damping of the coated samples were significantly higher than for the uncoated substrates. Thermal cycling of the molybdenum-coated intermetallic between 600 °C and room temperature revealed a saturation increase in the modulus with a corresponding decrease in the mechanical damping. This behavior was attributed to crack healing occurring in the molybdenum coating during the thermal cycling process.

Keywords

coatings, intermetallic compounds, modulus, strength, Ti-Al intermetallics

1. Introduction

Ti_3AL-BASED INTERMETALLICS show tremendous promise in high-temperature structural applications. These intermetallics have the potential to serve in a variety of environments, depending on the type of application, including jet turbines and internal combustion engine components. These materials have been found to maintain good strength at temperatures up to 1000 °C (Ref 1-4).

Oxidation of these intermetallic materials at temperatures in excess of 500 °C is an important limitation. Since most of the high-temperature environments have an abundance of oxygen, it is necessary to address the oxidation problems in these materials. The resistance of a material to oxidation at higher temperatures is dependent on the potential of the material to form and maintain a protective oxide scale on the surface. Previous studies have shown (Ref 5, 6) that the oxide scale formed on the surface of Ti_3Al-based intermetallics does not adhere well to the surface of the substrate and tends to spall off. The oxide layer formed on the surface of the intermetallic develops discontinuities and does not prevent oxygen from diffusing into the substrate.

The use of plasma-sprayed coatings is a common method of protecting substrates from corrosive environments and high-temperature oxidation. The successful use of a 0.1 mm thick Al_2O_3 coating as an oxidation barrier for these intermetallics has been shown (Ref 7, 8). However, the major disadvantage of Al_2O_3 as a coating material is its inability to withstand large thermal cycles. The Al_2O_3 coatings were observed to spall off after repeated thermal cycling between 600 °C and room temperature. Thermal shock resistance is an important requirement in most of the applications these intermetallics are intended for.

In our present study we have investigated the use of molybdenum as a coating material for Ti-25Al-10Nb-3V-1Mo intermetallic substrates. We envisage the use of such coated intermetallics in applications demanding moderate temperatures (up to 600 °C) and low friction characteristics, including a number of internal combustion engine applications. The bending strength, elastic modulus, and mechanical damping of the molybdenum-coated Ti-25Al-10Nb-3V-1Mo were measured. The effect of thermal cycling on the modulus and mechanical damping was documented through ultrasonic measurements.

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2. Experimental Procedure

2.1 *Materials and Coating Procedure*

The Ti-25Al-10Nb-3V-1Mo intermetallic substrates used in this study were obtained in the form of cast plates from Howmet (Howmet Corporation, Greenwich, CT). The chemical composition of the plates is given in Table 1. The molybdenum coating was applied to the substrate by plasma spraying. The intermetallic plates were sand blasted prior to spraying. A Plasmadyne gun was used for spraying the molybdenum onto the intermetallic substrates. Trace amounts of iron and aluminum (less than 0.02%) were present in the molybdenum powder. Plasma spraying parameters used in the process are given in Table 2. The molybdenum coating had an average thickness of 0.112 mm (standard deviation 0.043 mm). The sprayed plates were cut into smaller samples using a slow-speed diamond saw.

Table 1 Chemical composition of the intermetallic substrate

	Element							
Measurement	**Ti**	**Al**	**Nb**	**V**	**Mo**	**Cu**	**Si**	**Fe**
wt%	56.3	14	23 4	3 87	2.07	0.15	0.1	0.08
at%	60.8	25	10	3	1	(a)	(a)	(a)

(a) Trace concentrations

2.2 *Determination of Bend Strength*

The strength of the coated intermetallic samples was measured in three-point bending. The samples were positioned in a hardened steel fixture and loaded by a central pin on a span of 19 mm. The ratio of loading span to specimen thickness for all the samples tested was 5.8, while the ratio of loading span to specimen width was 7.6. The samples were loaded in an Instron machine with a 5 kN load cell and tested at a crosshead speed of 0.1 mm/min. Eight coated samples were tested.

2.3 *Thermal Cycling*

Three individual samples of similar dimensions were thermally cycled at 600 °C. This temperature was chosen based on proposed use temperatures for such materials. The samples were heated in a box furnace to these temperatures, then were soaked in air for 1 h prior to air cooling to room temperature. Six thermal cycles were applied to each sample. This number was chosen based on our earlier studies (Ref 8), which showed spallation of the Al_2O_3 coating after six thermal cycles. Furthermore, changes in the Young's modulus and mechanical damping saturated after two thermal cycles.

2.4 *Measurement of Elastic Modulus and Damping*

The elastic modulus and vibration damping of the coated samples were measured at room temperature using the piezoelectric ultrasonic composite oscillator technique (PUCOT). Details of the technique are provided elsewhere (Ref 9-13). From the measurement of the mass density and length of the specimen, the resonant period of the drive and gage crystals, the resonant period of the system, and the drive and gage voltages, the values of the Young's modulus, strain amplitude, and vibrational damping were determined.

3. Results and Discussion

The results of a two-parameter Weibull analysis on the strength values of the molybdenum-coated intermetallic and uncoated intermetallic samples are presented in Table 3. The Weibull analysis was carried out using a simplified two-parameter Weibull equation:

$$P(\sigma_f) = 1 - \exp[-\alpha\sigma_f^\beta] \quad \text{(Eq 1)}$$

where P is the probability of failure at Weibull mean stress σ_f, β is the Weibull modulus, and α is the modified scale parameter.

Equation 1 was rearranged as:

$$\ln\ln[1/(1 - P)] = \ln\alpha + \beta\ln\sigma_f \quad \text{(Eq 2)}$$

The probability of failure P was obtained by arranging the strength values of the samples in ascending order, then assigning a probability of failure to each strength value using the estimator

$$P(\sigma_{fi}) = i/(1 + N) \quad \text{(Eq 3)}$$

where $P(\sigma_{fi})$ is the probability of failure corresponding to the ith strength value and N is the total number of samples tested.

The Weibull mean strength (σ_f), standard deviation (sd), and coefficient of variation (CV) were calculated as:

$$\sigma_f = \alpha^{-1/\beta}\,\Gamma[1 + 1/\beta] \quad \text{(Eq 4)}$$

$$sd = \alpha^{-1/\beta}[\Gamma(1 + 2/\beta) - \Gamma^2(1 + 1/\beta)]^{1/2} \quad \text{(Eq 5)}$$

$$CV = 100\ \ sd/\sigma_f \quad \text{(Eq 6)}$$

where

$$\Gamma(n) = \int_0^\infty e^{-x}\,x^{n-1}\,dx$$

The Weibull parameters for the uncoated intermetallic substrates were obtained from a previous study (Ref 8). From the results it is evident that the molybdenum coating decreased the strength of the intermetallic samples significantly. These results were not in agreement with the results of a study on a 0.1 mm Al_2O_3 coating. In that study (Ref 8) it was found that a 0.1 mm Al_2O_3 coating had no effect on the strength of the intermetallic substrate.

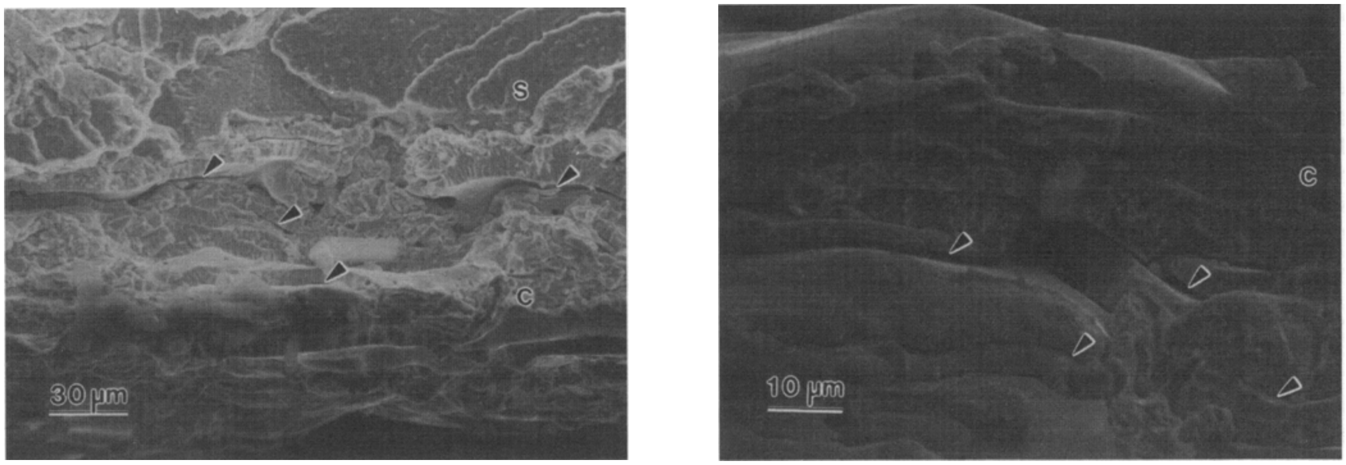
Scanning electron microscopy (SEM) carried out on the fractured surfaces of molybdenum-coated intermetallics revealed the cause for the decreased strength of the coated sam-

Table 2 Plasma spraying parameters used in the coating process

Item	Value
Plasma gun voltage, V	25
Plasma gun current, A	300
Gun to specimen distance, cm	7.5
Arc and powder gas	Argon
Atmosphere	Air

Table 3 Weibull parameters of the uncoated and molybdenum-coated intermetallic samples

	Weibull parameter						
Sample condition	α	β	Weibull mean strength, MPa	Standard deviation, MPa	Coefficient of variation, %	Correlation coefficient
Uncoated	7×10^{-26}	7.59	1751	291	16.6	0.95
Molybdenum-coated	3.3×10^{-20}	6.21	1213	226	18 6	0.93



(a) (b)

Fig. 1 Scanning electron micrographs of the as-coated samples. (a) Cracks (arrows) in the coating and at the coating(C)/substrate(S) interface. (b) High-magnification micrograph of the cracks in the coating

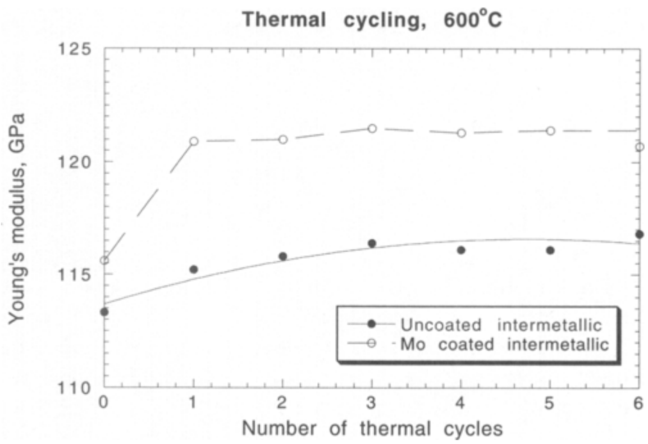


Fig. 2 Variation in the Young's modulus of the uncoated and molybdenum-coated samples with thermal cycling

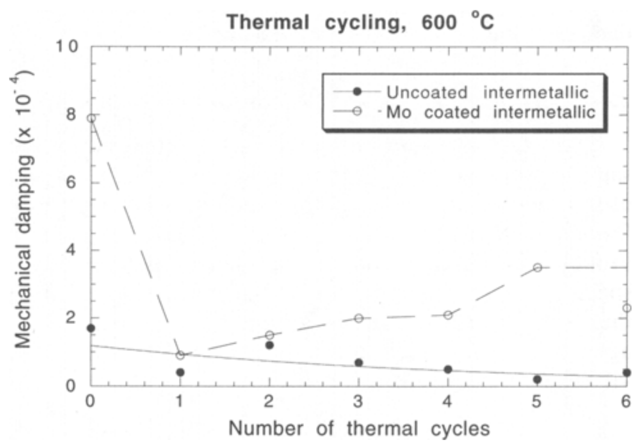


Fig. 3 Variation in the mechanical damping of the uncoated and molybdenum-coated samples with thermal cycling

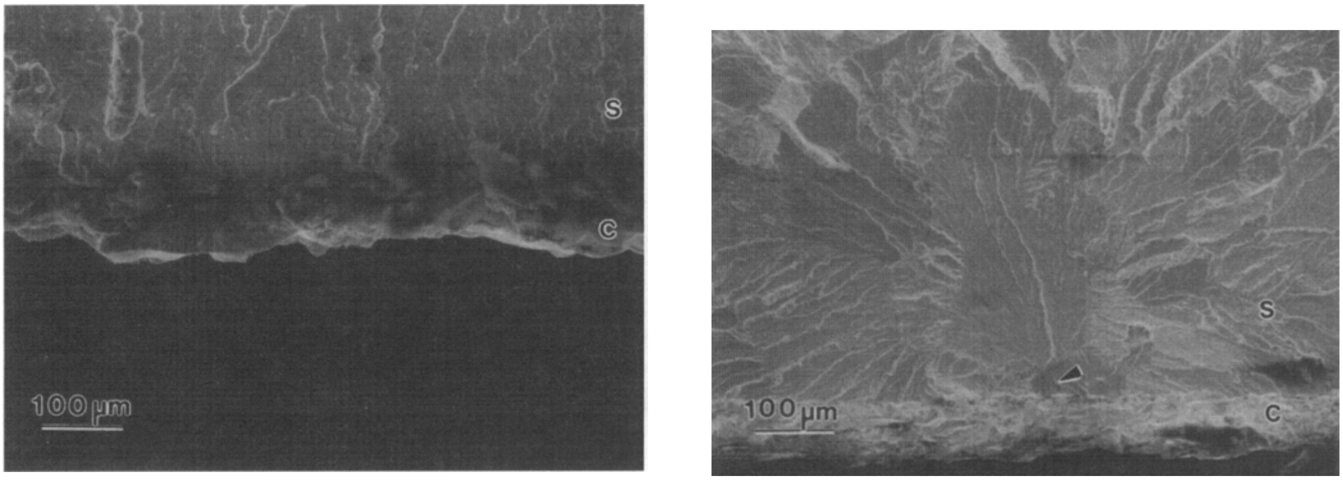
Table 4 Measured Young's modulus (*E*) and damping (internal friction, Q^{-1}) for the uncoated Ti-25Al-10Nb-3V-1Mo

Measurement	*E*, GPa	$Q^{-1} \times 10^{-3}$
1	113.3	4.8
2	113.9	0.6
3	112.8	1.2
4	112.7	1.5
5	113.7	0.5
Average	113.3	1.7
Standard deviation	0.5	1.8

ples. Cracks were observed within the molybdenum coating and at the coating/substrate interface (Fig. 1). The cracks at the coating/substrate interface are in most likelihood a result of the thermal stresses developed as a result of the thermal expansion mismatch between the substrate ($\alpha = 10 \times 10^{-6}$/°C) and coating ($\alpha = 4.3 \times 10^{-6}$/°C), and also as a result of the multiple runs used in applying the molybdenum coating to the substrate. These cracks would have developed during the plasma spray coating process.

Tables 4 and 5 show the results of the elastic modulus and damping measurements on the uncoated and as-coated samples, respectively. The measured modulus value of the molybdenum-coated samples was found to be higher than the measured modulus value of the uncoated samples. This was expected because molybdenum has a higher modulus (280 to 330 GPa) than the substrate (110 to 125 GPa). The damping in the molybdenum-coated samples was also larger than in the uncoated samples, presumably as a result of the presence of cracks in the coating.

The effect of thermal cycling on the stability and integrity of the molybdenum coating was determined, in order to evaluate the capabilities of using such a coating in practical applications. Figures 2 and 3 compare the variation in the Young's modulus and mechanical damping with increasing number of thermal cycles for the uncoated and molybdenum-coated samples, respectively. The uncoated samples exhibited only a slight increase in the modulus with increasing number of ther-



(a) **(b)**

Fig. 4 Scanning electron micrographs of the as-coated samples after one thermal cycle. (a) Absence of cracks as a result of healing. C denotes the coating and S denotes the substrate. (b) High-magnification micrograph revealing crack healing and rod-shaped molybdenum crystals in the coating

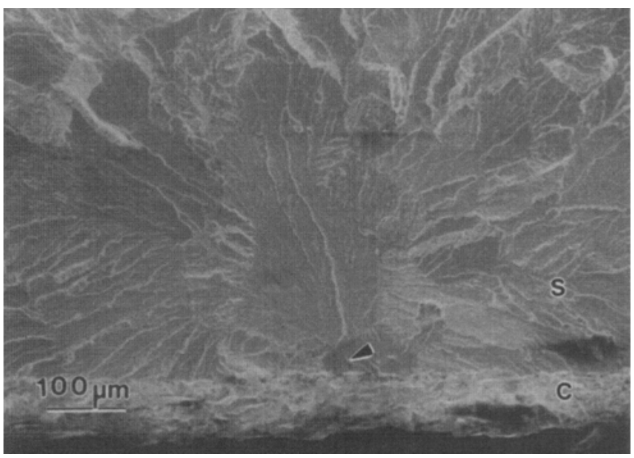


Fig. 5 Scanning electron fractograph revealing the presence of a coating(C)/substrate(S) flaw (arrow). Notice the overall fracture features.

mal cycles, with an attendant decrease in the damping. On the other hand, the modulus of the molybdenum-coated intermetallic samples increased significantly after one thermal cycle. The increase in the modulus was accompanied with a proportional decrease in the mechanical damping. Such behavior is consistent with crack healing. Furthermore, the molybdenum coatings were found to remain intact on the surface of the intermetallic substrates at the end of the thermal cycling experiments.

SEM observations of the surface of the thermally cycled molybdenum-coated intermetallic sample revealed the cause of increasing modulus and decreasing damping with thermal cycling. The cracks in the molybdenum coating formed during the plasma spraying process were observed to heal as a result of the thermal exposure (Fig. 4). The crack healing process was probably aided by the presence of trace amounts of aluminum in the molybdenum coating. The crack healing process was

Table 5 Measured Young's modulus (*E*) and damping (internal friction, Q^{-1}) for the 0.1 mm molybdenum-coated Ti-25Al-10Nb-3V-1Mo

Measurement	*E*, GPa	$Q^{-1} \times 10^{-3}$
1	116 4	8.4
2	115.9	10
3	114.6	6.1
4	115.2	4.2
5	115.8	11
Average	115 6	7.9
Standard deviation	0.7	2.8

also accompanied by significant grain growth in the coating. The increase in the modulus and decrease in damping are a direct consequence of this process.

Although bend strength measurements were not conducted on the molybdenum-coated samples after thermal cycling, we would expect the strength values of the coated samples to be comparable to those of the uncoated samples after one thermal cycle. Crack healing occurring during the thermal cycling would prevent strength sensitization of the substrate material.

Failure in all the coated intermetallic samples was initiated by failure of the coating on the tensile surface of the bend samples. Failure in the coating on the tensile surface in turn initiated a flaw at the coating/substrate interface and led subsequent failure of the coated system (Fig. 5). Fracture of the intermetallic substrate was of a "cleavage" type.

4. Conclusions

Although molybdenum has attractive properties as a coating material for Ti-25Al-10Nb-3V-1Mo, cracks formed in the coating during the plasma spraying process reduce the strength of the coated system. Thermal cycling of the coated samples at 600 °C was found to heal the cracks formed in the coating during the spraying process. This was reflected as a positive increase in the modulus and a decrease in the mechanical damping. Fracture of the coated samples initiated at flaws on the tensile surface of the sample. Fracture of the coated intermetallic samples exhibited "cleavage" features, similar to those observed on the uncoated samples. These results demonstrate the need for a crack healing heat treatment to be applied to the coated samples prior to use.

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