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Effects of Atomic Oxygen on the Thermochromic Characteristics of VO_2 Coating

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Thermochromic VO_2 coating is currently being developed for smart spacecraft thermal radiator application. Concerning the potential space environmental effects, in this study, coating samples are subjected to exposure to a ground-based atomic-oxygen flux for the equivalent of six months and three years in a typical low-Earth-orbit environment. Mass loss of the coating samples because of the exposure to atomic oxygen is measured. Characterization of total hemispherical emittance of the coating before and after atomic-oxygen exposure indicates that the atomic-oxygen erosion affects the thermal-optical performance of the coating to some extent. Detailed x-ray photoelectron spectroscopic analysis of the coating samples are performed, and an increase in the oxygen concentration in the outermost layer of the coating because of the atomic-oxygen exposure is identified. A possible mechanism for the change in thermo-optical property of the coating is discussed.

Introduction

THERMAL control has been a challenging technical issue in design of spacecraft because of the extreme thermal environment in space and constant drive to reduce the mass, volume, and power consumption of thermal control subsystem. Radiator, heater, and associated control unit constitutes a conventional thermal control subsystem. However, such a thermal control subsystem is bulky, heavy, and expensive,[1] particularly for high-power-consumption spacecraft. As the density of instruments on the spacecraft tends to be higher and the mission tends to be more complex, thermal control subsystem of higher performance in terms of mass, volume, and cost reductions and design simplicity than the conventional technique is needed. To meet these requirements, several technologies are currently under study and development, such as a microelectromechanical systems (MEMS)-based micromechanical louver[2] and the smart radiator using either thermochromic or electrochromic coatings.[3] Of particular interest is the thermochromic-coating-based smart thermal radiator, because of its passive mechanism and no need for sensor, control unit, and power consumption.

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VO_2 is a typical thermochromic material, which changes its thermal emittance, and the transmittance and reflectance, because of a metal-insulator phase transition upon change of its temperature.[4] By application of such material to the surface of spacecraft thermal radiator, it can be used to regulate heat rejection into deep space so as to achieve a passive thermal control for the spacecraft. Through doping, the transition temperature can be adjusted to meet the specific requirement for the spacecraft thermal control.[5] Coating can be deposited on different substrates using various methods including chemical vapor deposition,[6] electrobeam evaporation,[7] rf sputtering,[8] sol-gel technique,[9] and pulsed laser vacuum deposition.[10] Recent works by Kruzelecky et al.[11] and Soltani et al.[4] demonstrate that a tuneability of ~60% in emissivity of VO_2 coating can be achieved by proper control of the stoichiometry and microstructure of the coating. However, there is a concern that the space environment, particularly the atomic oxygen, might degrade the performance of the coating.[12] Such concern also arises from the fact that there exist several phases, such as VO_2 and V_2O_5, in the V-O compound family,[13] and atomic-oxygen bombardment on the coating can alter its surface stoichiometry composition and consequently its thermo-optical performance. It is for these reasons that in this study a ground-based atomic-oxygen exposure experiment on the coating samples is conducted. The objective is to determine the potential effects of atomic-oxygen flux on the thermochromic behavior of the coating and to understand the associated mechanism to facilitate the further technology development.

Experiment

Samples of 2-cm diam are prepared by depositing VO_2 coating on aluminum alloy substrates using laser-ablation deposition technical.[4] The reason to use aluminum instead of silicon as the substrate is because the aluminum is the standard material for spacecraft thermal radiator. A metallic vanadium target was used. A pulsed laser beam generated by a XeCl Excimer laser at a wavelength of 308 nm and pulse duration of 20 ns is introduced into the deposition chamber through a quartz window and focused by quartz lens on the target. The deposition is performed in a controlled gas phase

consisting of an O_2 and Ar gas mixture at a pressure of 90 mtorr so that the reaction between metallic vanadium atom vapor and oxygen produces desired VO_2 instead of other forms of vanadium oxide, such as V_2O_5. The substrate is heated and maintained at 520°C to facilitate the growth of polycrystalline VO_2 thin film. The final thickness of the coating after deposition is approximately 150 nm.

The microstructure of the coating samples is first analyzed using the x-ray diffraction (XRD) technique (Philips Diffractometers). The analysis is to determine crystalline structure of the coating and particularly whether a form of vanadium oxide other than VO_2 exists. A JOEL-6300F scanning electron microscope (SEM) was used to observe the surface microstructure of the coating, such as the surface texture and crystallization of the coating. An important objective of this study is to understand the mechanism of the potential effects of atomic oxygen on the microstructure of the VO_2 thermochromic coating. For this purpose, the surface of the coating samples before and after atomic-oxygen exposure is specifically analyzed using an ESCALAB 220I-XL x-ray photoelectron spectrometer (XPS) to determine possible changes in its surface chemistry.

The atomic-oxygen exposure experiment on the coating samples is performed using the Canadian Space Agency's space simulation apparatus. It is a rf plasma-based atomic-oxygen generator. Vacuum is generated using a Danielson Tribodyn 200/57 three-module molecular drag pump, with typical operating pressure at ~100 mtorr inside the test chamber for atomic-oxygen flux to be produced, although before the introduction of oxygen for producing atomic oxygen pressure on the order of 10^{-4} torr was achieved. The oxygen flow rate is set to 15 cc/m. Previous experiments on the characterization of the facility indicated that the atomic-oxygen source is approximately of energy level of 0.1 eV. Two coating samples were used in the atomic-oxygen exposure experiment. The exposure times were 2 and 12 h for the first and second samples, respectively. To determine the effective atomic-oxygen fluence so as to determine the equivalent low-Earth-orbit (LEO) exposure time, Kapton thin film was used as a witness sample during the atomic-oxygen exposure experiment in accordance with ASTM Standard E 2089-00. The change in thickness of the Kapton witness sample is used to calculate the effective fluence. The masses of two VO_2 coating samples before and after atomic-oxygen exposure are also measured in accordance with an American Society for Testing and Materials (ASTM) standard in anaerobic chamber using a microbalance with an accuracy of 0.002 mg.

Measurement of total hemispherical emittances of coating samples before and after atomic-oxygen exposure is performed using an AE Emissometer in accordance with ASTM-1371-04 testing standard. Standard samples (a blackbody and an aluminum samples), which are kept at same temperature as that of the testing sample, are used for calibration each time the measurement is performed. A series of measurements at different temperatures ranging from 25 to 65°C is performed to determine the thermochromic behaviors (change in total hemispherical emittance with respect to the change of temperature) of the coatings.

Experimental Results and Discussion

Figure 1 shows the result of XRD analysis of VO_2 coating sample deposited on an aluminum substrate. Because of the penetration of x-ray through the VO_2 coating, the diffraction peaks from the aluminum substrate are picked up and are relatively strong. The VO_2 diffraction peak is easily distinguished although it is relatively weak, indicating probably imperfect crystallization.

Concerning the effect of atomic oxygen on the coating, the mass losses of the coating samples subjected to atomic-oxygen exposures were measured. Table 1 lists the parameters of atomic-oxygen exposure experiment and the mass losses that occurred on two samples. Mass loss of the coating sample after equivalent six months LEO exposure was found to be too small to be accurately measured (within the error of microbalance). However, when the equivalent LEO exposure time increases to three years, mass loss of 0.018 mg for the sample of 2-cm diameter was measured. Giving the density[14] of VO_2 of 4.34 g/cm^3, the atomic-oxygen reaction efficiency Re of the

Table 1 Parameters of atomic-oxygen exposure experiment on VO_2 coating samples[a]

Parameter	Sample 1	Sample 2
Exposure time, h	2	12
Effective fluence, atoms/cm^2	1.56×10^{21}	9.5×10^{21}
Equivalent LEO exposure time	~6 months	~3 years
Mass loss, mg/cm^2	Negligible	0.006
Reaction efficiency ($\times 10^{-27}$ cm^3/atom)	——	0.13

[a]Calculation is based on typical LEO AO flux of 1×10^{14} atoms/(cm$^2 \cdot$ s) (Ref. 15).

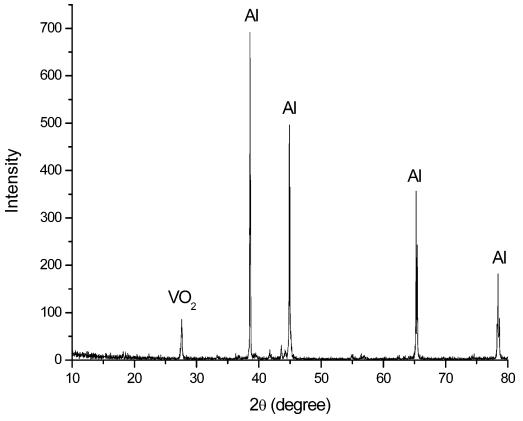

Fig. 1 XRD pattern of VO_2 coating deposited on aluminum substrate.

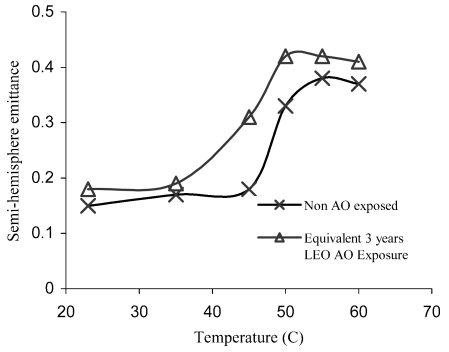

Fig. 2 Effect of AO exposure on the total hemispherical emittance of the VO_2 coating with respect to the change of temperature.

VO_2 coating can be calculated according to Eq. (1)[15]:

$$R_e = \text{volume of material lost}/F = (\Delta M/\rho)/F \qquad (1)$$

where ΔM is the mass loss of the sample for given surface area (g/cm^2), F the fluence of atomic oxygen (atoms/cm^2), and ρ the density of the material (g/cm^3).

From this result, it can be seen that the atomic-oxygen reaction efficiency (0.13×10^{-27} cm^3/atom) of the VO_2 coating is in the same order of magnitude as that of the SiO_2 protective coating ($<0.8 \times 10^{-27}$ cm^3/atom) for materials protection in the LEO environment. In other words, the surface erosion of VO_2 coating by atomic oxygen is rather limited from the mass loss point of view. However, degradation or change in the thermo-optical properties of the coating cannot be ruled out because other factors, such as the change in surface texture[16] and stoichiometry, can still affect the thermo-optical properties of the coating.

Figure 2 shows the thermochromic behaviors of VO_2 coating sample before and after equivalent three years LEO atomic-oxygen exposure. A significant feature of the thermochromic characteristic of the VO_2 coating is that its thermo-optical properties change drastically within a relative narrow temperature range, as confirmed by previous studies.[4,11] It can be seen from Fig. 2 that atomic-oxygen exposure elevates overall total hemispherical emittance

of the coating and also broadens the transition temperature range slightly. In a study by Dillon et al.[17] on VO_2 coating deposited on a single crystal Si substrate using the sputtering process, it was also found that plasma oxygen bombardment tends to increase the thermal emittance of the coating, although specific causes could not be identified. The VO_2 coating samples under this study, which are deposited on aluminum substrate by a laser ablation process, are somewhat different from samples used by Dillon et al.[17] in terms of thermo-optical properties, probably because of the difference in coating/substrate interfacial structure and deposition conditions. However, one conclusion that can be drawn from this experiment is that atomic oxygen can generally affect the thermo-optical property of VO_2 coating to an extent.

Characterization of the microstructure of the VO_2 coating before and after atomic-oxygen exposure was performed. Figure 3 shows the SEM observations of the surface of the coating samples before and after atomic-oxygen exposure. By comparison, it is evident that a small number of surface defects (holes) are created after the atomic-oxygen exposure. However, the creation of the defects of this size (up to a micrometer) is somewhat puzzling because stoichiometric VO_2 is not a volatile material. A possible explanation is that, on one hand, VO_2 coating has relatively high density of crystalline structure defects as indicated by weak XRD peak while on the other hand, the atomic-oxygen is quite reactive and can effectively introduce structure defects in oxide crystalline material through mechanisms of substitution, vacancy, and interstitial.[18] Upon atomic-oxygen exposure, the density of structure defects in the VO_2 coating is likely to increase substantially. This can result in possible concentration of defects at certain sites, forming small holes on the surface, as observed by the SEM. The formation of microscale surface defects can increase the microsurface roughness of the coating. This can be a contributing factor to the overall increase in the thermal emittance of the coating, because thermal emittance generally increases with the increase of surface microroughness.

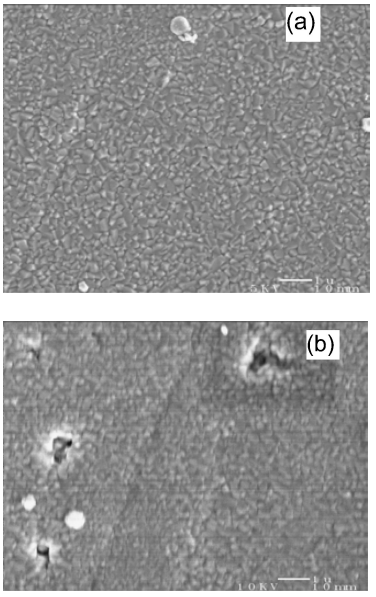

Fig. 3 SEM images of VO2 coating surface a) before and b) after equivalent three years of LEO atomic-oxygen exposure.

Characterization of the surface chemistry of the VO_2 coating before and after atomic-oxygen exposure was further performed. Figures 4a–4c show the XPS spectra of the VO_2 coating before and after equivalent six months and three years of LEO atomic-oxygen (AO) exposures. Quantitative analysis and comparison of the intensity, binding energies and half-widths of O_{1s}, $V_{2p1/2}$, and $V_{2p3/2}$ are shown in Table 2. It can be seen that after exposure to atomic oxygen for an equivalent three years in the LEO environment the

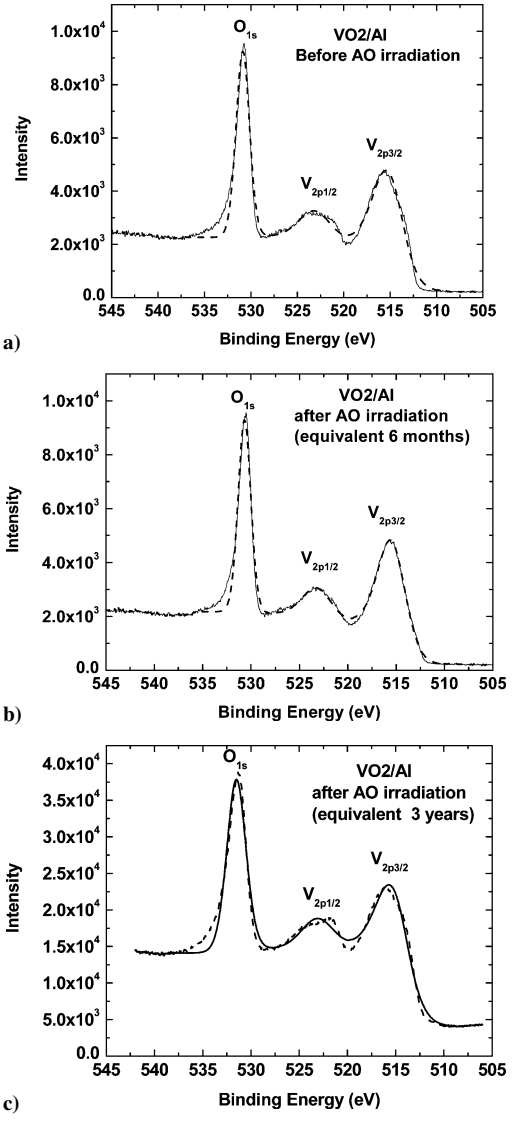

Fig. 4 Comparison of the experimental (——) and fitted (– – –) XPS spectra of VO_2/Al coating sample a) before atomic-oxygen exposure, b) after atomic-oxygen exposure for equivalent six months in a typical LEO environment, and c) after atomic-oxygen exposure for an equivalent three years in a typical LEO environment.

Table 2 Comparison of the intensity, binding energies, and half-widths of VO_2 core levels before and after atomic-oxygen irradiation

	O_{1s}			$V_{2p1/2}$		$V_{2p3/2}$	
Sample	Intensity	Position, eV	Width, eV	Position, eV	Width, eV	Position, eV	Width, eV
VO2/Al before AO exposure	1.0×10^4	530.8	1.7	523.1	3.8	515.1	3.7
VO2/Al exposed to AO for equivalent six months in LEO	1.0×10^4	530.6	1.6	523.1	3.5	515.4	3.3
VO2/Al exposed to AO for equivalent three years in LEO	3.7×10^4	531.5	2.3	523.1	3.8	515.2	3.9

intensity of the O_{1s} peak increases significantly, and its position shifts from 530.8 to 531.5 eV, an increase of 0.7 eV, and its half-intensity width increases from 1.7 to 2.3 eV. The increase in intensity of the O_{1s} peak is a clear indication of the increase in oxygen concentration in the outermost layer (<100 Å) of the VO_2 coating. This is further confirmed by quantitative analysis that the ratio of oxygen (O) to vanadium (V) for the coating has increased from stoichiometrically balanced 2.0 to 2.1 after equivalent three years of LEO atomic-oxygen exposure. Such an increase in O/V ratio certainly could create a stoichiometrical imbalance between O and V in terms of VO_2 coordination, and consequently, a large number of vacancies (defects) for vanadium atoms can be generated in the crystalline structure. The defects reduce the energy bandgap for photon emission. This is probably the main reason why the thermochromic behavior of the VO_2 coating is affected by atomic oxygen to some extent.

Conclusions

In this study, a thermochromic VO_2 coating sample, which is being developed for smart spacecraft thermal radiator application, is subjected to a test in ground-based atomic-oxygen flux to determine the potential effects of space environment on its thermo-optical property. Equivalent six months and three years LEO AO exposure experiments were performed on two samples, respectively. The experiment results show that VO_2 coating tends to have very good resistance to the atomic-oxygen erosion if purely from the mass-loss point of view. However, characterization of thermal emittance of the coating before and after atomic-oxygen exposure indicates that the atomic-oxygen exposure can affect the thermal-optical performance of the coating to an extent, increasing overall total hemispherical emittance and slightly broadening the transition temperature range. SEM and XPS analysis of coating samples before and after the atomic-oxygen exposure were performed to explore the causes for such change. The analysis suggests that an increased density of surface and crystalline structure defects, caused by atomic-oxygen bombardment, is probably the main reason responsible for the changes in the thermo-optical property of the coating.

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