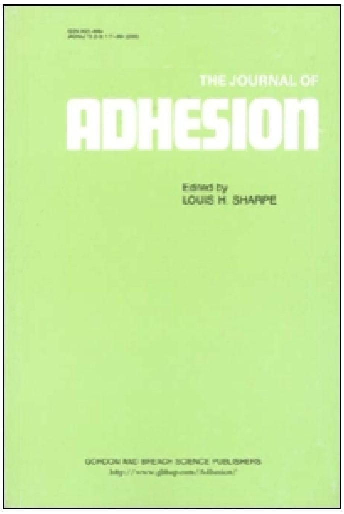
This article was downloaded by:
On: *22 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



The Journal of Adhesion
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

Interfacial Characterization of Epoxy-bonded Maraging Steel

H. Dodiuk[a]; N. Fin[a]; A. E. Yaniv[a]; S. Kenig[a]
[a] RAFAEL, Haifa, Israel

To cite this Article Dodiuk, H. , Fin, N. , Yaniv, A. E. and Kenig, S.(1990) 'Interfacial Characterization of Epoxy-bonded Maraging Steel', The Journal of Adhesion, 31: 2, 191 — 202

To link to this Article: DOI: 10.1080/00218469008048224

URL: http://dx.doi.org/10.1080/00218469008048224

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

J. Adhesion, 1990, Vol. 31, pp. 191–202
Reprints available directly from the publisher
Photocopying permitted by license only
© 1990 Gordon and Breach Science Publishers, Inc.
Printed in the United Kingdom

NOTE

Interfacial Characterization of Epoxy-bonded Maraging Steel

H. DODIUK, N. FIN, A. E. YANIV* and S. KENIG
RAFAEL, P.O. Box 2250, Haifa 26487, Israel

(Received March 24, 1989; in final form November 30, 1989)

KEY WORDS Spinel oxide; maraging steel; wedge test; epoxy adhesive; interfacial-cohesive failure; spectroscopy.

Downloaded At: 14:49 22 January 2011

INTRODUCTION

Adhesion phenomena involving polymer-metal interfaces have become a central subject for research and technological development, especially in view of adhesive bonding of metallic components in primary load-bearing structures. Since adhesion implies that some sort of chemical and/or physical interactions take place between the metal adherend and the polymeric adhesive, a great deal of attention has been devoted to identification and characterization of such interactions and to the development of techniques to study them. Among the most widely used methods for interfacial studies are: ESCA (Electron Spectroscopy for Chemical Analysis), AES (Auger Electron Spectroscopy), SIMS (Secondary Ion Mass Spectroscopy), IR spectroscopy, optical microscopy, and electron microscopy.

Maraging (Martensite-aging) steel is an advanced high-strength steel alloy that finds its use in high-strength applications such as rocket motor cases. The surface treatment of Maraging steel has a two-fold purpose. Firstly, to protect the motor case against corrosion in adverse atmospheres. Secondly, to provide a base for painting and an appropriate surface for adhesive bonding of internal insulation materials and external metal fixtures. Compared with aluminum and titanium, steel oxidizes relatively slowly. Consequently, in cases where the structural considerations are of secondary importance, bonding can be carried out directly to mechanically-treated steel. However, since the steel oxide adheres loosely to

---

* Deceased.

the metal and from interfacial durability considerations, steel is pre-treated prior to adhesive bonding for structural applications.

As a result of the scarcity of basic studies related to the interface properties of epoxy-bonded Maraging steel, the present investigation was aimed at characterizing the interface of epoxy-bonded pre-treated 250 Maraging steel. The pre-treatment of the steel alloy comprised sand blasting and superheated steam. The latter treatment results in spinel formation.[1,2] The effects of these surface treatments were investigated with respect to their macroscopic strength properties in the case of Maraging steel-aluminum bonded joints. Micro-characterization by SEM/EDAX, Auger and FTIR spectroscopies was used to determine the cohesive and interfacial crack propagation characteristics under opening mode loading of epoxy-bonded pre-treated Maraging steel.

Downloaded At: 14:49 22 January 2011

EXPERIMENTAL

Materials

Metal substrates The metal substrate for Wedge-test specimens (according to ASTM D-3762-79), used in this work, was 250 Maraging steel of nominal composition (weight percent) 18 Ni, 8.5 Co, 5 Mo, 0.4 Ti, 0.1 Al, and Fe the balance. It is a high-strength steel, its name deriving from martensitic structure and from aging necessary to strengthen the steel (mar-aging).

Another substrate used in this work was Al 2024 of nominal composition, Cu 4.4%, Mg 1.5%, Mn 0.6% and the balance Al which was pre-treated with unsealed chromic acid anodizing. The operating conditions of the anodizing are given elsewhere.[3]

Primer and adhesive BR 127 is a corrosion-inhibiting primer containing strontium chromate, a product of American Cyanamid (U.S.A.). The primer was applied by brushing to a thickness of 2.5–5 μm. The primer layer was air dried for 30 ± 5 minutes and then polymerized at 120 ± 5°C for 30 ± 5 minutes. FM-300K is an epoxy-based structural adhesive manufactured by American Cyanamid (U.S.A.) stored at −18°C prior to use. After heating to room temperature, the adhesive was cut to measure, applied to the primed specimens and polymerized at 175 ± 5°C and 40 psi in an autoclave or in a hot press, for 60 ± 5 minutes.

Surface treatments

Superheated steam treatment (*SHS*) The specimens were heat treated in superheated steam, in a Degussa Model DSU furnace. All specimens were pre-heated in argon up to 370°C. The furnace was purged with superheated steam and the specimens were further treated in this atmosphere at 485°C for 3 hours. Specimens were then cooled in air to room temperature. The resulting oxide is mainly spinel type, Fe_3O_4. It was shown in a previous work[1] that this oxide could act as a substrate for paints with very good results, and it was therefore assumed that, similarly, it could be used as a substrate for adhesive bonding.

Sand blasting Sand blasting was carried out with dry, chloride-free sand using a standard air gun. After sand blasting, the specimens were wiped with dry lint-free paper.

Solvent wipe Adherends were wiped with a paper towel soaked in acetone. This cleaning procedure was applied to each surface at least three times.

Mechanical tests

Single lap joints were prepared according to ASTM D-1102-72. The bonding strength was measured in a 5-ton Instron (crosshead speed of 0.2 cm/min) at 25°C. The mode of failure (adhesive or cohesive) was evaluated by visual inspection. Results are presented in Table I.

Wedge specimens for 250 Maraging steel adherends (3 mm thick) were prepared in accordance with ASTM D-3762-79. The wedge was inserted using a 2 Kg hammer. Each joint was then placed under a strong light source and a magnifying glass was used to locate the tip of the crack. The initial crack tip was marked and its length recorded (a_0). The specimen was then immediately placed in the humidity chamber (model BHK 4105, Associated Environmental Systems) at 50°C and relative humidity (R.H.) of 95% for one hour. After exposure to humidity, crack growth was measured at specific periods of time, as shown in Table II, using a Baush and Lamb stereoscope. Then the specimens were exposed to controlled ambient conditions (25°C, 50% R.H.) for an additional one year. In the final stage the specimens were split apart to examine and record the mode of failure.

Analytical methods

FTIR FTIR spectra of the adherend surfaces after fracture were taken in a Nicolet Model 5DX equipped with an external horizontal specular reflectance

TABLE I
Lap shear strength of CAA-treated 2024 bonded to 250 Maraging steel using primer BR-127 structural adhesive FM-300K

	Surface pretreatment for maraging adherends	Lap shear strength MPa	Mode of failure
1	T.C.E. degreasing, sand blasting, primer	40.33 ± 1.35	Cohesive
2	Degreasing, sand blasting, SHS, primer	34.05 ± 2.34	Cohesive
3	Machining to surface 22-28 CLA[a] degreasing, SHS, primer	0.70 ± 0.12	Spinel–Metal interface
4	Machining to surface 100 CLA,[a] degreasing, SHS, primer	2.07 ± 0.69	Spinel–Metal interface

[a] CLA—center line average height (microinch).

Downloaded At: 14:49 22 January 2011

TABLE II
Crack propagation in 250 Maraging steel/250 Maraging steel wedge test specimens bonded with primer BR-127 and structural adhesive FM-300K

	The length of the crack in mm*							
Time of exposuree Surface treatment	1 hour A.C.	1 hour H.C.	3 hours H.C.	24 hours H.C.	72 hours H.C.	11 days H.C.	17 days H.C.	1 year A.C.
SHS treatment	59 ± 2	66 ± 6	71 ± 10	79 ± 9	85 ± 9	93 ± 10	100 ± 8	104 ± 8
Sand blasting	57 ± 2.4	69 ± 7.5	78 ± 9	83 ± 9	90 ± 8	97 ± 6	101 ± 6	108 ± 7
Acetone wipe	58.5 ± 3	63 ± 5	70 ± 8	81 ± 10	90 ± 8	99 ± 9	104 ± 9	107.5 ± 10.5

A.C. = Ambient conditions, H.C. = Humidity chamber.
* Average of 9 specimens.

Downloaded At: 14:49 22 January 2011

accessory with incidence angle of 15° with respect to the normal to the surface and a gold mirror as a reference. 100 scans were taken for each spectrum.

Auger spectroscopy Auger spectra were taken in an Auger/SIMS spectrometer PHI model 545 M. Sputtering was performed with a differential pumped gun using Ar^+ ions.

SEM/EDAX The surfaces of the fractured specimens were examined in a Jeol SEM Model JSM 840 connected to an Energy Dispersive Analyser (Link Systems Model 860). The specimens were Au-Pd coated prior to examination to suppress charging of the surfaces.

RESULTS AND DISCUSSION

The present study was composed of two parts. The first was aimed at evaluating the shear strength and the mode of failure of Al-Maraging steel joints using single lap shear specimens and served as a screening step. The second part was designed to characterize the fracture surface and interface structure and composition of a crack derived by opening-type stresses of Maraging steel/Maraging steel epoxy-bonded specimens exposed to crack-accelerating hygrothermal conditions for various periods of time, and then to the ambient environment for a period of a year.

Shear strength

Table I summarizes the lap shear strengths of chromic acid anodized (CAA) Al-2024 adherends primed with BR 127 and bonded with FM300K structural adhesive to 250 Maraging steel adherends after various surface pre-treatments.

Downloaded At: 14:49 22 January 2011

It can be concluded that the superheated steam treatment (spinel type oxide formation) renders a surface which is inadequate for structural bonding, unless it is sand blasted prior to the steam treatment. The sand blasting treatment enhances the adhesion of the oxide to the steel to prevent premature failure at the oxide/steel interface under relatively low stresses (0.69–2.07 MPa).

The highest shear strength associated with cohesive failure was obtained in the case of sand blasted specimens. Second highest results were for specimens sand blasted prior to SHS.

It should be emphasized that although the values for treatment 2 (Table I) are slightly lower than for treatment 1, it is recommended as a standard procedure since it offers a protective oxide layer.

Crack propagation in opening mode loading

In the present investigation, the crack propagation characteristics in opening mode loading in ambient and humid environment was studied. Special emphasis was directed toward the various developing failure interfaces during the combined action of stress, heat and humidity. No effort was made to optimize the Maraging steel adherend thickness for the purpose of determining the absolute crack propagation rate.

The results for initial crack length and crack growth during exposure to combined heat and humidity are given in Table II. (The results are the average for 9 specimens). It can be seen that there are no appreciable differences in the length of the cracks and their growth rate between the three surface treatments, *i.e.* SHS, sand blasting and acetone wipe.

Visual examination of fracture surfaces

At the end of the loading procedure, the wedge specimens were split apart and visually inspected. Generally, five zones could be distinguished with regard to failure mode, as indicated schematically in Figure 1. The first zone comprised the

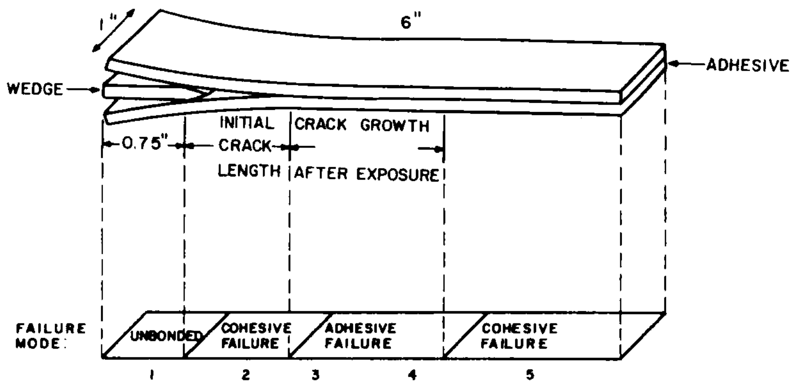


FIGURE 1 Wedge Test Specimen (According to ASTM-D-3762-79) and designated failure zones.

unbonded area of the specimen generated by the initial penetration of the wedge. The second region included the initial cohesive failure zone due to the opening mode stresses prior to environmental exposure. The third and fourth areas were of interfacial failure characteristics, resulting from exposure to heat and humidity and ambient atmosphere, respectively. The fifth zone is the manifestation of the final specimen splitting. In each case of adhesive or interfacial failure the adherends were defined by "adhesive side" (where adhesive was left) and by "metal side" (where the metal was bare).

SEM/EDAX

Apart from visual inspection, the adherend surfaces of SHS specimen after fracture were examined by SEM/EDAX, Auger and FTIR.

Figures 2–5 include SEM and EDAX micrographs of the SHS-treated specimens exposed to hot/wet conditions. As could be observed in Figure 2, the so-called "metal side" of zone 3, where visually interfacial failure has been observed, contains dark spots, approximately 1 mm in size, dispersed in a regular manner on the adherend. These spots were proven by EDAX (Figure 3) to composed of, among other elements, bromine. A replica pattern of missing material could be seen in the micrograph belonging to the so-called "adhesive side" (Figure 4). EDAX analysis (Figure 5) indicates that bromine is present all over the surface. It should be emphasized that EDAX analysis of both the primer BR-127 and the adhesive FM-300K has shown that only the adhesive contains bromine. Consequently, it seems that what appears to be an interfacial failure by visual inspection is really a mixed-mode failure. The shape and special pattern of the adhesive, on the "metal side," could be associated with the special weave of the adhesive carrier. Figure 6 depicts a cohesive failure surface of FM-300K. It is

Downloaded At: 14:49 22 January 2011

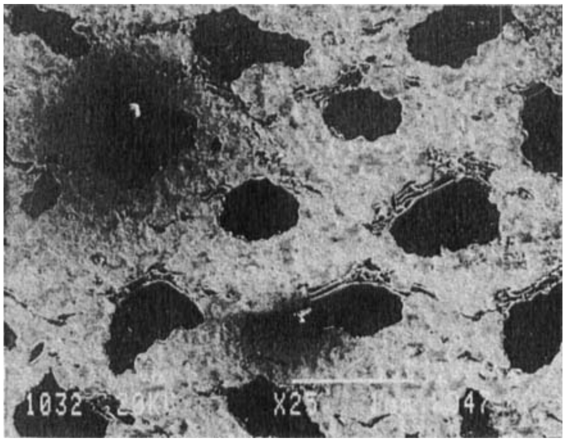


FIGURE 2 SEM micrograph of adherend with SHS treatment, zone 3 of "metal side," ×25.

Downloaded At: 14:49 22 January 2011

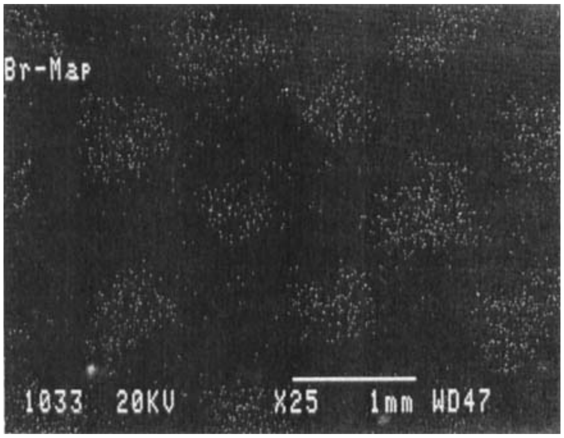


FIGURE 3 EDAX Bromine analysis of the region shown in Figure 2 (zone 3).

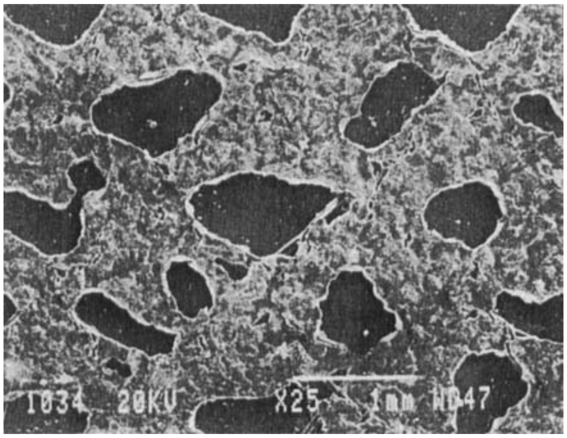


FIGURE 4 SEM micrograph of adherend with SHS treatment, zone 3 of "adhesive side" ×25.

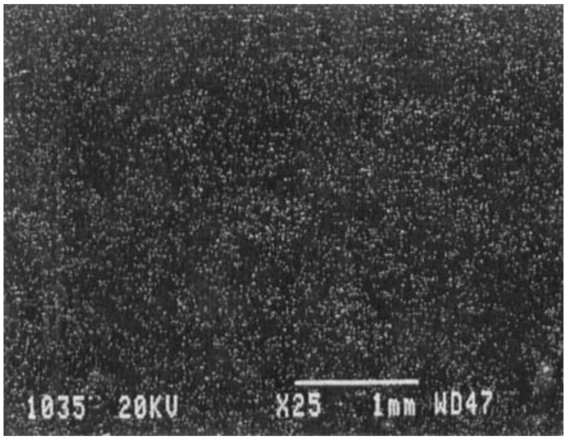


FIGURE 5 EDAX Bromine analysis of the region shown in Figure 4.

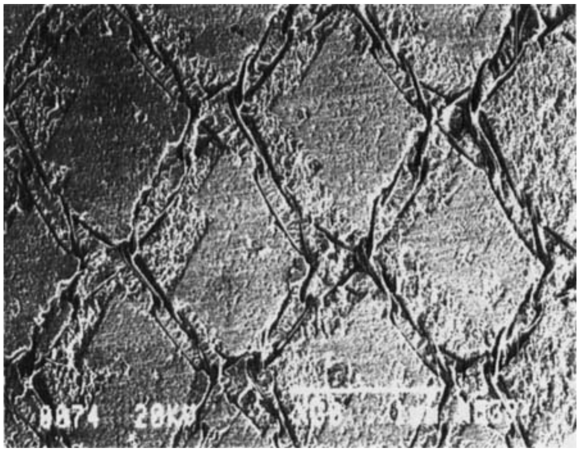


FIGURE 6 SEM micrograph of zone 2 failure surface.

Downloaded At: 14:49 22 January 2011

evident that the open net size, approximately 1 mm, of the carrier affects the morphology of the fracture surface. In the case of the interfacial failure zone (zone 3), the carrier is covered with the adhesive, hence only the imprint of the adhesive parts which have been detached from the adhesive are seen in Figure 2.

Auger spectroscopy

The "adhesive side" of the joint was heavily charged during the Auger analysis and it was impossible to analyze it. Therefore, only the results of the "metal side" are given.

The Auger spectrum of the "metal side" between the adhesive spots (Figure 7a) revealed that Fe, Ni, Co (marage) and O, N, C exist. After in depth sputtering of 3 nm (Figure 7b) the C peak decreased, whereas the Fe and O peaks increased indicating that the spinel layer, mainly composed of Fe_cO_4,[2] was reached.

Auger spectra of the adhesive spots on the "metal side" and after sputtering of 200 nm are given in Figures 8a and 8b, respectively. No Br was detected on the surface, and only minute quantities of Br can be seen in Figure 8b, suggesting that, on the surface, FM-300K adhesive is present.

As concluded from SEM/EDAX results, the Auger results confirm that microscopically the mode of failure is mixed, being interfacial between the adhesive and the metal oxide, in addition to areas of cohesive failure within the adhesive.

FTIR

FTIR spectra of the regions 1–5 (according to Figure 1) were taken (on the "adhesive side" of the fractured wedge test specimens) for the various surface-treated Wedge specimens.

Downloaded At: 14:49 22 January 2011

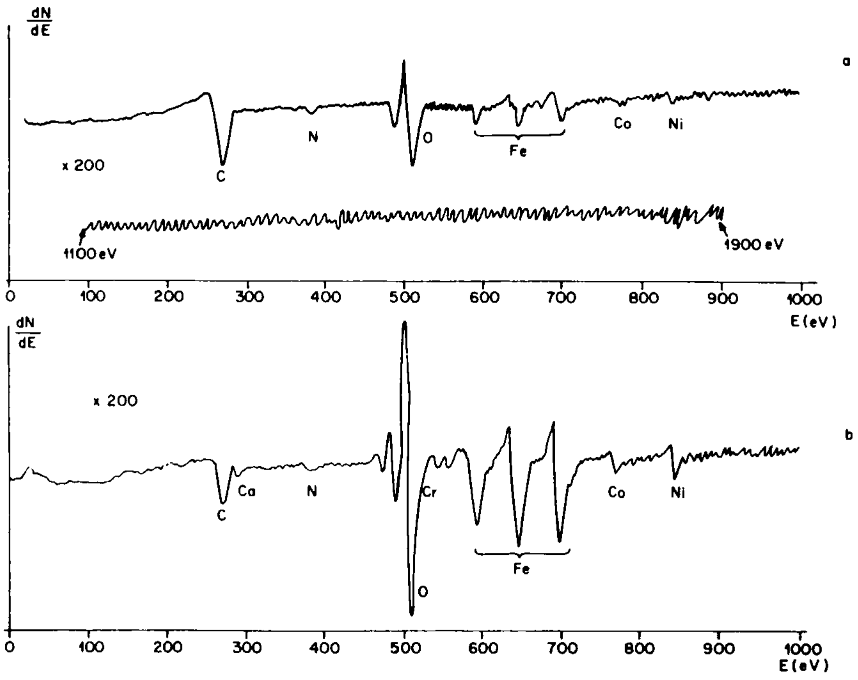


FIGURE 7 Auger spectra of "metal side," metallic region. a) surface, b) depth of 3 nm.

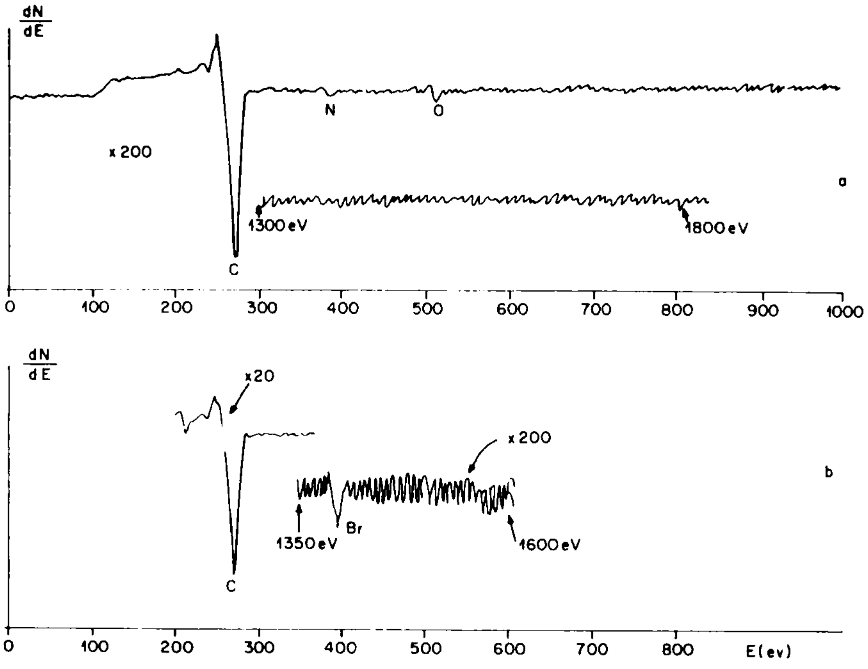


FIGURE 8 Auger spectra of adhesive areas on "metal side." a) near the surface (while sputtering), b) depth of 200 nm.

The main absorption peaks found were: A wide peak whose center is at ~3500 cm^{-1} (OH stretching corresponding mainly to absorbed water), 2920–2980 cm^{-1} (stretch of alkyl C—H), 2190 cm^{-1} and 2170 cm^{-1} (C≡N stretching typical of the dicyandiamide curing agent), 1247 cm^{-1} (stretch of aryl-O—C), 1515 cm^{-1} (stretch of C=C of an aromatic ring), 1085 cm^{-1}, 1041 cm^{-1}) stretch of C—O—C) and 829 cm^{-1} (C=C bend outside the plane of the benzene ring).

These absorptions are characteristic of the epoxy adhesive, FM-300K, used in the present work.[4,5] It is composed of a dicyandiamide cured 4,4′-(*N,N*′-tetraglycidyl methylenedianiline) epoxy resin film. An attempt was made to analyze quantitatively the changes during exposure to humidity. A rigorous examination of the infrared spectra of the five zones showed that changes during humidity conditioning took place mainly in two spectral regions. The first is at 3500–3400 cm^{-1} where a wide peak exists corresponding mainly to water absorption (the contribution of the epoxy hydroxyl groups is low and constant). The second is at 2190–2170 cm^{-1} where a doublet peak appears typical of dicyandiamide. Initially the 2190 cm^{-1} peak is more intense than the 2170 cm^{-1} one. However, the intensities change upon exposure. As has been pointed out by Pike *et al.*,[6] the doublet at 2190–2170 is characteristic of the carbondiimide (N=C=N) type linkage (due to the electronic resonance forms of the dicyandiamide). The doublet is affected by polar groups such as water.[5,6] In addition to changes of the 3500–3400 cm^{-1} and 2190–2170 cm^{-1} peaks due to water absorption and dicyandiamide, respectively, minor changes were observed at 1600 cm^{-1} corresponding to the C=NH group (a protonated tautomer of dicyandiamide) and absorbed water.

Two absorptions, i.e. the aromatic 1515 cm^{-1} and hydrocarbon 2920 cm^{-1}, were chosen as references, since they are supposed not to change during aging and to remain constant provided the adhesive thickness remains constant. This method was successfully used by Scola[5] and has been adopted by Dodiuk *et al.*[4].

The changes in the ratios of the absorption peak at 3500 cm^{-1} (during exposure to heat/humidity) as well as the peak at 2190 cm^{-1} to the aromatic peak at 1515 cm^{-1} are given in Table III in a normalized form with respect to region 2 for each pre-treatment.

From Table III the following conclusions can be drawn:

a) Generally, the highest amount of water absorbed was for specimens with acetone wipe and sand blasting. A lower amount of water was found in SHS-treated specimens. These findings indicate that SHS treatment is more effective concerning humidity absorption than acetone wipe or sand blasting (as expected).

b) There is an increase in water concentration upon transition from region 2 (before exposure to humidity) to region 3 (beginning of the hygrothermal exposure) for all three surface treatments. This corresponds to transformation of the failure mode from cohesive in region 2 to adhesive (visually) in region 3.

c) In the transition from region 3 to 4 (the end of propagation of the crack under hygrothermal conditions) a decrease in the amount of absorbed water took

Downloaded At: 14:49 22 January 2011

TABLE III
Normalized changes in ratios of water absorption and dicyandiamide concentration related to the aromatic peak at 1515 cm^{-1}

		Normalized Peak Ratios	
		Water	Nitrile
Surface treatment	Region (Figure 2)	$\frac{3500\,\mathrm{cm}^{-1}}{1515\,\mathrm{cm}^{-1}}$	$\frac{2190\,\mathrm{cm}^{-1}}{1515\,\mathrm{cm}^{-1}}$
Acetone wipe	2	1.0	1.0
	3	1.1	3.4
	4	1.3	2.1
	5	1.2	1.4
Sand blasting	2	1.0	1.0
	3	1.5	1.5
	4	1.3	1.0
	5	1.3	1.3
SHS treatment	2	1.0	1.0
	3	1.2	1.3
	4	0.9	1.1
	5	0.8	1.0

Downloaded At: 14:49 22 January 2011

place in the case of sand blasting and was more pronounced in the case of SHS. An increase in the amount of water absorbed took place in the case of acetone wipe. These results indicate that SHS is superior with regard to interfacial water absorption.

d) In the transition from region 2 to 3 an increase in the concentration of dicyandiamide was observed, the highest for acetone-wiped specimens and the lowest for SHS-treated specimens. This may be due to residual dicyandiamide extracted to the surface by absorbed humidity. High dicyandiamide concentrations in region 3 should correspond to high amounts of water absorption.

e) In the transition from region 3 to 4 a decrease in the concentration of dicyandiamide occurred except for the acetone-wiped specimens. This may be due to the lower concentration of absorbed water in this region.

f) In the transition from region 4 to 5 (cohesive failure) a decrease in the concentration of water and dicyandiamide occurred for most cases, as expected. However, since the bond line was exposed to humidity for a year, differences in dicyandiamide are expected.

CONCLUSIONS

Superheated steam treatment of Maraging-steel provides an excellent corrosion protection method due to formation of a uniform spinel type oxide layer. For an effective development of adhesion strength between the steel substrate, the spinel layer and a subsequent epoxy layer, sand blasting of the steel alloy (prior to SHS treatment) has been shown to be a critical step. This is due to the inferior adhesion at the steel-spinel interface.

The Wedge test, using Maraging steel adherends, has been shown to offer an appropriate experimental set-up to study the cohesive-adhesive failure modes and for subsequent surface and interface analysis, under combined hygrothermal and Mode I loading conditions. As expected, the failure mode changed from cohesive under ambient conditions to mixed of the adhesive-spinel interface when the crack was exposed to heat and humidity. A more rigorous analysis of the fracture surfaces, using SEM/EDAX and Auger spectroscopy, has indicated that what appears to be an interfacial failure mode, is really a cohesive one. FTIR data have shown that massive water absorption occurs on the propagating crack surface or stressed crack tip, while the joint was exposed to humidity. This is the cause of what appears to be adhesive failure under wet-hot conditions. In addition to its adverse effect on the adhesive-spinel interface, humidity proved to be detrimental to the specific adhesive studied (FM-300), due to its strong interaction with residual dicyandiamide (the curing agent) resulting in its solubilization and consequent void formation.

Downloaded At: 14:49 22 January 2011

Acknowledgments

The authors wish to thank Mrs I. Liran and Mr M. Anglowich for supplying the specimens used in this study.

References

1. (a) I. E. Klein, A. E. Yaniv and J. Sharon, *App. Surf. Sci.* **14,** 351 (1983). (b) I. E. Klein, J. Sharon and A. E. Yaniv, *Scripta Metalurgica* **15,** 141 (1981).
2. I. E. Klein, M. Levitzky and J. Sharon, *Rev. Coat. Corros.* **6,** 97 (1984).
3. A. E. Yaniv, I. E. Klein, J. Sharon and H. Dodiuk, *Surf. and Interface Analysis* **5,** 93 (1983).
4. H. Dodiuk, L. Drori and J. Miller, *J. Adhesion* **19,** 1 (1985).
5. D. A. Scola, Proc. 16th National SAMPE Technical Conference, October, 9–11, 1984, p. 328.
6. R. A. Pike, F. M. Lamm and J. P. Pinto, *J. Adhesion* **13,** 229 (1982).