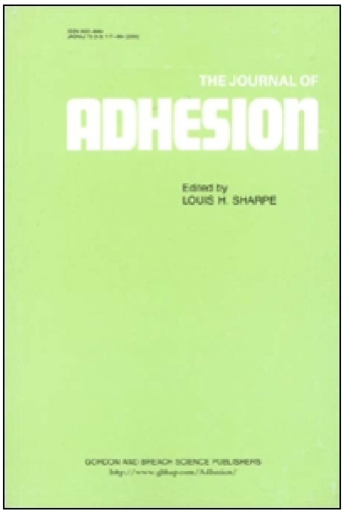


The Journal of Adhesion
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

Effect of Ultra-Clean Stainless Steel Surfaces on the Strength of Epoxide-Stainless Steel Butt Joints

F. S. Baker

To cite this Article Baker, F. S.(1979) 'Effect of Ultra-Clean Stainless Steel Surfaces on the Strength of Epoxide-Stainless Steel Butt Joints', The Journal of Adhesion, 10: 2, 107 — 122

To link to this Article: DOI: 10.1080/00218467908544618

URL: http://dx.doi.org/10.1080/00218467908544618

J. Adhesion, 1979, Vol. 10, pp. 107–122
0021-8464/79/1002-0107 $04.50/0
Printed in Scotland

Effect of Ultra-Clean Stainless Steel Surfaces on the Strength of Epoxide-Stainless Steel Butt Joints

F. S. BAKER

*Ministry of Defence, Propellants, Explosives and Rocket Motor Establishment,
Waltham Abbey, Essex, EN9 1BP, England*

(*Received January 25, 1979*)

Butt joints between stainless steel epoxy/stainless steel have been constructed from steel samples which have had their bonding surfaces subject to (a) argon–ion bombardment at 8 keV, total flux of 10^{18} ions cm^{-2}, (b) abraded with 180–220 mesh alumina grit and degreased, and (c) similar treatment to (b) but subjected to ion-bombardment. All the steel surfaces which were sputtered in argon at a background pressure of 10^{-5} Pa were not allowed to come into contact with air at ambient pressure even when forming the butt joints.

The ultimate tensile strength (UTS) of the joints were tested dry and after soaking in water at 40°C. Those joints made from the surfaces subjected to treatment (a) were always inferior to those subjected to (b) which in turn were inferior to those which had received treatment (c). In the last case, after soaking for a period of 10 weeks the UTS of the joints was 44% higher than the conventionally prepared samples (b).

INTRODUCTION

It is generally accepted that an adhesive used for joining metal surfaces will give a strong joint only if it is applied in the form of a liquid which completely wets the metal surfaces. Such complete wetting is indicative of strong bonding between the adhesive and metal which persists when the adhesive is subsequently transformed to its solid form by the evaporation of solvent, or by chemical means, as in the case of epoxy resins. It has been calculated that physical forces, van der Waals' forces, alone are sufficient to give a strong adhesive bond.[1] It is not necessary for good adhesion, therefore, to postulate the existence of chemical bonds between two mating surfaces.

Kinloch and Gledhill[2] have shown that the strength of a metal–metal bond made with an amine cured epoxy resin system will decrease with time if the joint is exposed to a hostile environment such as total immersion in distilled water at 40°C. The general theory put forward by these and other authors is that the thermodynamic work of adhesion between the epoxy and metal oxide interface changes from a positive to a negative value if the interface is covered with an adsorbed layer of water. It is known that water molecules diffuse through the resin. Thus, as the water reaches the interface, the change in the work of adhesion favours the debonding of the adhesive from the metal surface and the joint strength decreases with the time of exposure to the hostile environment.

It was reasoned that if the metal surface were clean, i.e., preferably free of oxide and certainly free of any adsorbed monolayer of hydrocarbons or other contaminants, then strong chemisorption forces between the metal and the epoxide resin should become possible. If such a state of affairs could be arranged then it is probable that the chemical bonds would not be so easily broken by water as the physical ones normally encountered.

The standard technique of abrading and solvent cleaning still leaves the surface of the metal covered in oxide, adsorbed hydrocarbons, solvent and any contaminants[3] which may be present in the atmosphere. At ambient pressure, there is no way of preventing this overall contamination, since the rate of coverage of the surface by these molecules is very fast.

The corollary, of course, is that the lower the pressure the lower will be the rate of contamination. An experiment was designed, therefore, in which a metal surface could be cleaned and kept clean whilst adding the adhesive.

This entailed constructing a high vacuum system in which the metal surfaces to be bonded could be cleaned by argon ion-bombardment and subsequently covered with sufficient adhesive to form a joint without exposing the cleaned surfaces to the atmosphere.

EXPERIMENTAL

The stainless steel specimens were made to the dimensions shown in Figure 1. Care was taken to ensure that the distance *d* from the ground shoulder to the ground surface *G* was known to within ±0.03 mm. This was important since a specially constructed gauge which bore on the shoulders was used to set the glue line thickness, Figure 2.

A block diagram and a photograph of the vacuum system are shown in Figure 3 and Plate 1 respectively. The line was pumped by an air cooled diffusion pump (Edwards FO2 $2\frac{1}{2}$ inch) which in turn was backed by a double stage 150 ls^{-1} rotary pump. The working fluid for the diffusion pump was a low vapour pressure polyphenylether (Trade Name, Santovac, Edwards High Vacuum International Ltd.).

The chamber in which the samples were sputtered clean, was separated from the vacuum chamber containing the adhesive so that there would be no hydrocarbon contamination from the glue whilst the surfaces were being bombarded. The connection between the two chambers was made via a port which could be sealed with a Viton "O" ring, Figure 4. This seal and the pot containing about 0.5–1 ml of adhesive were mounted on a turntable supported and directly coupled to a linear-rotary drive (A), designed and constructed for this work by Vacuum Generators Ltd. This particular drive contained a thrust bearing so that sufficient pressure could be exerted on the "O" ring to effect a vacuum tight seal.

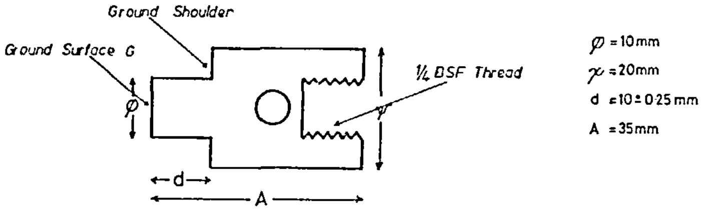


FIGURE 1 Butt Joint test pieces.

The specimens were suspended on steel pins held in position by forks which were electrically insulated from the rest of the apparatus so that the ion current falling on each sample could be monitored, Figure 4 and Plate II. The forks themselves were mounted on linear-rotary drives B and B′.

The argon-ion guns were of a type similar to the Fitch and Rushton design[4] and were supplied by Iontech Ltd. These devices produced a cone of ions. The current at the aperture of each gun was monitored as was also the total current drain from both guns. The overall energy of the ions could be varied from 0–10 keV.

The argon feeding the ion sources was supplied from BOC Spec pure 1 litre argon bulbs. The overall throughput of the gas was controlled by a leak valve. The argon used to flood the glue chamber and to bring the whole apparatus up to atmospheric pressure was supplied from a cylinder containing 99.99% pure argon.

The adhesive used in these experiments was an anhydride cured epoxy resin system, Araldite MY 750, Hardener 905, and Accelerator DY 063 (Ciba-Geigy Ltd). The components were mixed in the ratio 100 parts MY 750 to 100 parts 905 to 1 part DY 063. This adhesive was particularly suited to

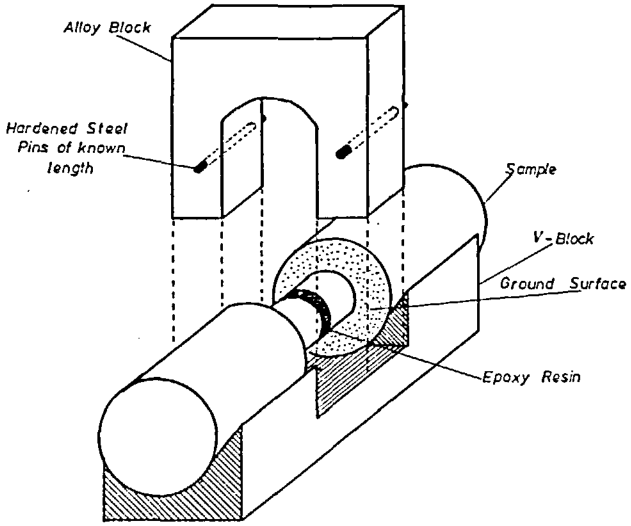


FIGURE 2 Holding jig to set glue-line thickness.

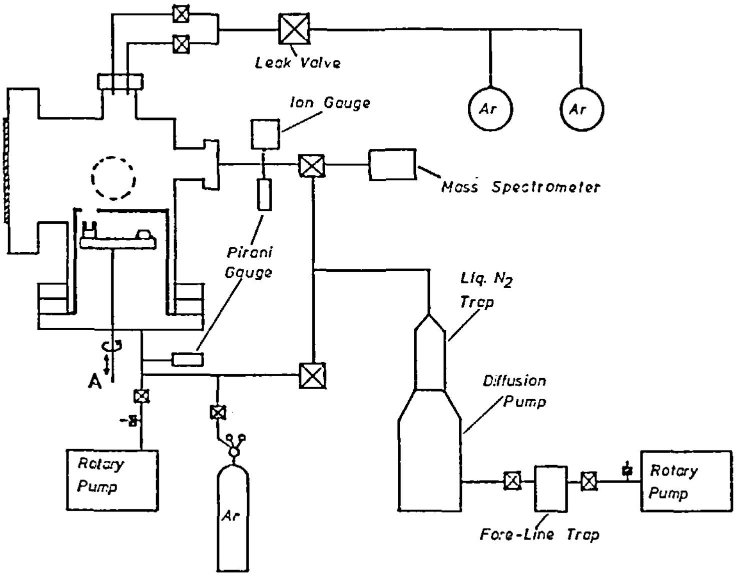


FIGURE 3 Block diagram of vacuum system.

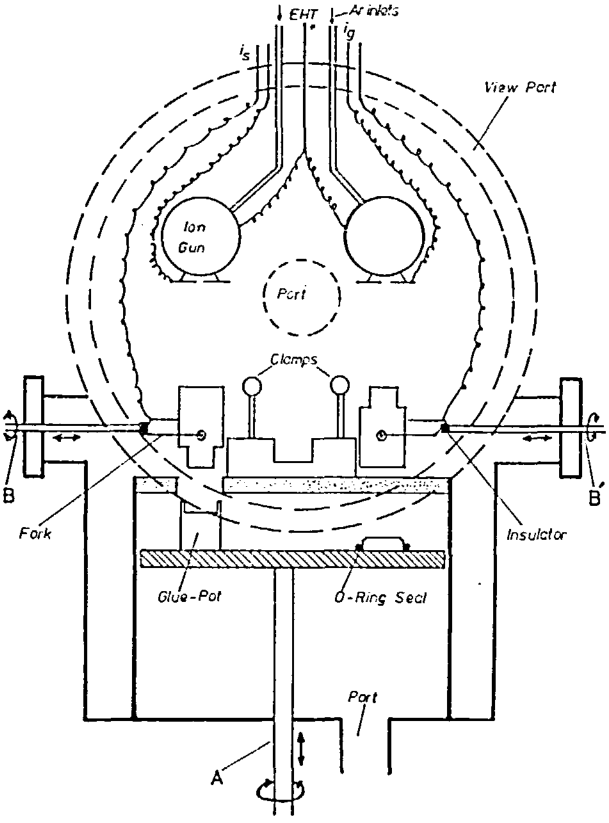


FIGURE 4 Vacuum chambers shown in open position with glue-pot to be raised to test piece for application of glue.

this work since it had a low vapour pressure and did not froth at reduced pressures; also its rate of cure could be controlled by the amount of accelerator present in the mixture. Part of the vacuum "work-up" procedure involved the baking-out of the ion source chamber at 170°C for 3½ hours, so it was essential that not only should the glue not cure during this cycle, but also that the viscosity of the adhesive should not increase to beyond a point where a sizeable drop could be transferred onto the two mating surfaces as described later. It was found that the addition of 1% accelerator to the mixture was sufficient to enable these conditions to be fulfilled.

A further bonus was that the pot-life of this adhesive system was sufficiently long when stored at 0°C to enable the same sample to be used throughout the duration of this particular programme which was 6 months.

EXPERIMENTAL PROCEDURE

The normal procedure governing the operation and handling of ultra high vacuum systems and components were followed. The techniques involved in making the joints will be described.

The glue pot was degreased and charged with 0.5–1.0 ml of the adhesive. It was then screwed into position on the turntable via the inter-connecting port. The table was lowered, rotated, and then raised so that the "O" ring was in position to effect a seal.

The stainless steel specimens were washed in isopropanol to remove any gross contamination from their surfaces and mounted on their respective forks. The PTFE coated V-block fitted with clamps was placed against its locating blocks and held in position by the clamping screw as shown in Plate II.

Both chambers were then pumped down to 10^{-1} Pa and held there for a few minutes to outgas the glue. The glue chamber was isolated from both the ion-source chamber and the pumping line and then filled with argon to a pressure of 8 mm. At such a pressure the mass spectrometer showed that very little argon leaked into the ion-source chamber.

The system was left to pump overnight and the following morning the ion-source chamber was baked-out to 170°C for $3\frac{1}{2}$ hours. With this schedule a background pressure of approximately 3×10^{-5} Pa was consistently obtained. Mass spectroscopy showed that the bulk of the contaminants was in the region of 40–60 atomic mass units, with an appreciable contribution at mass 19, indicating that the contamination may very well be coming from the considerable amounts of PTFE present in the chamber, i.e. from the V-block, Viton "O" ring, and PTFE tubes used for insulating the EHT line to the ion-sources.

When the system had cooled to room temperature, the ion-guns were switched on. The samples were manoeuvred under the ion beams such that all the surface to be bonded was bombarded. The ion flux density was adjusted by controlling the amount of gas flowing through each gun so as to give the same ion current on each sample. During sputtering the samples were rocked from side to side to ensure that the surfaces were being eroded as evenly as possible. The bombardment gave ion-beam energies of 7–8 keV, giving ion currents on each sample of 120 μA, i.e. a flux density of approximately 150 $\mu\text{A cm}^{-2}$ on each specimen surface. The duration of the bombardment was typically 25 minutes. Under these conditions 1.4 to 2 μm of the surface were removed.[5]

On completion of sputtering, the voltage supplying the ion sources was switched off, the ion-source chamber was isolated from the pumps and the

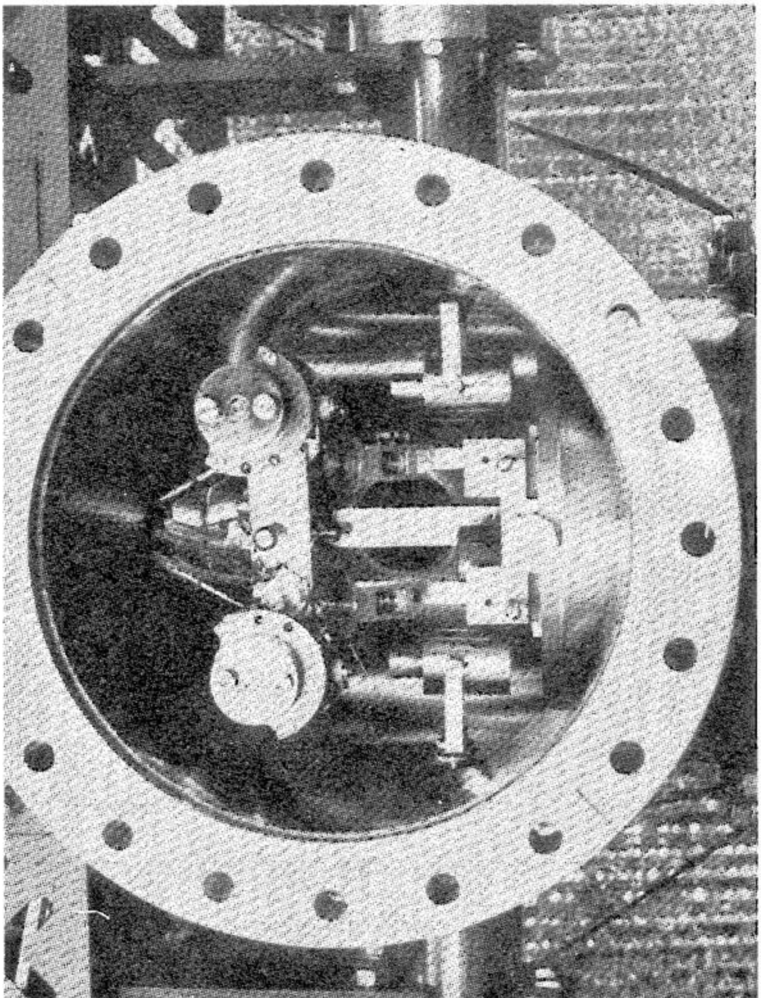


PLATE II View of ion-bombardment chamber.

argon pressure in the chamber was allowed to increase until it matched that in the glue pot chamber. The "specpure" argon supply was switched off and the seal between the two chambers broken. The turntable was rotated until the glue pot was under the port and raised so that on rotation of the left-hand specimen its cleaned surface could be immersed in the adhesive.

The pot was lowered sufficiently for the specimen with its surface covered with a blob of glue to be rotated into an upright position and driven forward onto the "V" block so that it tipped into a horizontal position. The other sample was similarly manoeuvred and the two were allowed to contact so that both sample surfaces were covered with adhesive. Should there not have been enough material transferred to give a glue line of the order of 0.25 mm then the left-hand specimen was withdrawn and dipped into the glue pot and the operation repeated until the desired thickness of adhesive was reached.

Once this state of affairs had been attained, the pressure in the system was raised (with argon from the cylinder) to that of the atmosphere. The samples, lightly clamped to the "V" block, were removed from the apparatus. The glue line was set accurately to 0.25 mm with a specially engineered gauge which used the ground shoulders on the specimens as reference points, Figure 2. Excess adhesive was wiped away from the joint with a fine nickel spatula. The bond was then cured on the "V" block by baking in an oven for 3 hours at 120°C.

The strengths of these butt joints were measured on an Instron Tensile Testing Machine set to a cross-head speed of 1.27 mm min^{-1}. In all cases the joints were tested only after they had come to equilibrium with the temperature of the room housing the Instron.

RESULTS

Joints were made from samples which had received the following treatments prior to bonding:

a) Type S No surface treatment, save for ion-bombardment.

b) Type A Cleaned by the standard process of degreasing in trichloroethylene, abrading with 180–220 mesh alumina grit, followed by further degreasing in solvent.

c) Type AS Cleaned as in (b) but subjected to ion-bombardment.

These samples were tested dry and after immersion in water at 40°C for given periods of time. The results are listed in Table I and Figure 5, the latter being a plot of mean strength against time.

From these results it is clear that the type S joints were considerably weaker than the conventionally made type A samples. The initial joint strength was some 16% below the type A samples and after immersion in water for 4 and 6 weeks fell to 35 and 30% respectively below the mean strength of the latter.

The situation is reversed when comparing type AS joints with type A. Although the initial strengths of the type AS joints were not measured, their strength would be of the same order as or even higher than the breaking

TABLE I

Effect of water on joint strengths

Joint type	Time in water at 40°C (hours)	Joint strength (M.Pa)	(Mean and standard error)
S	0	45.1	47.64±2.27
		49.82	
		42.80	
		52.84	
	648	29.97	
		24.92	29.99±1.84
		33.51	
		31.54	
	1008	20.37	
		24.97	25.74±3.34
		31.87	
A	0	49.84	
	648	54.36	
		54.69	56.81±4.00
		69.33	
	648	42.74	
		43.4	42.96±0.22
		42.74	
	1752	23.26	
		34.82	29.0 ±3.34
		28.92	
AS	672	53.92	
		50.63	51.29±1.37
		49.31	
	1776	44.42	
		43.70	41.75±2.32
		37.13	

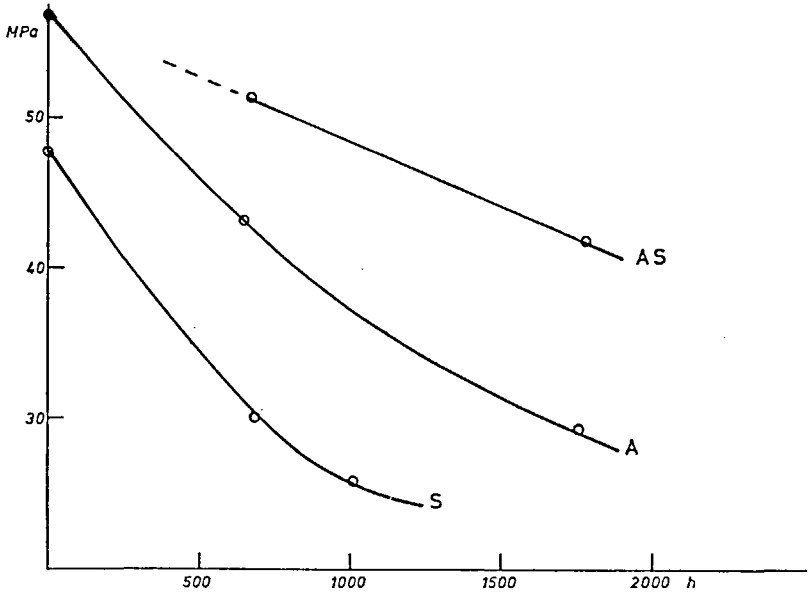


FIGURE 5 Mean joint strength as a function of time of immersion in water.

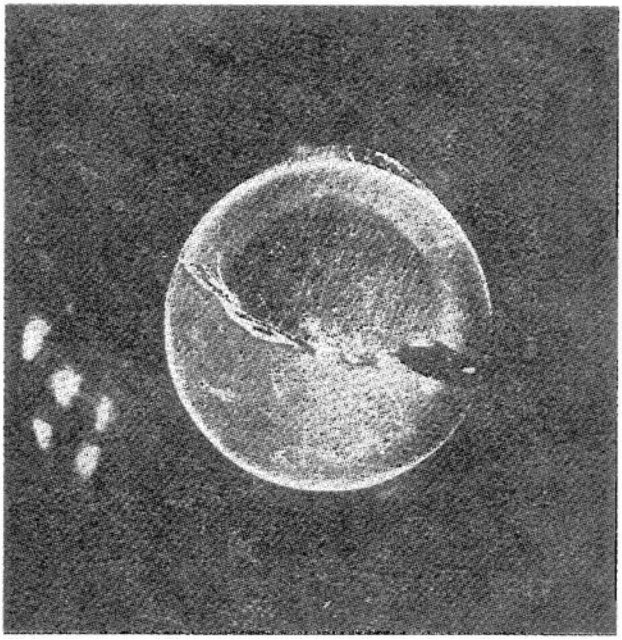


PLATE III Fracture surface of joint made with ion-bombarded substrate.

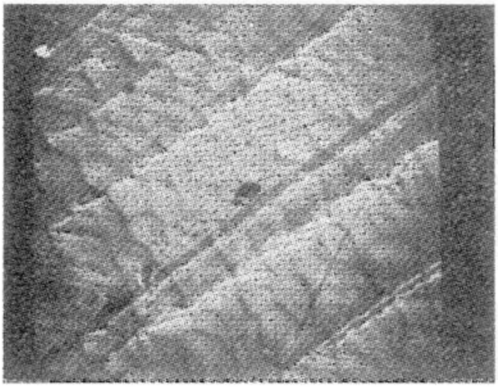
stress of the type A samples; it is unlikely that they would be lower. Based on the assumption that the strengths are of the same order then it can be seen that the type AS samples lost only 26.5% of their strength after soaking in water for 10 weeks, whereas the conventionally treated samples, type A, lost 48.9% of their strength over a comparable immersion time. Certainly in terms of absolute strength the mean value of 41.75 MPa obtained for the AS joints immersed for this period is 44% higher than that measured for the type A samples. This represents a considerable increase in the durability of the joints.

An interesting feature of this work was the appearance of rings on the fractured surfaces of those specimens which had been subjected to ion-bombardment. The rings ran round the periphery of the surface as shown in Plate III. Closer examination showed that they consisted of an annulus of adhesive which had undergone a type of conchoidal fracture similar to that observed by Bascom *et al.*[6] The thickness of the adhesive diminished towards the centre of the sample and in some cases was apparently absent altogether. This ring formation was not observed for any of the type S samples which had been soaked for 4 weeks or more. It was always present for the type AS samples, but was never observed in the conventionally prepared type A joints.

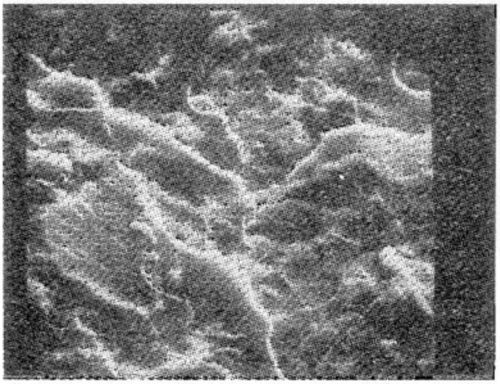
A detailed examination of the ring structure with the Scanning Electron Microscope, showed pronounced differences in the nature of the conchoidal fracture surface between the ion-bombarded only (type S) and the abraded-bombarded (type AS joints). The type S surfaces showed shallow cusp-like fractures reminiscent of those observed by Bascom *et al.* in his mixed mode system, whereas the type AS surface showed very pronounced thick cusp structures with upturned edges, Plates IV(a), (b) and V(a), (b) respectively. In both cases the open end of cusp pointed towards the centre of the sample. As the centre of the specimen was approached so these structures became less pronounced, disappearing altogether a few millimetres from the periphery of the sample.

It is tempting to suggest that these ring features are due to the fact that the ion beam did not remove the material uniformly across the surface of the sample, the sputtering rate being higher at the centre of the beam than at the edges. Two observations make this hypothesis unlikely; the samples were rocked from side to side during the bombardment process to ensure that the ion flux density impinging on the sample surface was evenly distributed, and, the ring had been observed to follow the outline of a flaw, such as an "air" bubble in the adhesive for those few cases in which such flaws existed.

After soaking in water the type S specimens gave fracture surfaces resembling a mixed cohesive/interfacial failure similar to that obtained with type A samples before and after a 10 week soak. It should be noted that the latter joints seemed to go from a mixed cohesive/interfacial pattern when dry, through what would appear to be a purely interfacial failure on soaking for 4 weeks, to a mixed failure pattern as described above. Except for the presence of the rings a similar sequence was observed for the type AS joints.



(*a*)



(*b*)

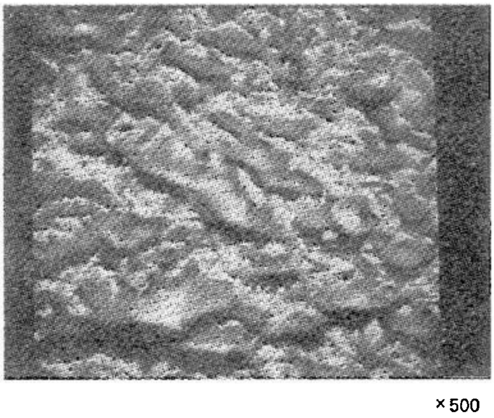
PLATE IV Fracture surface from S-type joints viewed in SEM.

DISCUSSION

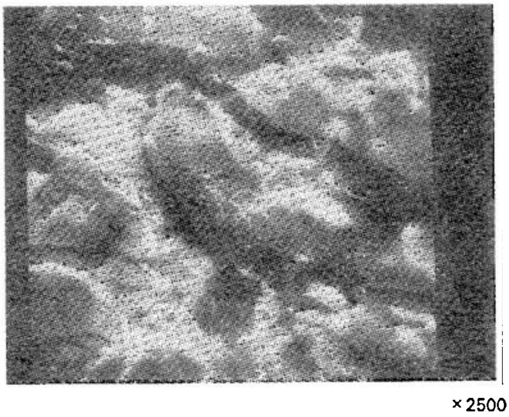
It is generally recognized[7] that rugosity can play an important role in increasing the strength of a bonded joint. The main considerations are that the area in contact with the adhesive is increased, that a large number of scarf joints very close to the interface are provided, and that the tendency for adhesive to spread along the surface is enhanced.[8] It is not surprising therefore to find that the breaking strength of abraded (type A) joints is higher than for non-abraded, ion-bombarded (type S) samples.

On the other hand type AS specimens showed a distinct improvement in joint strength compared with type A joints after immersion in water. The following factors will contribute to this difference in behaviour:

1) Under the low pressure (1 Pa) conditions of the experiment the chance of having air or argon trapped at the metal surface by the adhesive during



(a)



(b)

PLATE V Fracture surface from AS-type joints viewed in SEM.

the making of the joint is very low compared with type A specimens which were made at atmospheric pressure.

2) Sputtering can increase the rugosity of the surface, but this is a minor factor here since a total flux density of only 10^{18} ions cm^{-2} was used. Large changes in the surface roughness of stainless steel are obtained only after exposure to at least 10^{19} ions cm^{-2}.[9]

3) If any oxide is present on the surface after ion-bombardment it will be very thin and probably of a different nature to that found on standard abraded surfaces.

4) The metal surfaces after ion-bombardment are extremely active and there is every possibility that strong chemisorption occurs between the oxygen atoms of the resin and the metal.

5) Because there is more intimate contact between the sputtered steel surfaces and the adhesive polymer, charge transfer effects may be more important than for joints made at ambient pressure.

All these factors lead to a more durable bond between the adhesive and stainless steel surface and if displacement by water is important then this will occur at a much slower rate with joints made from sputtered surfaces.

Not only did the strengths of joints made from abraded sputtered specimens remain superior to that of joints made from abraded samples after immersion in water but also the mode of failure was different. With the former joints the surfaces after testing showed a ring of adhesive round the periphery which was never observed for specimens which had not been subjected to ion-bombardment.

Closer examination by scanning electron microscopy, revealed that the fracture surface of the adhesive was very similar in appearance to that observed by Bascom *et al.*,[6] for a joint which had failed by a mixed-mode mechanism.

This type of failure occurs by a crack starting in the adhesive and then progressively moving towards the metal/adhesive interface as it propagates towards the centre of the butt joint. It only occurs if the bond between the metal and the adhesive is strong enough to withstand the high tensile loading present at the edge of the joint, so that the adhesive itself fails under the high shearing loads to which it is subjected in this region.[10]

Since no "ring" structure was observed with failure surfaces from abraded only joints, the bond between metal and epoxy resin must be higher for ion-bombarded samples. It is also possible that because the adhesive was put onto a very clean surface the metal may have caused some orientation of the polymer at the metal/polymer interface, thus altering its modulus close to the surface. In either case the "displacement by water" mechanism postulated by Kinloch and Gledhill will be thermodynamically hindered and therefore will proceed at a much slower rate.

CONCLUSIONS

Simply cleaning the stainless steel adherend surfaces by ion-bombardment will not give joints as strong as those made from specimens abraded and cleaned in the normal way. This presumably is because the latter have a much rougher surface which considerably enhances the joint strength.

Subjecting abraded adherend surfaces to ion-bombardment appreciably increases the ultimate tensile strength of joints which have been soaked in water. This increase amounts to 44% with joints soaked in water at 40°C for 10 weeks.

Mixed-mode fracture has been observed for all joints made from surfaces cleaned by ion-bombardment. After a few weeks soaking in water the mode of failure for the non-abraded specimens reverts to that of the conventionally prepared samples. It is proposed that the mixed-mode failure pattern is indicative of the formation of strong interfacial bonds between the epoxy resin and the sputtered metal surface, and/or there is present at the interface a thin layer of adhesive with a different modulus from that of the bulk.

Acknowledgements

The author wishes to express his thanks to Messrs A. A. Hazel, S. Smith, J. Williams and R. Watkins for their technical assistance in the design and construction of some of the equipment.

References

1. D. D. Eley and D. Tabor, *Adhesion*, D. D. Eley, Ed. (Oxford University Press, 1961), p. 9.
2. R. A. Gledhill and A. J. Kinloch, *J. Adhesion* **6**, 315 (1974).
3. F. S. Baker, A. J. Kinloch and M. Gettings, *J. Appl. Polym. Sci.* **21**, 2375 (1977).
4. R. K. Fitch and G. J. Rushton, *J. Vac. Sci. Tech.* **9**, 379 (1972).
5. K. Kanga, K. Hojou, K. Koka and K. Toki, *Jap. J. Appl. Phys.* **12**(9), 1297 (1973).
6. W. Bascom, C. Timmons and R. Jones, *J. Mater. Sci.* **10**(6), 1037 (1975).
7. C. W. Jennings, *J. Adhesion* **4**(1), 25 (1972).
8. D. H. Kaelble, *Treatise on Adhesion and Adhesives*, *Vol I.*, R. L. Patrick, Ed. (Dekker, New York, 1967), p. 175.
9. M. J. Whitcomb, *J. Mater. Sci.* **9**, 551 (1974).
10. R. S. Alwar and Y. R. Nagaraja, *J. Adhesion* **7**, 279 (1976).