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Structure–property correlation in Al-diffusion coated steels

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Mild steel and stainless steel samples were pack-calorized under varying conditions and the calorized specimens were characterized by optical microscopy, microhardness data and X-ray diffraction. The mechanical, fatigue and creep resistance properties were also determined. The concept of favourable and unfavourable phases has been introduced, based on the Pilling–Bedworth ratio for compatibility with the base. In the Fe–Al system, only FeAl and Fe_3Al have been found to satisfy this criterion and are therefore desired. The formation of phases such as $FeAl_3$ and Fe_2Al_5 is considered undesirable. The process parameters have therefore been varied and optimized to form only favourable phases. It is found that a lower Al activity pack such as Fe–35 wt% Al gives better results than a higher Al activity pack. The optimum temperature and time of calorizing for both mild and stainless steel are found to be 900 °C for 2 to 4 h. Physical characteristics of the pack such as small, uniform size powder of homogeneous composition are also important to give reproducible results. The mechanical properties of selected calorized (900 °C, 2 and 4 h) mild steel specimens using an Fe–62 wt% Al pack show that there is an appreciable rise (more than 100%) in surface hardness and only a small (around 5%) fall in reduction in area while the percentage elongation remains unaltered on calorizing. There is a considerable fall in high-cycle fatigue properties under push–pull vibration while, under a three-point loading high-frequency fatigue test, the probability to failure and crack initiation reveal an improvement.

1. Introduction

Aluminide coatings are known to protect steel at elevated temperatures in sulphurous, fused salt and marine atmospheres as well as providing satisfactory wear and scaling resistance. The coatings retain their efficacy below 900 °C, above which Al diffuses deeper into the base leaving the outer surface impoverished in Al [1]. If the level of Al drops below 8% in the outer layer, the protective properties are inadequate [1]. Steels with outer aluminide layers have been considered as substitutes for costly alloy steels in high- and ambient-temperature corrosive atmospheres [2]. Of particular significance is the potential of the aluminized steels in minimizing harmful carburizing at the elevated temperatures which process heater tubes experience in the hydrocarbon industry, such as in oil refineries [3]. Apart from these, aluminide-coated steels find prominent use as components in automotive exhaust systems, heat exchangers, furnace parts and pre-engineered building construction [4] etc.

Calorizing involves aluminization of materials of complex shape in a cementation pack consisting of an activator and donor material aluminium, either in pure form or as a compound of an alloy. Pack aluminizing of steel in an unalloyed Al pack is reported to yield non-uniform, brittle $FeAl_3$ and Fe_2Al_5 coatings [2]. On the other hand, a ferro-aluminium pack with an activator (usually a halide) is known to yield a smooth, adherent and uniform coating [2]. In the pack cementation process, aluminium is transported from the pack to the substrate in the form of gaseous Al halides. The halide then decomposes on the metallic surface, releasing Al atoms to react with the surface of the steel and leading to the formation of solid solutions or intermetallic compounds with iron. Al also diffuses into the interior through the metal surface or through the existing coated layer and forms intermetallic compounds of varying stoichiometry. The kinetics of aluminium transport in aluminizing packs have been extensively studied in the literature both for pure Al packs [5–10] as well as for Al alloy packs [11–14]. There is a generally held view [15] that the surface chemical reactions are so fast that the vapour phase is essentially in local thermodynamic equilibrium with the sample surface and alloy particles in the pack for a variety of activators and over a wide temperature range.

The growth of the coating layer is found [2] to be mostly parabolic. Further, the rate of aluminium deposition in a single-phase alloy pack is controlled by diffusion in the solid and gaseous phases rather than by the rate of surface reactions [6–10, 15] since the last step is very fast. Another feature of the pack cementation process as contrasted with hot-dip aluminizing is that in the former, the alloy layer composition does

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not change gradually from that of the donor pack on the outside to that of the substrate in the interior. In pack calorizing, sharply defined (optically distinct) layers form [16].

As mentioned above, apart from α-solid solution [17–19], intermetallic compounds of various stoichiometry ($FeAl_3$, Fe_2Al_5, FeAl, Fe_3Al etc.) can form when Al atoms interact with Fe [20–27]. The actual compounds, their extent and morphology depend on process parameters such as the composition of the pack and activator, the temperature and time of the treatment process as well as the chemistry of the specimen. There are, however, divergent reports on the phases formed, due primarily to differences in the process parameters and difficulty in determining phase compositions in small volumes.

The oxidation resistance provided by the Al-rich layer is primarily due to the formation of Al_2O_3. However, in atmospheres such as that of chloride, this layer breaks down and the main protection is believed to be the sacrificial nature of Al atoms with respect to Fe atoms [4, 16]. Whereas oxidation and corrosion resistance properties of steel improve upon calorizing, the mechanical properties by and large deteriorate. The brittle intermetallic compounds reportedly [28] begin to crumble and separate immediately on application of a load, but the ductile part of the coating adjacent to the base sticks to it even after the specimen fails. However, thin cases of 0.05–0.07 mm produced by calorizing at 850 °C can be cold- or hot-worked. It is believed [11] that the reduction in mechanical strength of calorized steels is due to reduction in the effective cross-section of the material, the assumption here being that the cross-section where the interaction between diffusing Al and Fe atoms takes place is ineffective for load-bearing. Some fatigue properties have been reported and it has been shown that the thicker the coating, the lower is the fatigue life [29]. There are some investigations to show that coatings improve the low-cycle fatigue life [30]. Calorizing decreases the creep strength and stress rupture strength [13].

The present investigation was undertaken to investigate the influence of the composition of the donor mix, and of calorizing temperature and time on a variety of steels. Attention was focused on the phases formed and their morphological features, as well as on mechanical properties including fatigue of the coated material.

2. Experimental procedure

Samples of cleaned, degreased, finished mild steel (0.26% C) and 304 (18/8 austenitic) and 430 (17% Cr) stainless steel were prepared. The pack consisted of powdered Fe–Al alloy of two compositions, 35 and 62 wt % Al, together with diluent and inert filler material (sintered alumina) to avoid sintering or coalescence of Al powders, and an activator or carrier NH_4Cl which acts as a flux and facilitates the initial reaction between Al and steel. The sample and the pack materials were sealed hermetically in an Fe–Cr–Ni alloy retort and the assembly was held at 850–950 °C for 2–4 h. The specimens were cooled *in situ*. The packing conditions were standardized and both mild steel as well as stainless steel samples were packed together in a batch calorizing process with the Fe–62% Al pack. The samples were metallographically prepared by polishing and etching the transverse section with 2% nital solution. These were used for optical metallography and microhardness measurements as well as for phase analysis by X-ray diffraction using CrK_α radiation. Analysis of deeper layers by X-ray diffraction was done by removing the layers electrolytically. Calorized mild steel samples (900 °C, 2 or 4 h using Fe–62% Al alloy as pack material) as well as uncalorized material were subjected to tensile and fatigue tests. Rotating bending fatigue tests were carried out in a rotating bending cantilever fatigue testing machine at a stress level of 240 MPa and a frequency of 50 Hz. Fatigue crack initiation tests were conducted under three-point loading in a high-frequency Vibrophore machine at a mean stress of + 123 MPa and dynamic stress of ± 106 MPa and frequency of 90 Hz. The criterion for crack initiation was taken as a 1 mm crack from a V-notch, having a stress concentration factor of 2.27.

3. Results

The complete structural characterization of calorized mild steel (MS) using Fe–62% Al and Fe–35% Al alloys shows that for MS the calorizing condition 850 °C/2 h does not give sufficient coating thickness, but at higher temperature and longer time there is an increase in coat thickness from 13 to 185 μm and an increase in microhardness from 200 to 390 VHN. The favourable phases FeAl and Fe_3Al (satisfying the Pilling-Bedworth condition) form mostly except at 950 °C/4 h when $FeAl_3$ also forms. However, calorizing with a lower Al activity pack (35 wt % Al) produces favourable phases only under the calorizing conditions of 950 °C/4 h (Table I).

Pack-calorized 304 and 430 stainless steel (SS) show two distinct layers of coating compared to a single layer in calorized MS, although the total coat thickness appears to be thinner in SS (45–130 μm) especially under 900 °C/4 h conditions. Table II shows the structural characterization of calorized 304 SS. The average microhardness is much higher, starting with 480 VHN at 850 °C/2 h and going up to 680 VHN at 950 °C/4 h. Unlike MS, the unfavourable phases are also forming at lower temperature and time for SS. The calorizing parameters found to produce only favourable phases in 304 SS are 950 °C/4 h. Also, it was noticed that the *d* values of phases are much higher in specimens calorized at lower temperatures, while they approach accurate *d* values at 950 °C/4 h. Table III shows structural data for calorized 430 SS, which shows mostly the presence of the favourable phase FeAl except at 850 °C/4 h. Both stainless steels pack-calorized with Fe–35% Al at 950 °C show the favourable phase FeAl only, as in MS (Tables II and III).

Figs 1–3 show the microstructures of MS, 304 SS and 430 SS, respectively, when calorized under ident-

TABLE I Properties of calorized MS

Pack	Calorizing conditions (°C/h)	Average coat thickness (μm)	Average microhardness (kg mm^{-2})	Intermetallic phases (by XRD)
Fe–62 wt % Al	850/2	13	193	–
	850/4	67	221	FeAl, Fe_3Al
	900/2	93	243	FeAl, Fe_3Al
	900/4	106	290	FeAl, Fe_3Al
	950/2	119	317	FeAl, Fe_3Al
	950/4	185	390	FeAl, Fe_3Al, $FeAl_3$
Fe–35 wt % Al	900/2	75	234	FeAl
	950/2	140	286	FeAl
	950/4	150	362	FeAl

TABLE II Properties of calorized 304 SS

Pack	Calorizing conditions (°C/h)	Average coat thickness (μm)	Average microhardness (kg mm^{-2})	Intermetallic phases (by XRD)
Fe–62 wt % Al	850/4	45	477	FeAl, Fe_2Al_5, Fe_3Al, $FeAl_3$
	900/2	48	500	FeAl, Fe_2Al_3 Fe_2Al_5
	900/4	112	610	Fe_2Al_5, FeAl
	950/2	70	613	Fe_2Al_5, FeAl
	950/4	115	677	FeAl (on surface, 20 μm below and 50 μm below)
Fe–35 wt % Al	950/4	74	677	FeAl

TABLE III Properties of calorized 430 SS

Pack	Calorizing conditions (°C/h)	Average coat thickness (μm)	Average microhardness (kg mm^{-2})	Intermetallic phases (by XRD)
Fe–62 wt % Al	850/4	45	–	FeAl, Fe_2Al_5, Fe_3Al, $FeAl_3$
	900/2	–	–	FeAl, Fe_2Al_3, Fe_2Al_5
	900/4	103	–	Fe_2Al_5, FeAl
	950/2	–	–	Fe_2Al_5, FeAl
	950/4	130	613	
			550	FeAl: (on surface, 30 μm below and 55 μm below)
Fe–35 wt % Al	950/4	64	613	FeAl

ical and standard pack conditions. In contrast to a single-layer coating in mild steel, there is multiple-layer coating in both the stainless steels. Table I shows that the outermost layer in both SS and MS is the hardest, and this layer generally consists of a mixture of favourable and unfavourable (e.g. Fe_2Al_5, $FeAl_3$ etc.) phases. On the other hand, the inner layers are softer and contain favourable phases. The standard microhardness of known phases in the Fe–Al system is given in Table IV. On batch calorizing of MS and SS it can be said (Table V) that the calorizing conditions have been optimized for MS and for 430 SS as

TABLE IV Approximate microhardness of intermetallic compounds in Fe–Al system [31]

Phase	Microhardness (kg mm^{-2})
Fe_3Al	350
FeAl	640
Fe_2Al_3	820
$FeAl_2$	1030
Fe_2Al_5	820
$FeAl_3$	990
Fe_2Al_7	1080

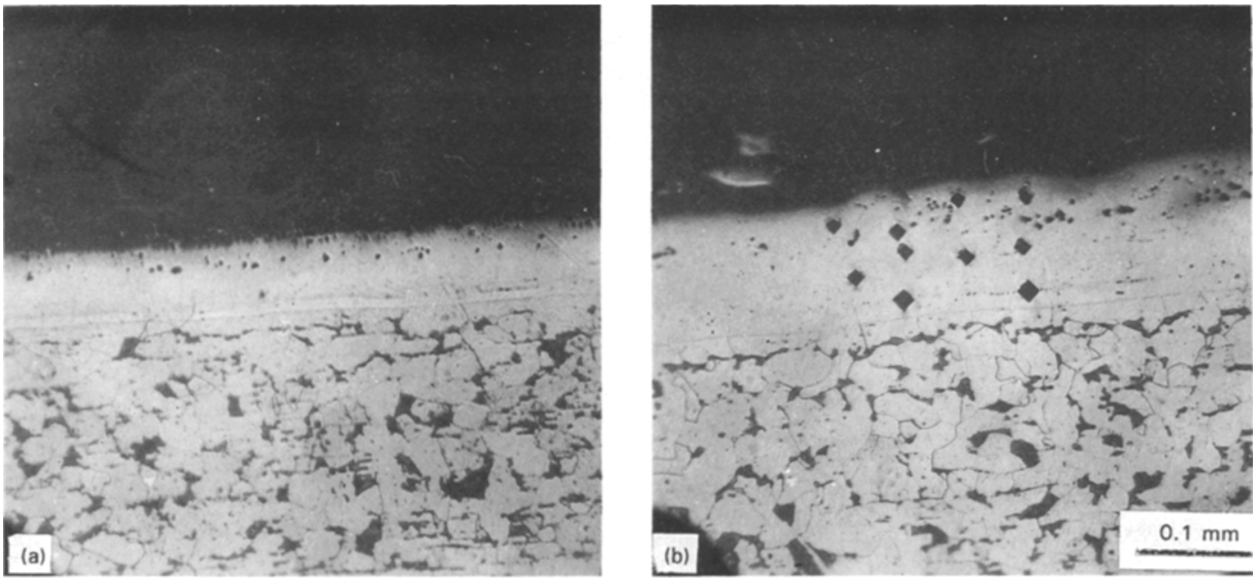

Figure 1 MS calorized at (a) 900 °C/4 h and (b) 950 °C/4 h.

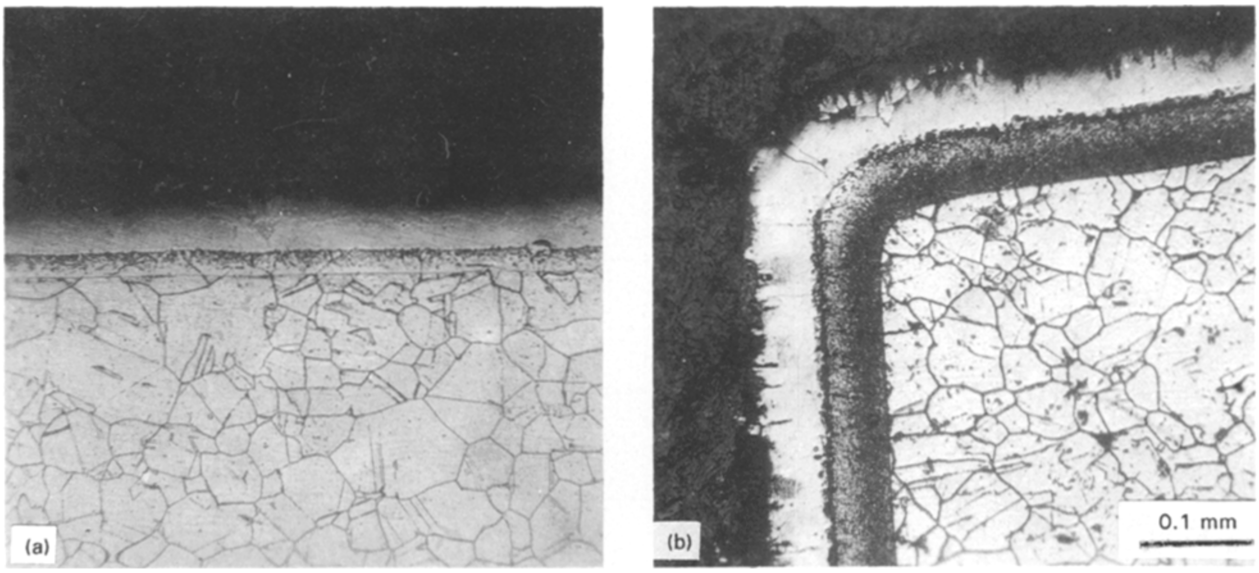

Figure 2 304 SS calorized at (a) 900 °C/4 h and (b) 950 °C/4 h.

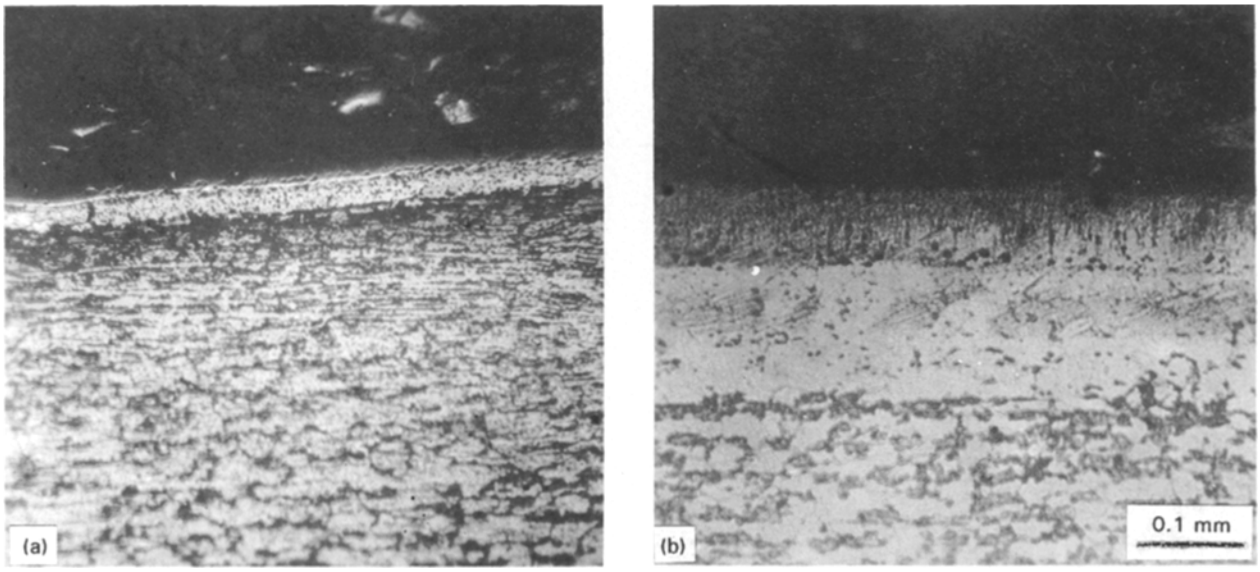

Figure 3 430 SS calorized at (a) 900 °C/4 h and (b) 950 °C/4 h.

TABLE V Properties on batch calorizing of MS and SS

Specimen	Calorizing conditions (°C/h)	Average coat thickness (outer + inner layer) (μm)	Distance from outer edge (μm)	Microhardness (kg mm^{-2})	Phases identified by XRD
MS	900/4	63	7–10	515	FeAl (on surface)
			22	439	
			25–29	378–329	
			47	185	FeAl, Fe_3Al (50 μm below)
	950/4	124	15–22	515	FeAl, Fe_3Al, $FeAl_3$ (on surface)
			35–55	475–440	FeAl (30 μm below)
			65–75	410–378	FeAl (60 μm below)
			104–110	230–205	
304 SS	900/4	40 + 45	10–12	610–750	FeAl, Fe_2Al_5, $FeAl_3$, Fe_3Al (on surface)
			30	–	FeAl (30 μm below)
			60	378	
	950/4	50 + 105	10–15	710–753	FeAl, Fe_3Al, $FeAl_3$, Fe_2Al_5 (on surface)
			20	852	FeAl, Fe_2Al_5 (20 μm below)
			62–75	378–329	FeAl (50 μm below)
			97	229	
430 SS	900/4	40 + 43	–	–	FeAl (on surface)
			20	–	FeAl (20 μm below)
			52	439	FeAl (50 μm below)
	950/4	85 + 80	–	–	FeAl, Fe_3Al, Fe_2Al_5 (on surface)
			–	–	FeAl (50 μm below)
			95	515	FeAl (90 μm below)
			116–126	378–290	–
			175	186	–

TABLE VI Tensile properties of MS uncalorized and calorized at 900 °C/4 h with Fe–62% Al pack

Property tested	Uncalorized specimen	Calorized specimen	Change in property due to calorizing
Hardness (VPN)	156	363	132% increase
UTS, R_m (MPa)	480	452	5% increase
Elongation, A(%)	40	40	No change
Reduction in area, Z(%)	73	66	9% decrease

900 °C/4 h. However, in 304 SS favourable phases were not formed on the surface even under these conditions.

In comparison with an uncalorized tensile specimen, calorizing (Table VI) produces a 132% increase in hardness, a 5% decrease in reduction in area, no change in percentage elongation and a 5% decrease in ultimate tensile strength (UTS). Fig. 4 shows a considerable decrease in high-cycle fatigue properties in calorized mild steel due to multiple crack initiation sites. The calorized layer peeled off during the test. From Fig. 5, the probability to failure and cycles to crack initiation were determined using the median rank values, assuming a log–normal distribution. The data reveal that MS calorized at 900 °C for 2 h has better fatigue properties than that calorized for 4 h.

4. Discussion

The types of intermetallic phase that form on the surface and at different depths below the surface of the coating have been studied in this work. A simple analysis can be made on the basis of the Pilling–Bedworth (PB) condition to assess the intermetallic phases that form on the surface and at different depths below the surface of the coating. In its original form, the PB condition stipulates that if an oxide formed occupies a larger volume in its uncompressed state than the metal destroyed, the coating must be compact and protective. This condition has been extended to cover other types of metallic coating such as aluminides obtained during calorizing:

$$1 < \frac{V_{MAl_x}}{V_M} < 3$$

where V_{MAl_x} = volume of metal aluminide and V_M = volume of metal used in forming aluminide. As can easily be imagined, the ratio between the volume of aluminide and the volume of substrate metal expended in the formation of aluminides characterizes the continuity of the coating and the level of internal stresses formed in the coating due to phase transitions. This ratio has been found to lie within the limits given above for the intermetallic

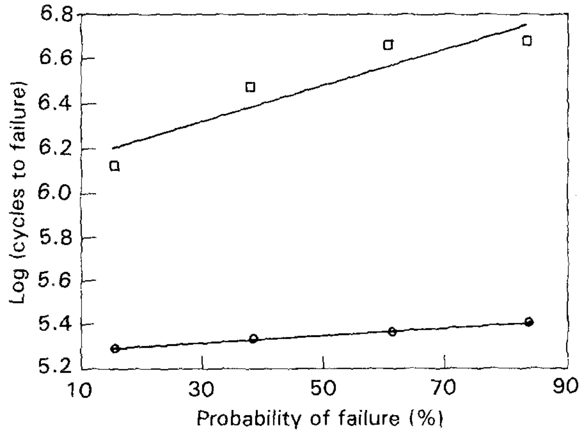

Figure 4 High-cycle fatigue properties of MS (Rotating bending, $S = 240$ MPa): (□) uncalorized, (○) calorized 900 °C/4 h.

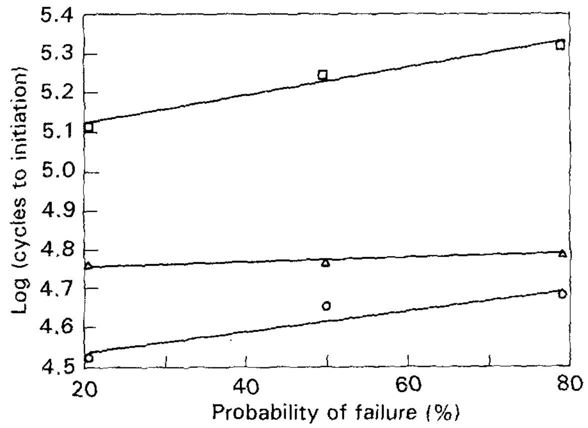

Figure 5 Fatigue crack initiation tests on MS (three-point bend, U notch): (□) uncalorized, and calorized (△) 900 °C/2 h, (○) 900 °C/4 h.

compounds FeAl (2.09) and Fe_3Al (1.37), while it is greater than 3 for all other compounds in the Fe–Al system [22]. Thus the formation of compounds such as $FeAl_2$, $FeAl_3$, $FeAl_6$ etc. may be harmful because of poor compatibility with the matrix.

In the present study, X-ray diffraction of coated layers and microhardness across a cross-section of the coating indicates that in the case of MS under the experimental calorizing conditions and with the higher-Al pack, favourable phases like FeAl and Fe_3Al generally form except in the case of 950 °C/4 h when the unfavourable phase $FeAl_3$ also forms on the surface. The deeper layers (~30 μm and more), however, contain only FeAl. On the other hand, calorizing with the lower-Al pack (35 wt % Al) gives rise to the formation of only FeAl, including at 950 °C/4 h, and other Al phases do not form. It is to be expected that in the latter pack, because of the lower Al (35 wt %), phases rich in Al like $FeAl_3$ and Fe_2Al_5 may not form. Consequently 950 °C/2 h appears to be an optimised condition in MS for material in either pack. Lower temperature retards the process and higher temperature impairs the quality of the protective deposit. Fe_3Al was not reported for the lower-Al pack but it may still be present and because of the presence of texture, the exclusive diffraction lines (1 1 1, 3 1 1, 3 3 1) may not have been observed.

In the case of SS calorized separately with the higher-Al pack, the calorizing parameters of 850 °C/4 h give a combination of all possible phases and 950 °C/4 h appears to be suitable for both types of steel. However, during standardized conditions of batch calorizing (using small and uniform size powder) with the Fe–62% Al pack, especially in the case of 304 SS, a mixture of favourable and unfavourable phases forms on the surface and only favourable phases form ~30 μm and more below the surface. Standardization of the pack is important for getting reproducible results. SS calorized with the lower-Al pack shows only the favourable phase FeAl on the surface and in deeper layers as in the case of MS. A pack of low Al activity such as Fe–35% Al is in general more helpful in getting desirable phases on the surface and inside the calorized coatings.

The reduction in the values of UTS and yield strength is in line with similar previous observations by others [28]. The reduction in area is appreciably deteriorated. This indicates that there is some embrittlement, as others have observed [28]. From the fatigue crack initiation properties, it is seen that MS calorized at 900 °C/2 h has better fatigue properties than that calorized for 4 h. This is due to the former having a smaller thickness. The thickness of the coating, it is believed, plays an important role in deciding the overall mechanical properties. Since the intermetallic compounds are themselves much stronger than the matrix, the slight fall in UTS may indeed be due to decohesion between the aluminides and the matrix.

In the literature, very few results on the effect of calorized coatings on fatigue properties are reported. The results can vary considerably, e.g. it is shown [28, 29] that an increase in the thickness of Al diffusion coat in the range 0.045–0.2 mm leads to reduced high-cycle fatigue lives. The adverse effect is due to the brittleness of the intermetallic case. Due to the larger volume of the aluminides, a compressive residual stress is to be expected on the calorized surface. This should lead to an improved performance in fatigue in monolithic samples. However, the deterioration in the present case would be attributed to the large difference in moduli between the aluminide and matrix that may induce fatigue–more so, if the layer is thicker. Inherent properties of the aluminide coat such as its strain-bearing capacity may also detrimentally affect the fatigue behaviour of the component. Although the literature provides some reasons, such as loss of load-bearing cross-section and modification of chemical composition, it is believed that further work is required to pinpoint the causes.

5. Conclusions

1. A pack of low Al such as 35 wt % gives rise to intermetallic phases favourable for corrosion protection under the experimental calorizing conditions.
2. A pack containing 62 wt % Al gives rise generally to a mixture of favourable and unfavourable phases on the surface of the coating.

3. The calorizing conditions of 900 °C for 2 or 4 h are suitable for producing favourable phases only on the surface of MS and 430 SS in both lower- and higher-Al packs.

4. For 304 SS, a lower-Al pack always produces desirable phases, but with a higher-Al pack only a thin undesirable top layer forms, which when removed results in desirable phases.

5. From a fatigue point of view a thinner coating (e.g. 900 °C/2 h for MS) is to be preferred.

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References

1. N. D. TOMASHOV, "Theory of Corrosion and Protection of Metals" (Macmillan, New York 1966) p. 119.
2. R. SIVAKUMAR and E. J. RAO, *Oxid. Met.* **17** (1982) 391.
3. C. J. BOLTON and I. R. McLAUCHLIN, in "Corrosion and Mechanical Stress at High Temperatures", edited by V. Guttmann and M. Merz (Applied Science Publishers, London, 1981).
4. R. D. JONES and D. P. JONES, in "Coatings and Surface Treatment for Corrosion and Wear Resistance", edited by K. N. Strafford, P. K. Datta and C. G. Googan, (Ellis Horwood, Chichester, 1984) p. 103.
5. K. NISHIDA and T. NARITA, *Trans. JIM* **14** (1973) 431.
6. S. R. LEVINE and R. M. CAVES, *J. Electrochem. Soc.* **121** (1974) 1051.
7. R. SIVAKUMAR and L. L. SEIGLE, *Metall. Trans. A* **7** (1976) 1073.
8. B. K. GUPTA, A. K. SARKHEL and L. L. SEIGLE, *Thin Solid Films* **39** (1976) 313.
9. B. K. GUPTA and L. L. SEIGLE, *ibid.* **78** (1980) 365.
10. N. KANDASAMY, L. L. SEIGLE and F. J. PENNISI, *ibid.* **84** (1981) 17.
11. C. DURRET and R. PICHOIR, in "Coatings for High Temperature Applications", edited by E. Lang (Applied Science, London and New York, 1983) p. 33.
12. K. VASHCHENKO, V. ZHIZHCHENO and A. FIRSOV, "Bimetalliche Skie Otlivki Zhelezo–Aluminu" (Mashinostroenie, Moscow, 1966).
13. A. MINKEVICH, "Khim–Term, Obrabotka Metallov Splavov" (Mashinostroenie, Moscow, 1965).
14. A. N. MUKHERJEE and P. PRABHAKARAN, *Anti Corr. Meth. Mater*, **25** (1978) 5.
15. T. H. WANG and L. L. SEIGLE, *Mater. Sci. Eng.* **108** (1989) 253.
16. R. M. BURNS and W. W. BRADLEY, "Protective Coatings for Metals", (Reinhold, New York, 1967) p. 281.
17. N. S. GORBUNOV, "Diffusion Coating on Iron and Steel" (Acad. Sci., Moscow, USSR, 1958) p. 91.
18. E. FITZER and H. J. MAURER, in "Materials and Coatings To Resist High Temperature Corrosion", edited by D. R. Holmes and A. Rahmel (Applied Science Publishers, London, 1978) p. 253.
19. W. A. McGILL and M. J. WEINBAUM, *Met. Progr.* **115** (1979) 26.
20. D. P. MOSES and G. G. POPHAM, *Metallurgia* **45** (1952) 70.
21. B. N. ARZAMASOV and A. A. KONE-PLEVA, *Metal Sci. Heat Treatment* **20** (1978) 957.
22. D. R. ANDREWS, *Metallurgia* **62** (1966) 153.
23. G. V. SAMSONOV (ed.), "Protective Coatings on Metals" (Consultants Bureau, London, 1973) p. 5.
24. S. L. CASE, *Steel Proc.* **36** (1950) 435.
25. E. GEBHARDT and W. OBROWSKI, *Z. Metallkde* **44** (1953) 154.
26. G. GURTLER and L. SAGEL, *ibid.* **46** (1955) 738.
27. T. I. ARTYUSCHCHENKO, in " Protective Coatings on Metals", edited by Samsonov, Vol. 5 (Consultants Bureau, New York, 1969) p. 124.
28. G. V. KARPENKO, V. I. POKHMAROVSKII, V. B. DALISOV and V. S. ZAMIKHOVSKII, "Influence of Diffusion Coatings on the Strength of Steel", edited by A. Aladjen (Trans Tech, Switzerland, 1979) p. 123.
29. R. S. BARTOCCI, in ASTM STP 421 (American Society for Testing and Materials, Philadelphia, 1967) p. 169.
30. C. H. WELLS and C. P. SULLIVAN, *ASM Trans.* **61** (1968) 149.
31. L. N. LARIKOV, V. M. FAL' CHENKO, D. F. POLISHCHUK, V. R. RYABOV and A. V. LOZOVSKAYA, in " Protective Coatings on Metals", edited by G. V. Samsonov, Vol 3, (Consultant Bureau, New York, 1971) p. 66.

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