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Corrosion and oxidation resistance properties of titanium-containing low-alloy steel

Abstract An innovative technique of using conventional low-alloy steel as the prefabricated starting material and pure titanium and aluminium as alloying additions has been employed in this study for obtaining titanium-containing corrosion and oxidation resistant low-alloy steel. Corrosion resistant iron-titanium alloys have also been developed, which may find use in the hardware of phosphoric acid making plants and other equipment. The corrosion and oxidation resistance properties of these alloys have been exhaustively studied using modern electrochemical techniques. Initially the alloying element compatibility range was worked out for titanium in iron, by determining the optimum physicochemical properties of the iron-titanium matrix corresponding to a particular titanium percentage. This value was then extrapolated to the low-alloy steel matrix, assuming the prefabricated low-alloy steel (SAE 8620) to be an impure iron (due to the lower concentration of alloying elements like Mn, Si, P, S, Cr, Ni, Mo, etc.), for obtaining a resistant low-alloy steel. Ti 5%-SAE 8620 low-alloy steel matrix revealed superior resistance to oxidation and corrosion compared to SAE 8620 alloy.

Introduction

High-strength low-alloy steels (HSLA) and microalloyed steels are basically low-alloy steels (LAS), having alloying additions of Mn, Ni, Cr, Mo, Nb, Ti, V, Al and B. In the case of the microalloyed variety, the total alloying content may vary between 0.3% and 0.4%. The presence of elements like Mo, Nb, Ti, V, Al and B impart superior resistance to corrosion and oxidation to these materials. In the case of conventional LAS, the total alloying elements may be around 8–9 wt%. Both these varieties may be considered under the broad spectrum of the family of LAS, varying in their specific strengths as a function of the composition and texture of the matrix. The superior strength properties revealed by the microalloyed steel matrices may be attributed to strengthening by grain refinement, by precipitation within the matrix and solid solutioning effects. Pronounced grain refinement and precipitation strengthening are produced by the addition of niobium, while that of moderate precipitation coupled with lower grain refinement are attained by the addition of vanadium. Substantial precipitation, along with moderate grain refinement, is obtained by titanium addition. Manganese is the principal strengthening element of the plain carbon high-strength structural steels when present over 1%, being one of the major contributors to the toughness of the matrix. However, manganese functions here as a mild solid solution strengthener and as an element responsible for the decrease of the austenite to ferrite transformation temperature, resulting in the refinement of ferrite grain size.

The capability of titanium [1–6] to form a strong and adherent passive film, in almost all types of aggressive media, has virtually opened the cover of a Pandora's box for the development of resistant materials and other protection technologies. Higher specific strength (strength to weight ratio) and higher thermal stability have bestowed added advantages to the titanium metal. Moreover, titanium is not a very expensive metal, compared to the beneficial effects it provides. The solubility of titanium in iron is 6.9% at 1300 °C and decreases to 2% or less at room temperature. The incapability of ordinary structural and LAS to sustain an aggressive environment, and one containing chloride ions, has led the authors of this paper to fabricate a not too expensive LAS, based on titanium as an alloying addition. The iron-titanium alloy, having 5% titanium, has been found to be compatible towards phosphoric acid, revealing comparatively lower leaching rates and indicating the possibility of use in the hardware of phosphoric acid manufacturing plants. This paper

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discusses all these aspects, laying emphasis on the properties concerning the corrosion and oxidation resistance of these matrices. The prefabricated SAE 8620 alloy used in this study is basically a manganese-containing LAS, and its subsequent alloying with 5% titanium keeps the alloying elements within the limit of solubility, forming less acicular interaction products.

Experimental

A conventional plasma arc-cum-induction melting furnace fitted with vacuum pumps and gas-filling facilities (inert gas) has been used in this study. Pure iron (99.99%) and commercially pure titanium (99.99%) and aluminium (99.99%) have been employed for preparing the iron-titanium and iron-titanium-aluminium alloys, in the arc-furnace facilities using argon gas as an environment.

SAE 8620 alloy steel matrix has been used for making the titanium-modified LAS. As such, the SAE 8620 matrix forms the prefabricated LAS, which is used as the starting material for obtaining its titanium-modified version. Both pure titanium and aluminium are added to the prefabricated SAE 8620 matrix for obtaining the titanium-modified SAE 8620 matrix using the arc-cum-induction furnace facilities. Initially, Fe-Ti alloys, having 5% Ti, 8.5% Ti and 8.5% Ti with 0.5% Al were studied for their corrosion and oxidation resistance properties, for determining out the optimum %Ti, at which the Fe-Ti matrix is most stable in terms of resistance to oxidation and corrosion. Finally, the prefabricated SAE 8620 alloy was induction melted using that optimum Ti concentration for developing a resistant LAS.

All these induction-melted alloys are furnace cooled before retrieval from the mould and hence have a superimposed annealing effect on the samples. The retrieved ingots are analyzed by the conventional wet analysis process. Tafel extrapolation and linear polarization techniques, have been employed for obtaining electrochemical parameters like I_{corr}, E_{corr}, b_a, b_c, etc., using a potentiostat (EG&G Par model 366). All the electrochemical parameters are expressed with reference to saturated calomel electrode (SCE). Anodic polarization studies of the iron-titanium group of alloys have been conducted using H_2SO_4 or H_3PO_4 as the electrolyte. The thickness of the passive film formed during the anodic polarization studies has been measured using the ellipsometric technique. A conventional impedance set-up, fitted with an electrochemical interface and a lock-in amplifier, was employed for obtaining the R_p values. Weight-loss corrosion rate values have been obtained from experiments based on the determination of the extent of material leaching, as per ASTM G31/71 standard. Oxidation rate values have been obtained from experiments conducted inside a muffle furnace, under an ambient air environment. Hardness values have been recorded, using a Rockwell machine and were converted to the brinnel number (BHN) scale using appropriate conversion tables. All the chemicals employed in this study are of analytical reagent grade. Standard metallographic techniques comprising grinding, polishing, etching and microphotographing have been employed for the metallographic examinations conducted on the

iron-titanium, iron-titanium-aluminum and titanium-aluminium modified SAE 8620 group of alloys.

Results and discussion

Iron-titanium group of alloys

The physical and chemical properties of the Fe-Ti group of alloys, with and without aluminium addition, compared to that of mild steel is given in Table 1. It is seen that the hardness values of this group of alloys remain more or less in the range of mild steel, varying within 100–165 BHN. Considering the Fe-Ti group of alloys as a separate class and a difference of 50 units to be due to the variations in the composition and texture of the matrix, it appears that an increase in the level of total alloying elements (addition of Al) increases the matrix hardness values marginally. It is assumed that the small annealing effect experienced by these induction-melted alloys during the cooling down is negligible and is present in all the induction-melted alloys, and need not be considered in the evaluation of the matrix. The oxidation gain values of mild steel and Fe91.5-Ti8.5 are on a higher level compared to those of Fe95-Ti5 and Fe91-Ti8.5-Al0.5 alloys. Aluminium addition in the Fe matrix appears to provide ceramacity to these alloys, probably being able to generate Al_2O_3 uniformly dispersed within the surface oxide layer. Corrosion rate values in 5% H_2SO_4 reveal a maximum for the Fe91-Ti8.5-Al0.5 matrix, while it gives identical values for Fe95-Ti5 and Fe91.5-Ti8.5 alloys. In the case of the 10% H_3PO_4 medium, corrosion rate values increase in the order Fe91-Ti8.5-Al0.5, Fe91.5-Ti8.5 and Fe95-Ti5 alloys, although differing only marginally within 0.3 units of corrosion current.

Table 2 shows the oxidation resistance values of Fe95-Ti5 alloys and mild steel at various temperatures, supported by observations from scanning electron microscopy (SEM). It is seen that the average oxidation gain values of the Fe-Ti alloy has not been affected by the increase in temperature up to 600 °C. It is also observed that, compared to the mild steel, the average oxidation gain values of Fe-Ti alloys are less, indicating a lower degree of temperature susceptibility. Unlike mild steel, the oxidized surface of the Fe-Ti group of alloys reveals specific grained structure without cracks being observed, even at 600 °C.

Table 1 Physical and chemical properties of the Fe-Ti group of alloys, with and without aluminium additions

Material	Hardness (BHN)	Micro-exam (500×)	Oxidation rating × 10^{-4} (mg/cm^2/h)	Corrosion current I_{corr} (µA/cm^2)	
				5% H_2SO_4	10% H_3PO_4
Mild steel	165	fine grain	280	0.90	1.0
Fe95-Ti5 alloy	100	grainy	100	0.65	0.65
Fe91.5-Ti8.5 alloy	156	precipitated phases at grain boundary	202	0.65	0.50
Fe91.0-Ti8.5-Al0.5 alloy	165	dendritic network and precipitated phases at grain boundary	55	2.8	0.30

Table 2 Oxidation resistance of Fe95-Ti5 alloy at various elevated temperatures, supported by SEM surface observation (duration of oxidation 2 h)

Material	Average oxidation gain (mg/cm^2)			SEM surface observation for the oxidized surface (175×) (surface oxidized at 600 °C for 2 h)
	200 °C	400 °C	600 °C	
Fe95-Ti5	0.20	0.20	0.20	specific types with distinct pattern of smaller oxide grains observed with no cracks (Fig. 2)
Mild steel	0.112	0.224	0.56	oxide pattern observed with crack (Fig. 3)

Table 3 Film thickness and SEM microstructures of the passive film formed on Fe91.5-Ti8.5 alloys as a function of electrolyte

Material	Passivation potentials (E_p), passivation current (I_p) and the thickness of the passive film in Å						SEM microstructure of the passive film (1000×)
	40% H_3PO_4			10% H_2SO_4			
	Å	E_p (mV)	$I_p(\mu A/cm^2)$	Å	E_p (mV)	I_D ($\mu A/cm^2$)	
Mild steel	2700	+550	64	600	+550	1.5	porous passive film in H_2SO_4 and H_3PO_4 media
Fe91.5-Ti8.5 alloy	2700	+600	21	140	+600	1.1	passive film in H_3PO_4 medium
Fe95-Ti5 alloy	2700	+650		140	+650		compact low-porosity film in H_2SO_4 and H_3PO_4 media
Fe91.0-Ti8.5-Al0.5 alloy	2700	+600	33	650	+650	2.0	compact low-porosity film in H_3PO_4 medium

Table 4 Electrochemical behaviour of deformed and heat-treated Fe95-Ti5 alloy in 3% NaCl medium

Material	Potential (mV vs. SCE)				Potential shift in negative direction (mV)	Ratio of initial potential to potential shift in the negative direction	Polarization resistance (ohm)
	5 h	10 h	15 h	25 h			
Mild steel	−380	−380	−390	−450	70	5.43	80
Fe95-Ti5 alloy + 85% deformation	−240	−300	−400	−500	260	0.92	125
Fe95-Ti5 alloy + 85% deformation + stress relieving at 50 °C for 15 h	−300	−300	−300	−340	40	7.5	225
Fe95-Ti5 alloy + 85% deformation + stress relieving at 50 °C for 15 h + double annealing	−400	−400	−400	−410	10	40	85

Table 3 gives the passivation potentials, film thickness and the SEM microstructures of the passive films formed on the Fe-Ti group of alloys in 40% H_3PO_4 or 10% H_2SO_4 electrolytes. It is seen that in H_3PO_4 medium the alloy forms a thicker film whereas the film thickness values are comparatively lower in the H_2SO_4 medium. The Fe91-Ti8.5-Al0.5 alloy generates a compact low-porosity film in 40% H_3PO_4 medium. This may be attributed to the effect of aluminium, which tends to be oxidized to aluminium phosphate type of compounds, providing protection to the surface.

The corrosion resistance of Fe-Ti alloys in acidic solutions revealed that the dissolution rates of the Fe_2O_3-TiO_2 film was found to be significantly smaller [7–8] and no dissolution occurred at anodic potentials in 1 M H_2SO_4 [9]. The Fe-Ti alloy containing more than 39 at% and 57 at% Ti can be passivated by anodic polarization in 5 M HCl [10]. The dissolution rate of Fe_2O_3-TiO_2 films is smaller than that of the Fe-Ti alloys (arc melted) by approximately two orders if they are compared at the same film composition in 5 M HCl. Overall consideration of the above discussion clearly reveals that Fe-5%Ti alloy may be considered as a superior general purpose engineering alloy, revealing resistance to both oxidation and corrosion.

Table 4 lists the electrochemical behaviour of the deformed and heat-treated Fe95-Ti5 alloy in 3% NaCl medium. It is clearly observed that 85% deformation of the Fe95-Ti5 matrix, followed by heating, shows comparatively better electrochemical properties, while subsequent double annealing deteriorates the surface by shifting the potential to a more negative direction. The polarization resistance (Rp) values also reveal a minimum for the panel deformed and heated at a lower temperature for 15 h and followed by double annealing. It appears that deformation, followed by only low-temperature prolonged stress relieving, helps in the process of homogenization of the titanium-containing

phases, along with deactivation of the surface stress spikes, such that the surface potential tends towards a more positive direction. The negative potential shift is a maximum for the only deformed state and, followed by a drastic reduction in the negative potential shift in the case of the deformed and prolonged stress-relieved state, clearly indicates the highly dynamic nature and unsuitability of the only deformed state, where titanium-containing phases are non-uniformly distributed along the length and breadth of the cross section. As such, the surface undergoes progressive denoblement, accompanied by leaching of the surface. Prolonged post-stress relief at a lower temperature appears to improve the uniformity of the Fe-Ti complexes and other stressed phases, as revealed by the drastic reduction of the level of the final negative potential shift. The ratio of the initial potential to the negative potential shift also reveals an optimum value of 7.5 indicating control in both the levels of the initial potential and the negative shift for the deformed and stress-relieved matrix, compared to that followed by double annealing.

Titanium-containing LAS

The extent of the high-melting alloying element (Ti) to be accommodated in the fabricated LAS matrix required a previous study of the conventional Fe matrix with different concentrations of Ti for determining the critical alloying-element concentration at which there is an optimum combination of properties, within the more or less easy diffusibility limit of Ti in the Fe matrix, forming softer matrix products. The optimum concentration of the high-melting Ti alloying element was then extrapolated to the prefabricated LAS matrix, ignoring the effects of other alloying elements, which are only marginal. Such an extrapolation of the difficultly soluble Ti obviated the conventionally followed laborious homogenization steps, as mentioned earlier. Accordingly, 5% Ti was alloyed with the conventional SAE 8620 alloy, using a induction-cum-arc furnace facility, as 5% Ti addition to pure iron revealed optimum improvement in its resistance to oxidation and corrosion, indicating an easy diffusibility limit of Ti in Fe matrix.

SAE 8620 alloy is a very common LAS used in the mining industry, combining an optimum extent of strength and ductility along with reasonable resistance to corrosion and oxidation. Incorporation of 5% Ti in such a

Table 5 Composition of SAE 8620 low-alloy steel (LAS) and the induction-melted titanium-containing LAS

Element	Base LAS (SAE 8620 alloy)	Induction-melted titanium-containing LAS
Carbon	0.16	0.16
Silicon	0.30	0.31
Manganese	0.80	0.70
Chromium	0.70	0.64
Nickel	0.45	0.53
Molybdenum	0.25	0.26
Titanium	0.15	5.03
Copper	0.04	0.10
Sulfur	0.02	0.025
Phosphorus	0.02	0.012

matrix may provide additional strength and hardness, along with resistance to corrosion abrasion and oxidation.

Table 5 gives the composition of the induction-melted titanium-containing LAS, along with the base SAE 8620 LAS matrix. It is clearly seen that the fabricated titanium-containing LAS only marginally differs in composition from that of the base SAE 8620 alloy, except that the fabricated alloy has 5.03% titanium while the base alloy has a titanium content of 0.15%.

Table 6 lists the physicochemical properties of the Ti- and Al-containing induction-melted LAS matrices. It is observed that the matrix hardness and tensile strength of the Ti-modified LAS reveals lower values compared to the base SAE 8620 alloy. It is attributed to the absence of acicular harder phases and simultaneous generation of softer phases of solid solutions of Ti in the Fe matrix. The marginal annealing effect experienced by the induction-melted alloys may be neglected for all practical purposes, as all the alloys experience an identical annealing effect. The base SAE 8620 alloy, which is used as the standard for comparison for the newly fabricated alloys, also experiences a mild annealing effect during manufacture in the form of massive sand castings, from which it is retrieved. The corrosion rate values of the 5% Ti-containing induction-melted LAS matrix registers a reduction of about 1/13 of that of the base LAS, while for the 5% Ti- and 0.6% Al-containing LAS it is 1/7 of that of the base LAS. The 5% Ti-containing LAS shows 1/3 of the oxidation (in ambient air) of the base LAS, while there is a drastic increase of the oxidation value for the Al- added Ti-modified base LAS matrix. Comparatively higher corrosion rate values of Ti- and Al-containing LAS is probably attributed to matrix heterogeneity due to

Table 6 Physicochemical properties of the induction-melted titanium- and aluminium-containing LAS

Material	Hardness (BHN)	Tensile strength (TSI)	Weight loss corrosion rate $\times 10^{-5}$ (gm/cm^2/h) (3% NaCl)	Oxidation rating at 600 °C $\times 10^{-5}$ (gm/cm^2/h)
Base LAS (SAE 8620)	450	93	9.10	27.19
Induction-melted Ti-containing LAS[a] (5% Ti)	225	49	0.69	9.47
Induction-melted 5.03% Ti- and 0.5% Al-containing LAS[b]	229	53	1.29	60.30

[a] The starting materials melted for the LAS were SAE 8620 alloy and pure titanium
[b] The starting materials melted for the LAS were SAE 8620 alloy, pure titanium and pure aluminium

interaction products of Al with residual elements like Mn, Si, Mo, S, P, etc., present in the SAE 8620 matrix, and the galvanic strains thereof. However, very high oxidation rate values of LAS containing Ti and Al is also attributed to matrix heterogeneity and unfriendly acicular-type complex formation, which results in stress mismatch and subsequent spalling of the surface oxide products. In the case of the Fe-Ti matrix, Al addition probably reduces the oxidation by formation of a friendly net work of inert Al_2O_3 throughout the surface. On the other hand, Al forms unfriendly acicular interaction products with the residual alloying elements like Mn, Si, Ni, Mo, S, P, etc., present in the base SAE 8620 matrix.

Table 7 gives the Tafel parameters of the induction-melted Ti- and Al- containing LAS fabricated using the base SAE 8620 alloy. The electrochemical parameters have been recorded in both 3% NaCl and synthetic seawater medium. It is seen that the I_{corr} value of the 5% Ti-modified matrix is much lower than that of the base alloy and also that of the 0.6% Al-modified 5% Ti-containing alloy. The E_{corr} value is more or less identical in all the panels, indicating the basic thermodynamic similarity of these matrices. The Al- and Ti-containing alloy appears to have a galvanically incompatible surface, resulting in higher I_{corr} and marginally more negative E_{corr} values. The b_a and b_c values of the 5% Ti-containing matrix reveal identical levels, indicating that both anodic and cathodic types of interactions are effective in controlling the surface reactions and their optimization. The polarization resistance (R_p) values of the LAS, the induction-melted Ti and Ti-Al containing LAS in media like natural sea water and 3% NaCl clearly reveal that the Ti-modified alloy reveals an extremely high polarization resistance value, compared to that of the base and 0.6% Al plus 5% Ti modified matrices, indicating its superiority.

Comparison of the iron-titanium group of alloys and titanium-containing LAS

Figure 1 compares the physicochemical properties of the iron-titanium group of alloys and the induction-melted modified (with Ti and Al) alloys. It is seen that the hardness
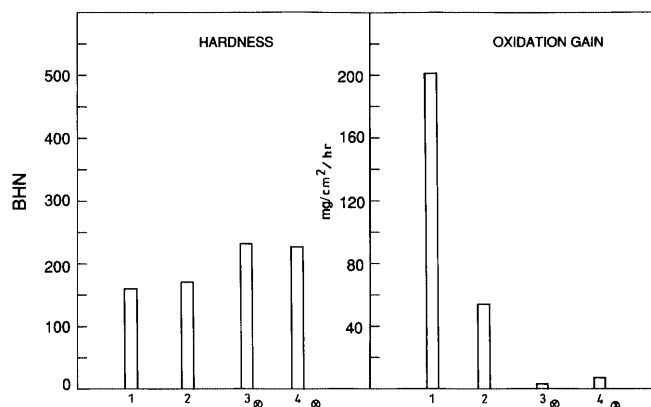

Fig. 1 Comparison of the physicochemical properties of Fe-Ti alloys and Ti-modified low-alloy steels: *1* Fe-5% Ti; *2* Fe-5% Ti-0.6% Al; *3* 5% Ti-SAE 8620; *4* 5% Ti-0.6% Al-SAE 8620

of the Fe-Ti and Fe-Ti-Al alloys is almost identical, owing to the basic similarities of these two groups of alloys. However, the Ti-SAE 8620 alloys, with and without Al addition, appear to reveal higher levels of hardness compared to their Fe-Ti counterparts. This may be attributed to the inherently lower hardness level of the Fe matrix, compared to that of the SAE 8620 matrix. The oxidation gain values of the Fe-Ti group of alloys are higher than those of the Ti-containing SAE 8620 group, indicating the better physicochemical properties of the latter compared to the former. The beneficial effect of the Al addition on the oxidation resistance properties of the Fe-Ti group of alloys contrasts with that of the Ti- and Al- containing SAE 8620 alloy. The absence of complex intermetallic formations in the former allows the Al to be distributed uniformly as a protective oxide network within the surface scale reinforcing the film, while in the latter case the formation of a complex intermetallic of Al with the residual alloying elements of SAE 8620 (Mn, Si, S, P, Ni, Cr, Mo, etc.) induces stress mismatches on the oxidized products, resulting in the subsequent spalling of the film. Figure 2 shows the grained pattern of oxides on the surface of the Fe-Ti alloy and Fig. 3 reveals the grained oxides observed on the surface of mild steel. It is seen that the oxidized Fe-Ti surface reveals no crack, while a crack is clearly observed on the oxidized mild steel surface.

Table 7 Tafel parameters for the induction-melted titanium- and aluminium-containing LAS (electrolyte = 3% NaCl or natural seawater)

Material	3% NaCl (vs. SCE)					Natural seawater (vs. SCE)				
	I_{corr} (μA/cm^2)	R_p	E_{corr} (mV)	Tafel slope		I_{corr} (μA/cm^2)	R_p	E_{corr} (mV)	Tafel slope	
				b_a	b_c				b_a	b_c
Base LAS (SAE 8620)	30.0	20	−535	55	15	27.0	112	−530	60	20
Induction-melted Ti-containing LAS (5% Ti)[a]	0.70	2800	−425	75	75	2.2	3000	−485	90	90
Induction-melted 5.03% Ti- and 0.5% Al-containing LAS[b]	5.0	134	−545	85	50	20.0	132	−545	90	15

[a] The materials melted for the LAS were SAE 8620 and pure titanium
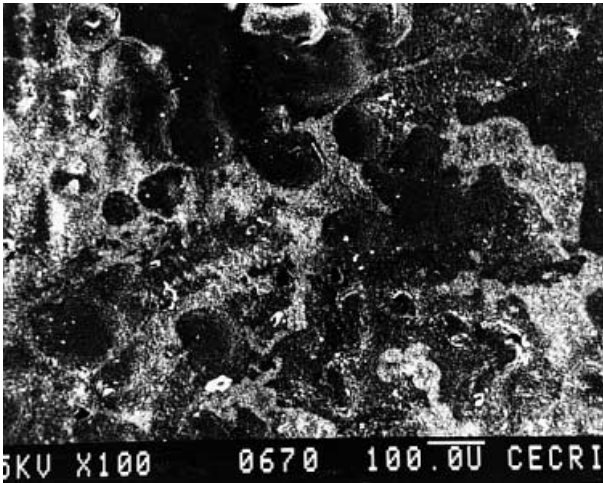[b] The materials melted for the LAS were SAE 8620, pure titanium and pure aluminium

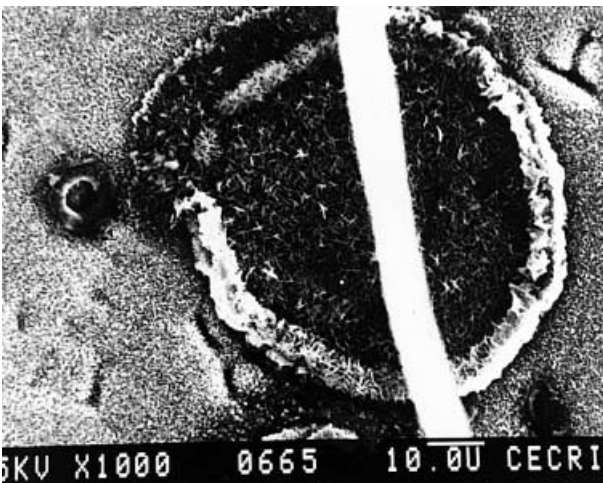**Fig. 2** Grained oxidized layer on Fe-Ti alloy

Fig. 3 Grained oxidized layer on mildsteel with crack

Conclusion

It appears from this study that the Fe95-Ti5 matrix is resistant to both corrosion and oxidation and Fe91-Ti8.5-Al0.5 is particularly resistant to the dilute phosphoric acid medium. It is possible to modify the conventional SAE 8620 LAS matrix in an induction cum arc furnace, using pure Ti and Al, where the starting base matrix is the prefabricated SAE 8620 alloy.

Fe-5%Ti alloy and 5% Ti-modified SAE 8620 alloy reveal resistance to both corrosion and oxidation. The addition of Al introduces complications in the dry oxidation step for the Ti-modified LAS, although it favours oxidation resistance and resistance to corrosion in phosphoric acid medium for the Fe-Ti system of alloys. Addition of aluminium destabilizes both the resistance to corrosion and oxidation of the induction-melted Ti-modified SAE 8620 matrix. The Fe-Ti group of alloys form a compact film in H_2SO_4 medium, while they form thicker porous films in H_3PO_4 medium.

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