SCIENCE CHINA
Technological Sciences

February 2012 Vol.55 No.2: 505–509
doi: 10.1007/s11431-011-4700-x

Improvement in the liquid zinc corrosion resistance of high Nb-TiAl alloys by pre-oxidation in a SiO_2-powder pack

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Received September 5, 2011; accepted November 24, 2011; published online December 28, 2011

The influence of pre-oxidation on the liquid zinc corrosion resistance of high Nb-TiAl alloys was investigated. The pre-oxidation was performed by heating the specimens, buried in silica powder and encapsulated in a silica tube under a vacuum of 1.3×10^{-3} Pa at 950°C for 12 h. Experimental results showed that the preoxidized sample exhibited much higher liquid zinc corrosion resistance than that for the comparative samples. This excellent liquid zinc corrosion resistance was attributed to the formation of high-quality oxide scale during peroxidation. The corrosion of all the samples in liquid zinc was caused by a localized breakdown in the oxide scales. The continuous and dense oxide scale formed during preoxidation substantially may prevent the liquid zinc from diffusing to the substrate, and its good continuity may also reduce the possibility of localized breakdown in the oxide scale.

liquid zinc, corrosion, preoxidation, TiAl-Nb intermetallic compound

Citation: Sun P F, Zhang L Q, Zhang L, et al. Improvement in the liquid zinc corrosion resistance of high Nb-TiAl alloys by pre-oxidation in a SiO_2-powder pack. Sci China Tech Sci, 2012, 55: 505–509, doi: 10.1007/s11431-011-4700-x

1 Introduction

In continuous hot-dip galvanizing lines, the immersed bath hardware, such as bearings, sink, stabilizer, and corrector rolls, is subject to corrosive attack by the molten bath material. Current materials used for the bath hardware rolls in hot-dip galvanizing are WC–Co coating sprayed by high velocity oxygen fuel (HOVF) on stainless steel. The WC–Co coating may serve in liquid zinc for approximately 1–3 weeks [1]. Numerous materials are currently being developed and tested to assess their effectiveness in the bearing application of a continuous hot-dip galvanizing lines [2, 3]. In recent years, increasing research interest has been seen in the development of intermetallic compounds. Intermetallics usually have many exciting and advantageous properties for use in a wide variety of applications. These materials are currently used in aerospace, automotive engines, heating elements, and corrosion-resistant coatings. Among them, TiAl–Nb alloys have been paid more and more attentions owing to their attractive properties such as low density, excellent high temperature strength, and good oxidation resistance at elevated temperatures [4–6].

In previous studies, Wang et al. reported that the TiAl–Nb alloys exhibit excellent liquid zinc corrosion resistance [7]. It is believed that this excellent isothermal liquid zinc corrosion resistance may be related with their oxide resistance, that is, the better oxide resistance, the higher liquid zinc corrosion resistance. To make a further understanding, we studied the isothermal corrosion of TiAl-Nb alloy with three different surface states in liquid zinc at 450°C in this paper. The three kinds of surface state included non-treated (bare), electrical discharge machined (cut), and preoxidized.

Preoxidation of TiAl alloy with powder pack under low

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oxygen pressure at high temperature can significantly improve the oxidation resistance of the coupon [8, 9]. It is believed that the excellent oxidation resistance should be attributed to the preferential formation of Al_2O_3 under the low oxygen pressure. In our previous studies, the resistance of Ti-45Al-8Nb coupons to cyclic oxidation at 900°C in air also was significantly improved by similar preoxidation method. This excellent oxidation resistance is attributed to the formation of dense Al_2O_3-rich layer and the extremely dense rutile layer.

2 Experimental procedures

2.1 Specimen preparation

The nominal chemical compositions of the experimental materials were Ti-45Al-8Nb and Ti-45Al-8Nb-0.3Y. The alloys were prepared by tungsten-arc melting in an argon atmosphere, using titanium granular sponge (99.9%), pure aluminum pig, and niobium-aluminum alloy, for four times. To obtain the duplex microstructure, the ingot was heat treated at 1250°C for 12 h in a furnace followed by furnace cooling.

The samples for corrosion test were cut from the ingot using an electrical discharge machine (EDM) with dimensions of 40 mm×10 mm×2 mm. For convenience to observe the structures of the oxide scales, some coupons were cut from the ingot by EDM with dimensions of 10 mm×10 mm ×1 mm.

2.2 Preoxidation and cyclic oxidation

Before the preoxidation, the specimens were polished up to 1200 grit SiC paper, and cleaned ultrasonically for 10 min in acetone. Then the polished and cleaned specimens were buried in silica powder, and the whole mixture was encapsulated in a silica tube of 12 mm inner diameter under a vacuum of 1.3×10^{-3} Pa. The preoxidation was performed by heating the capsule in a muffle furnace at 950°C for 12 h. This condition was chosen by some experiments which have not been reported.

Some cyclic oxidation tests were carried out in order to investigate the relationship between oxidation resistance and liquid zinc corrosion resistance of the specimens. These tests were carried out in a cyclic oxidation furnace with an auto moving beam; the specimens were inserted into and removed from the hot zone of the furnace within a few seconds to guarantee a rapid heating and cooling. One cycle consisted of oxidation for 1 h at 900°C and 11 min at ambient temperature. The specimen mass measurements were taken after oxidation for every 20 cycles.

2.3 Corrosion test

Before the corrosion test, all of the specimens were cleaned ultrasonically in acetone. The liquid zinc containing 0.2 wt.% aluminum was melted, brought to the desired testing temperature, and stabilized. The lower three-fourth of the specimens was immersed in liquid zinc.

The previous studies [7] showed that TiAl-Nb alloy exhibited a long incubation time during which no attack virtually occurred in liquid zinc. After this incubation time, the corrosion rate increased noticeably. Considering these results, the specimens were removed from the liquid zinc to observe every three days. When the zinc could not be removed any more or macro corrosion was observed, the test would be stopped.

2.4 Examination

The outer surface and cross-section of samples after peroxidation and cyclic oxidation were examined by means of scanning electron microscopy (SEM) combined with an energy dispersive X-ray spectroscopy (EDS). Nickel was deposited on the specimen surfaces via chemical plating to protect the oxide scales when the cross-sectional morphologies were observed.

3 Results

3.1 Corrosion life of the immersed specimens

As same as the previous studies [7], all the specimens exhibited an incubation period without any corrosion in liquid zinc, and then the immerged side showed a total dissolution after several days.

Figure 1 shows the incubation period of the three groups of specimens in liquid zinc at 450°C. For Ti-45Al-8Nb, the incubation periods of the bare, cut and preoxidized specimens were about 30, 57, and 87 d, respectively. Meanwhile, the incubation periods of Ti-45Al-8Nb-0.3Y were about 33, 69, and 102 d, respectively. The bare specimen had the lowest corrosion resistance while the preoxidized specimen had the highest corrosion resistance for each alloy. It can be

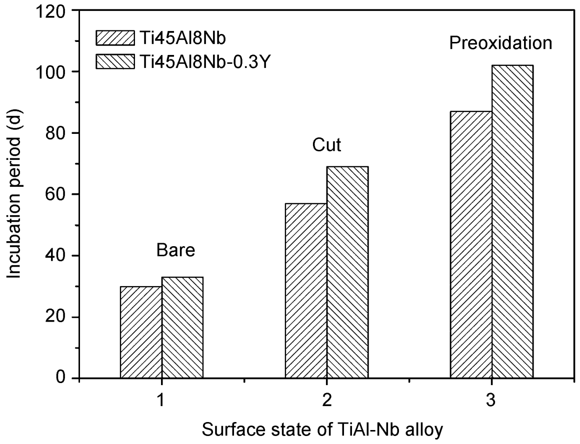

Figure 1 The incubation periods of the three groups of specimens in liquid zinc at 450°C.

observed that the Y addition can increase the incubation period for each surface state, though it's not very obviously for the bare specimens.

3.2 Observation of the macroscopical TiAl–Nb alloy after immersion in liquid zinc

Figure 2 shows the optical macrographs of the Ti-45Al-8Nb specimens from liquid zinc at 450°C right after the incubation period. We could see clearly that all the three specimens were partially corroded, and the corrosion locations were mainly at the edges and corners. It should be noticed that there was nearly no zinc stuck on the areas where no corrosion occurred. The liquid zinc did not wet the plate surfaces of the specimens, therefore the corrosion didn't occur at all. We also took the cross-sectional BSE micrographs of the corrosion locations, and they were exactly like the previous studies [7], and consisted of meniscoid corroded pits and zones where no corrosion took place.

We can notice that the bare specimen's surface was covered by a very thin oxide scale, which makes it look like blue. Actually, since the liquid zinc did not wet the alloy at all in the initial one or two days, there was adequate interspace between the bare specimen and the liquid zinc to make the formation of the oxide scale. This oxide scale is very protective at 450°C, and quite like the aluminum's oxidation behaviors at the ambient temperature. That's the reason why the bare specimen had a similar corrosion behavior of the other two specimens. However, as shown in Figure 3, when the temperature was raised to 900°C, this oxide scale was not protective any more.

4 Discussion

The corrosion occurred preferentially at the edges and corners, as shown in Figure 2. That may be attributed to the Marangoni effect and stress concentration. But in this paper, we want to discuss the effect of the oxide scale itself on the liquid zinc corrosion resistance of the specimens.

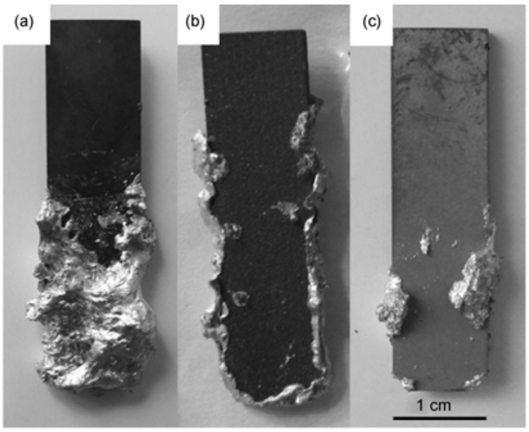

Figure 2 The optical macrographs of the Ti-45Al-8Nb specimens from liquid zinc at 450°C right after the incubation period. The three specimens are the bare specimen (a), the cut specimen (b), and the preoxidized specimen (c), respectively.

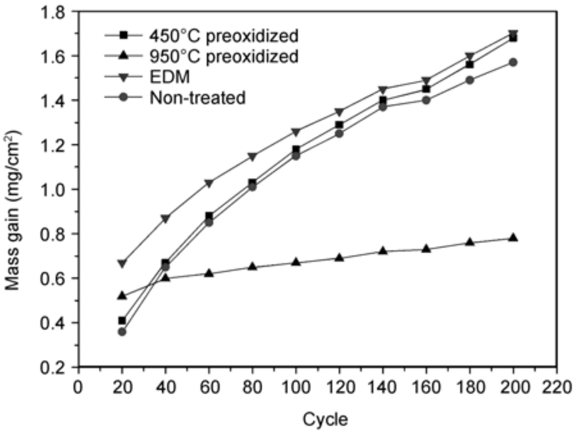

Figure 3 Cyclic-oxidation curves at 900°C in air of the Ti-45Al-8Nb specimens with different surface states. One cycle corresponds to 1 h at 900°C and 11 min at ambient temperature.

4.1 The relationship between oxidation resistance and liquid zinc corrosion resistance

The cyclic-oxidation curves of the Ti-45Al-8Nb specimens with different surface state are summarized in Figure 3. It shows that the specimen preoxidized with powder pack at 950°C exhibits much higher oxidation resistance than the other specimens. On the contrary, the oxidation resistance of cut specimen is even lower than that of the bare one. It might be pointed out that the preoxidation at 450°C was carried out in a common muffle furnace without powder-pack for 1day. In Figure 1, we found that the cut specimen showed an incubation period about twice that of the bare one. Therefore, it seems that we can't make the conclusion that the higher oxidation resistance, the better liquid zinc corrosion resistance.

Figure 4 shows the outer surfaces of cut specimen and preoxidation specimen. Although both the two specimens are covered by oxide scales, their morphologies are totally different. The oxide scale of preoxidation specimen consists of comparatively coarse and nearly same size oxide grains. On the contrary, the cut specimen's oxide scale is extremely dense, but with many micro-cracks at the meantime. The EDS analyses of points A and B in Figure 4 are shown in Table 1. It shows that the oxide grains in Figure 4(a) are TiO_2, and the oxide scale of cut specimen is complicated and consists of a mixture of alumina and titania. The AES analysis shows that the oxide scale of cut specimen is very thin with a thickness about 100 nm, therefore it's hard to make the cross-sectional micrographs. Actually, since the oxide scale of cut specimen is very thin, the EDS data of point B is not very accurate. However, it indicates that the surface of cut specimen is covered by oxide scales so that

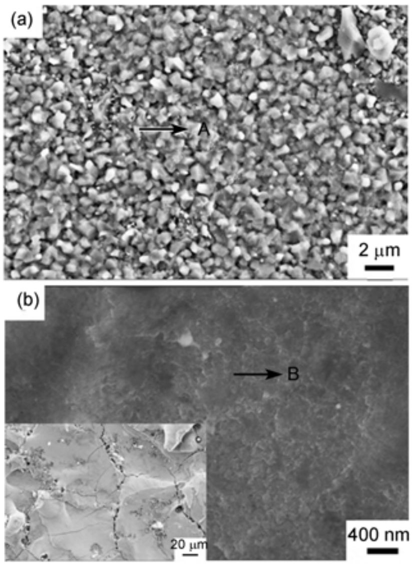

Figure 4 Outer surfaces of the preoxidized specimen (a) and the cut specimen (b). The inset in (b) is the less magnification SEM micrograph of the surface of cut specimen.

Table 1 Results of EDS (atom%)

Point	O	Al	Ti	Nb
A	73.88	3.8	21.66	0.24
B	51.13	20.62	23.7	4.49

we can compare it with the preoxidized specimen in the liquid zinc corrosion experiment.

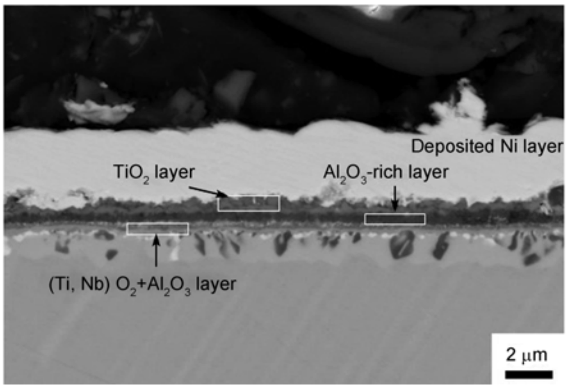

Figure 5 The cross-sectional BSE micrograph of specimen preoxidized at 950°C.

Figure 5 shows the cross-sectional morphology of specimen preoxidized at 950°C. Figure 6 shows the result of EDS line scan. In Figure 6, stage I is the matrix, stage II is the Al-depleted layer, and stage III is Nb-rich phase. We can observe that the oxide scale consists of three layers including stage IV, stage V and stage VI. Stage IV is complicated without any apparently element segregation, stage V is very rich in Al, and stage VI almost only consists of titania. Since it's the typical oxide scale structure of TiAl- Nb alloys [6, 10], we can conclude that the structure of the scale is in the order of TiO_2 layer/Al_2O_3-rich layer/(Ti, Nb)O_2+Al_2O_3 layer from outside. It should be noticed that the Al_2O_3-rich layer of preoxided specimen is more continuous than the oxide scale formed in air. The dense Al_2O_3-rich layer is very effective in preventing the diffusion of oxygen atoms [8]. Additionally, the other layers are also continuous and relatively low porosity, which means that this scale is not subject to occurring any localized breakdown. That's why the preoxidized specimen has not only a higher oxidation resistance but also the higher liquid zinc oxidation resistance than the cut specimen.

For the cut specimen, the micro-cracks in the oxide scale result in the bad oxidation resistance, as shown in Figure 3. But in the liquid zinc, the surface tension makes the liquid zinc not wet the oxide scale at all, and so that the zinc atom can't diffuse via these cracks. So although the oxidation resistance of cut specimen is even lower than the bare one, its liquid corrosion resistance is much higher.

4.2 The effect of Y addition

Recent research showed that Y addition in TiAl-Nb alloys changed the growth mechanisms of oxide scale, and 0.3 at.% Y-added alloy got the best oxidation resistance in air [10]. It was observed in Figure 1 that 15 days increased in the incubation period after the Y addition for the preoxidized specimens, which may be attributed to the better quality oxide scale. Figure 7 shows the outer surfaces of Ti-45Al-8Nb and Ti-45Al-8Nb-0.3Y preoxidized specimens. They look like similar, and actually their cross-sectional

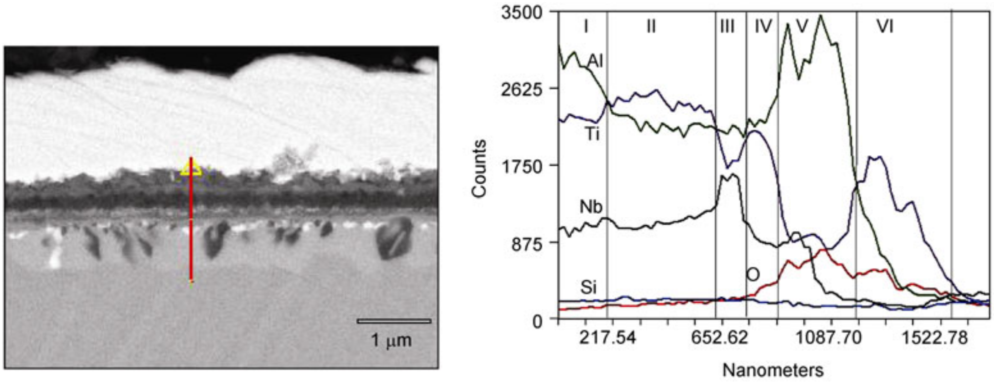

Figure 6 The result of cross-sectional EDS line scan of specimen preoxidized at 950°C.

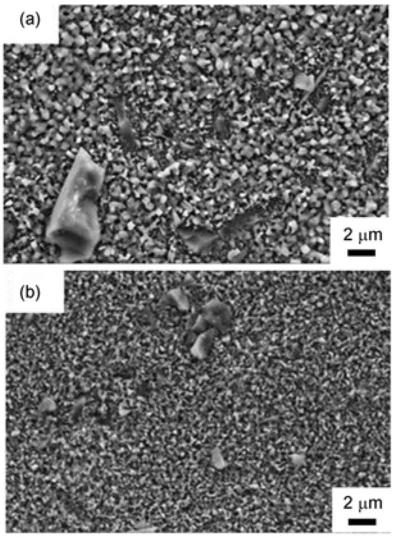

Figure 7 The outer surfaces of preoxidized Ti-45Al-8Nb specimen (a) and Ti-45Al-8Nb-0.3Y specimen (b).

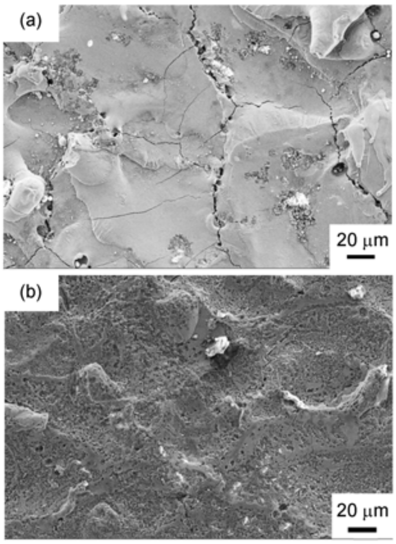

Figure 8 The outer surfaces of cut Ti-45Al-8Nb specimen (a) and Ti-45Al-8Nb-0.3Y specimen (b).

morphologies are similar too, both in the order of TiO_2 layer/Al_2O_3-rich layer/(Ti, Nb)O_2+Al_2O_3 layer from outside. However, the oxide grains of Ti-45Al-8Nb-0.3Y are much smaller than those of Ti-45Al-8Nb. In other words, the oxide scale of Ti-45Al-8Nb-0.3Y is more compact and continuous, therefore the localized breakdown would less possibly occur. Since it is believed that the corrosion of TiAl-Nb alloys is initially caused by a localized breakdown in the oxide scales [7], Y addition can improve the isothermal liquid zinc corrosion resistance of the preoxidized specimens.

For the cut specimens, 12 days increased in the incubation period because of the Y addition. The mechanism is similar to that for the preoxidized specimens. Figure 8 shows the surfaces of Ti-45Al-8Nb and Ti-45Al-8Nb-0.3Y cut specimens. We can observe that the oxide scale of Ti-45Al-8Nb-0.3Y specimen has less micro-cracks than the other one. For the bare specimens, 0.3 at.% Y addition didn't have much effect, as shown in Figure 1. Considering the truth that Y addition can drastically refine the microstructure of TiAl-Nb alloy [10], we can say that the microstructure's effect on the liquid zinc corrosion resistance is not visible.

5 Conclusions

Preoxidation with silica powder-pack at high temperature can improve the liquid zinc corrosion resistance of TiAl-Nb alloys. This excellent liquid zinc corrosion resistance should be attributed to the formation of high-quality oxide scale during peroxidation. The corrosion of all the samples in liquid zinc was caused by a localized breakdown in the oxide scales, and preferentially occurred in the edges and corners. The continuous and dense oxide scale formed during preoxidation substantially prevents the liquid zinc from diffusing to the substrate, and its good continuity also reduces the possibility of localized breakdown in the oxide scale. Y addition doesn't improve the bare specimen's liquid zinc corrosion resistance visibly. However, because of refining the oxide grains, Y addition increases more than 10 d in the incubation period of both the cut and preoxidized specimens.

According the discussion in section 4.1, one more conclusion can be drawn. That is, there is no inevitable relationship between oxidation resistance and liquid zinc corrosion resistance of TiAl-Nb alloys. Due to the surface tension, the micro-cracks in the oxide scale will not become the channels of liquid zinc touching the substrate, but they can't prevent the oxygen atoms' diffusion.

This work was supported by the National Natural Science Foundation of China (Grant No. 50871127) and the National Basic Research Program of China ("973" Project) (Grant No. 2011CB605500).

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