HEAT TREATMENT OF LOW CARBON STEEL (LCS) TUBES TO IMPROVE CORROSION RESISTANCE

Del Aguila D

Rio Tinto Alcan Queensland R&D Centre (QRDC), Brisbane, QLD, Australia

Abstract

Heat exchangers in the Bayer process are routinely cleaned with dilute sulphuric acid to dissolve Desilication Product (DSP) scale attached to the internal surface of the tubes. The scale deposit reduces the heat transfer coefficient of these units consequently reducing the energy efficiency of heat recovery.

During the cleaning process, the tubes become exposed to the dilute acid cleaning solution causing corrosion that reduces the life of the tubes. The corrosion attack is minimised by adding corrosion inhibitors to the acid solution but the damage still remains significant for the life expectancy of the tube.

Another variable with significant impact on corrosion resistance under these conditions is the type of microstructure produced in the metal of the heat exchanger tube during manufacture. Optimum microstructures can double tube life based on laboratory results. This type of microstructure can be obtained by selective heat treatment at the steel mill.

The paper shows the results of different heat treatments on the microstructure of standard LCS heat exchanger tubes. The improvement in corrosion performance is verified using a laboratory simulation acid circulation rig (ACR) with state-of-the-art electrochemical monitoring.

1. Introduction

Bayer liquor returning from precipitation to the digestion area is mixed with incoming mill slurry to extract aluminous phases from bauxite. The extraction is carried out at high temperatures, 150 – 270°C depending on the alumina phases and other bauxite characteristics. The liquor feed to digestion is heated usually with steam from flash tanks in shell and tube heat exchangers (HEX).

During this heat recovery, silica dissolved in the liquor precipitates as scale on the internal surface of the tubes with a detrimental effect on heat recovery. When the heat recovery becomes insufficient, the scale formed in the tubes is removed by cleaning with dilute sulphuric acid in order to bring the system back to acceptable operating conditions.

Major issues with corrosion in HEX tubes occur during the use of dilute sulphuric acid for cleaning. A minor factor with corrosion in these units is Bayer liquor itself, due the formation of a passive corrosion layer when the liquor contacts the mild steel surface. Corrosion is an issue before this protective layer is formed, however once this layer is formed the corrosion attack by liquor is negligible.

The conventional DSP scale management method that is simple and affordable for most alumina refineries at present is acid and mechanical cleaning. This procedure together with optimised and well implemented plant practices can bring satisfactory outcomes.

Alumina refineries use low carbon steel (LCS) tubes to maintain their process heaters (regenerative units) and most of their live steam heaters. The most common metallurgy standards used are ASTM 179 and ASTM 192. Both have the same chemical composition and differ only in tolerances for application purposes. Heat treatment is the last stage of the manufacturing process of HEX tubes in the steel mill and is the stage with major impact on corrosion performance.

Extensive work has been carried out in Rio Tinto Alcan QRDC and other laboratories to evaluate the corrosion performance of these materials under Bayer process conditions. It was found that different tubes fabricated under the same ASTM standard have different corrosion performance. The more resistant material corresponds to a specific type of microstructure characteristic of a specific type of heat treatment. It was also found that this type of microstructure is selective to certain types of corrosion inhibitors and the best performance at plant level is achieved with the right selection of tube and corrosion inhibitor.

Low carbon steel (hypoeutectoid steel = < 0.8% C) means heat treatment is based on the iron-carbon binary phase diagram. The type of microstructure that proves high corrosion resistance has been identified as "spheroidised cementite". This type of microstructure, which in this paper is defined as the "final outcome", can be obtained using different metallurgical procedures, generally a combination of annealing temperatures around the critical temperature Ac1, holding time and cooling rate. Some may not be applicable or cost efficient for the steel mill. The procedure to be chosen has to be simple and applicable at the mill without incurring a significant increase per unit price.

This paper illustrates an optimal approach to management of HEX corrosion in current use at Rio Tinto Alcan alumina refineries. To minimise corrosion attack on the internal surface as a result of acid cleaning, a better quality HEX tube material is developed to be more resistant to corrosion under normal plant acid cleaning conditions. This, combined with selection of the optimum corrosion inhibitor and dose, increases the life expectancy of the tube and reduces maintenance costs. Some alumina refineries are inadvertently using this approach but at generally high tube prices. The current integrated approach has been successfully accomplished for quality and cost advantages by collaborating directly with the tube manufacturer.

2.0 Methodology

Extensive laboratory heat treatment work has been carried out to determine the parameters that lead to the various types of tube microstructure. The mill supplied test samples for heat treatment and the work was carried out using a programmable laboratory furnace. The samples for metallographic imaging were sectioned, ground, polished and etched with 2% Nital at CSIRO metallographic facilities, and the microstructures observed using an Olympus PMG3 microscope. The samples were evaluated for corrosion performance using the Rio Tinto Alcan QRDC acid circulation rig (ACR). This is a setup equipped with state of the art electrochemistry instrumentation including a Linear Polarisation Resistance (LPR) technique to measure corrosion rates.

Some heat treatment profiles were undertaken in a steel mill with advice from QRDC, and their corrosion performance subsequently validated in the ACR.

3. Experimental Design

The following heat treatments were undertaken in this work:

Test ID	Before HT	After HT	Heat Treatment
Test 1	AR-R	1HT	Below critical temperature, 2hours
Test 2	AR-R	2HT	Cycled around the critical temperature, 3hours
Test 3	AR-S	3HT	Close to critical temperature 1hour
Test 4	AR-S	4HT	Closer to critical temperature, 0.5hours
Test 5	AR-R	5HT	Thermal shock, austenite/pearlite

Description of Samples:

AR: As Received from the mill in the laboratory
- R: Heat treated previously at the mill
- S: Stressed sample from third drawing stage at the mill
HT: Heat Treated subsequently in the laboratory

The five tests identified above successfully achieved the target spheroidised cementite microstructure.

During the spheroidisation process, as in other annealing processes, the final outcome is driven by the pre-existing condition (with or without mechanical stress) and the annealing process parameters (temperature, time, rate).

The experimental work used two pre-existing conditions and adjusted the parameters to obtain the "final outcome". Tests 1, 2 and 5 were without mechanical stress and Tests 3 and 4 with mechanical stress. Test 5 is not affected with pre-existing condition because the sample reaches austenisation (950 °C). In this case, the stress relieved condition was chosen.

The pre-existing conditions and the parameters for this work were chosen from heat treatment of low carbon steel literature and related publications currently in the public domain. These heat treatments are based on the Fe-C Binary Phase Transformation Chart. There is a large amount of information about heat treatment of low carbon steel for different applications but only a few relate to acid cleaning at Bayer process conditions.

4. Laboratory Results

Standard HEX tube material manufactured under ASTM 192 specification was used for the test. Some alumina refineries are currently successfully using this metallurgy standard of tube. The tube dimensions were 38.1 mm OD and 2.6 mm WT (wall thickness) and were cut into rings 10 mm long to be used as test samples.

The chemical composition of this material was:

Samples	C	Mn	Si	S	P	Ni	Cr	Mo	Cu	Nb	Ti
	%	%	%	%	%	%	%	%	%	%	%
China STD	0.08	0.48	0.21	0.01	0.01	0.05	0.04	0.01	0.19	<0.01	<0.01

Test 1

The test was carried out with as received sample identified as AR-R. This sample has already been heat treated at the mill and is a tube material that the mill considers as an end product. The furnace was preheated below the critical temperature and the tube sub-samples were placed inside. The sub-samples were then cooled down to room temperature at a controlled rate. The oxidised layer formed on the surface during cooling was removed manually prior to metallographic and corrosion evaluation.

Test 2

For this test, the same starting sample identified as AR-R was used as in Test 1. The furnace was preheated to the same annealing temperature and the samples were placed inside for some time with cycling above and below the critical point. The samples were then cooled down to room temperature, and the oxidised layer was removed manually prior to metallographic and corrosion evaluation.

The effect of these heat treatments on corrosion rate at a range of doses of a single inhibitor is shown in Figure 1. Corrosion rates at typical inhibitor doses are reduced to about one third by the laboratory heat treatment subsequent to the inherent treatment at the steel mill.

Microstructure of the sample before heat treatment (AR-R) is shown in Figure 2. Microstructures of samples after treatment, 1HT and 2HT were identical; sample 2HT is shown in Figure 3. The microstructure showed clear spheroidisation. The cementites have come out from the matrix as globular particles, but remain relatively localised within the ferrite matrix.

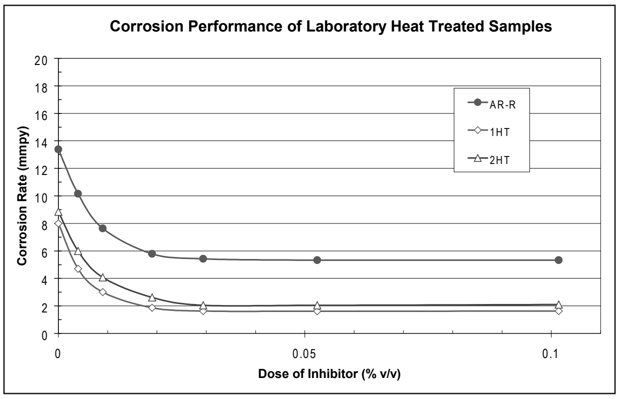

Figure 1. Corrosion Performance of sample 1HT & 2HT

The change of microstructure as a result of these heat treatments is showed in Figures 2 and 3.

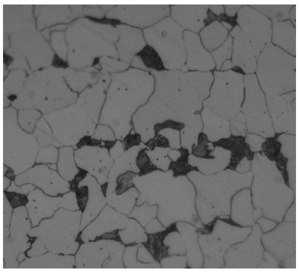

Figure 2. Sample AR-R, X 500

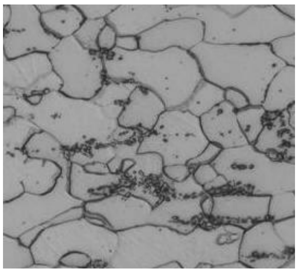

Figure 3. Sample 2HT, X 500

Test 3

For this laboratory test, the sample identified as 3AR-S was used. This sample was obtained from the mill after a third drawing stage of the manufacturing process. The sample was under mechanical stress as a result of consecutives drawings and no extra heat treatment had been applied at the mill prior to the heat treatment test in the laboratory. The laboratory furnace was preheated below critical temperature then the sub-sample was placed inside the furnace for annealing. The samples were then cooled down to room temperature at a controlled rate. The samples were prepared for evaluation as before.

Test 4

For this test, the starting sample identified as 4AR-S was used, the same used for Test 3. The furnace was preheated below critical temperature but closer this time, and then samples placed inside the furnace and kept at this temperature. The samples were then cooled down to room temperature at a controlled rate and prepared for evaluation as before.

The effect of these heat treatments on corrosion rate at a range of doses of a single inhibitor is shown in Figure 4. These gave identical corrosion results. Corrosion rates at typical inhibitor dose are reduced significantly, to about one tenth by the laboratory heat treatment, subsequent to the inherent third draw at the steel mill.

Microstructure of sample before heat treatment (4AR-S) is shown in Figure 5. Microstructures of samples after heat treatment, 3HT and 4HT were again identical; sample 4HT is shown in Figure 6. The microstructure showed clear spheroidisation with the cementites separating from the ferrite matrix as globular particles and are more dispersed than those in the 2HT sample.

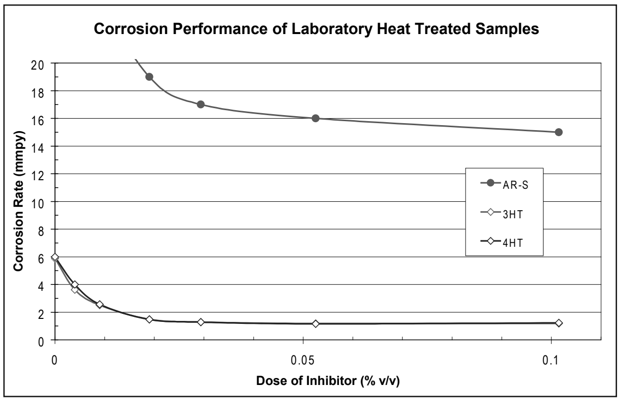

Figure 4. Corrosion Performance of sample 3HT & 4HT

The change of microstructure as a result of these heat treatments is showed in Figures 5 and 6.

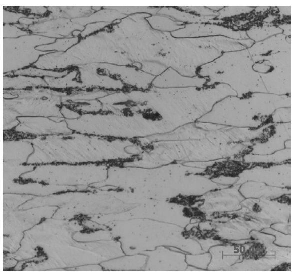

Figure 5. Sample AR-S, X 500

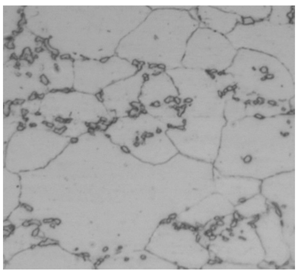

Figure 6. Sample 4HT, X 500

Test 5

For this test, the sample identified as AR-R was used; the same sample used in Tests 1 and 2. The furnace was preheated to the austenitic temperature then samples placed inside the furnace and kept for a short time. They were then quenched to the martensitic temperature in a salt bath of sodium nitrate and potassium nitrate, and then isothermally annealed close to the critical point for very short time, and then air cooled to room temperature.

The result of Test 5 was that the corrosion rate reduced to one third of that of the sample from the steel mill (See Figure 7).

Microstructure of sample before heat treatment (AR-R) is shown in Figure 8. Microstructure of sample after heat treatment, 5HT is shown in Figure 9. The microstructure showed the clear spheroidisation stage. The cementites come out from the ferrite matrix as globular particles and seemed to be more scattered than the ones in 2HT.

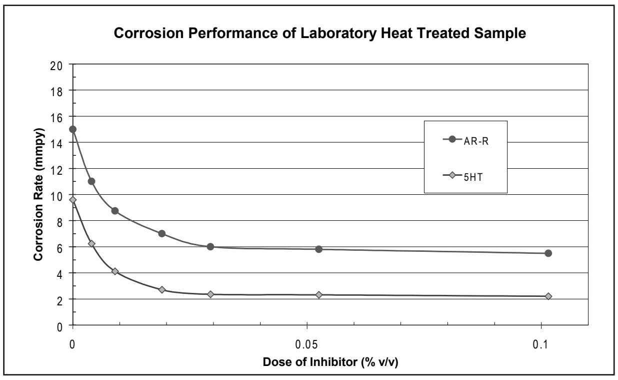

Figure 7. Corrosion Performance of sample 5HT

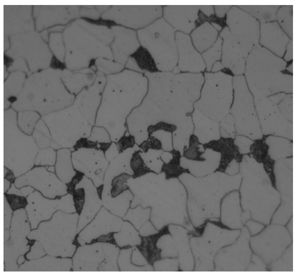

Figure 8. Sample AR-R, X 500

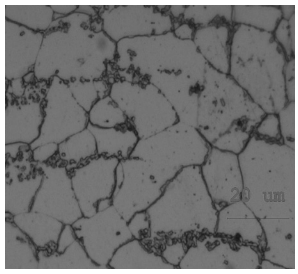

Figure 9. Sample 5HT, X 500

5. Overall Comparison

From a "final outcome" perspective, the five tests described above successfully achieved the target microstructure and showed the expected good corrosion performance. Perhaps the best cases were samples 3HT and 4HT (Figure 4) where corrosion rates were consistently below 2.0 mmpy corrosion rate, compared to a commercial benchmark tube at 1.8 mmpy). Other samples, 1HT, 2HT and 5HT showed 1.9, 2.0, and 2.5 mmpy corrosion rate respectively (Figures 1 and 7).

It is important to emphasise the effect of residual mechanical stress from the manufacture process on corrosion performance. Sample AR-S (stressed) in Figure 4, had about 3 times more corrosion than sample AR-R (relieved) shown in Figure 1. It also appeared that the better corrosion behaviour was obtained by heat treating a stressed material.

In summary outcome, heat treatments 3HT and 4HT were slightly better than heat treatment 1HT, 2HT and 5HT.

From the "parameters" point of view, a remarkable reduction of furnace holding time to obtain the "final outcome" was observed with sample 5HT, compared with samples 1HT, 2HT, 3HT and 4HT. Higher heat treatment temperatures were also undertaken with sample 5HT.

In summary, heat treatment 5HT used a rapid spheroidisation process but was based on prior sample conditioning.

6. Mechanism

Two mechanisms are defined: the conventional and the thermal shock. In the conventional mechanism, iron transforms to pure ferrite or a combination of ferrite/austenite. For the thermal shock mechanism, iron is fully transformed to an austenite phase.

The decomposition kinetics for conventional isothermal annealing to achieve spheroids of cementite (Tests 1, 2, 3 and 4) is well defined (Chen-Chia Chou; 1989). It begins with recrystalisation followed by grain growth and agglomeration of the carbides. The prior history of the steel is therefore an important factor.

However, for the thermal shock Test 5, there is little information on the decomposition kinetics of super-cooled austenite into globular pearlite. Lifshitz (Lifshitz; 1961) describes the kinetics process as "coalescence", the growth of large grains of the new phase by the incorporation of the small grains. Chen-Chia Chou (Chen-Chia Chou; 1989) does not fully agree with Lifshitz and implies that the mechanism may follow the conventional isothermal annealing and differs only on the time to reach a stable condition. It seems the mechanisms in this heat treatment cannot be completely described at this stage.

7. Results of Implementation at a Steel Mill

Four heat treatment tests were carried out at a steel mill, transferring the experience of the laboratory heat treatments and corrosion tests. At the mill, the heat treatment parameters were less flexible in the large furnace, as would be expected. The application at the mill of any heat treatment profile also can depend on the cost ceiling of the finished HEX tube.

Nevertheless a more favourable microstructure was achieved at the mill with isothermal annealing below the critical point. This proved to be more corrosion resistant to dilute sulphuric acid as tested on subsequent samples in the laboratory using the ACR.

8. Laboratory/Plant Assessment

In Tests 1 and 2, heat treated samples that were already heat relieved at the mill was used. The final favourable corrosion results can be obtained with either isothermal annealing or cycling treatment around the critical point. Both conditions require longer exposure times that may be difficult to be applied at the mill due to the effect on other stages of the continuous cold-draw manufacturing process.

In Tests 3 and 4, heat treated samples that had been under great mechanical stresses (third draw) were used. More favourable microstructures can be obtained with subcritical annealing at close or very close to the critical point. Exposure times are considerably reduced compared to Tests 1 and 2. These two profiles are also more suitable for a mill application.

Test 5 also used a heat treated sample that was already heat relieved at the mill. The results showed very rapid formation of the desired microstructure (< 2 minutes). However, the process requires an intermediate process that is out of the conventional cold drawing regime, and may significantly increase the cost of the final product. This heat treatment has the potential to significantly simplify the spheroidisation process once the intermediate stages are optimised.

9. Conclusions

The favoured "spheroidised cementite" microstructure for corrosion resistance can be obtained under various heat treatment conditions. The most suitable procedures with a high possibility to be applied at the mill are the ones with relatively rapid recrystallisation kinetics.

These results highlight the potential for Bayer refineries to establish favourable heater tube characteristics for corrosion resistance by collaborating with the mill manufacturing process. The collaboration is feasible for certain heat treatment conditions, with the goal to provide a more cost effective outcome for tube lifetime and supply price.

Acknowledgements

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