

Failure mechanism of blast furnace tuyeres

Natasa Vuckovic-Spitzer, Institute of Metallurgy, Clausthal University of Technology, Germany

Tatjana Mirkovic, Salzgitter Flachstahl GmbH, Germany

Rainer Beusse, Salzgitter Mannesmann Forschung GmbH, Germany

Jürgen Pethke, Salzgitter Flachstahl GmbH, Germany

Arnold Adam, Institute of Inorganic and Analytical Chemistry, Clausthal University of Technology, Germany

Karl-Heinz Spitzer, Institute of Metallurgy, Clausthal University of Technology, Germany

Contact data:

Natasa Vuckovic-Spitzer, Institute of Metallurgy, TU Clausthal, Robert-Koch-Str. 42, 38678 Clausthal-Zellerfeld, Germany

Tel.: +49 53 23 72 2800, Fax: +49 53 23 72 3120, E-mail: natasa.vuckovic@tu-clausthal.de

Key Words: blast furnace, tuyeres, failure mechanism, copper corrosion

Abstract

The damage of a blast furnace tuyere, requiring its replacement, disturbs normal operation of the blast furnace and reduces the economic efficiency of production. In this paper, the failure mechanism of blast furnace tuyeres was investigated by metallographic examination of sections cut from failed tuyeres and laboratory experiments directed towards a simulation of tuyere operation and failure. The obtained results revealed a complex failure mechanism which consists of two main phases: the phase of local damage by corrosion and the phase of melting of damaged areas. The corrosion of tuyeres is caused by the presence of aggressive chemical compounds in the blast furnace, primarily chlorine-containing compounds. The corrosive attack on a tuyere results in the formation of intergranular cracks and microporosity in the tuyere copper. Such defects affect severely the cooling of the copper in the affected areas. Thermal load on the tuyere surface through the splashing of hot metal and slag and reduced thermal conductivity of the copper in the areas affected by corrosion lead to the overheating and finally localized melting of the tuyere. This process can take place repeatedly until the tuyere is completely damaged, which is accompanied by leakage of water into the furnace.

Introduction

Tuyeres are used for supplying preheated air into blast furnace and are commonly made of highly pure copper. High temperatures originating from coke combustion (up to 2200 °C) and splashing of molten iron and slag in the tuyere zone of blast furnace cause a high thermal load on tuyeres. Also, tuyeres are permanently exposed to mechanical action (abrasion) of the burden materials.

Some of the chemical compounds encountered in the blast furnace process such as chlorine- and sulphur-containing compounds can attack and corrode the tuyere copper. Moreover, elements like alkalis (K and Na), Zn, Pb and Cl can circulate in the blast furnace alternating between condensed and gaseous state

[1-3]. This results in accumulation of these elements in the furnace, whereby the possibility of corrosion attack increases.

Under such severe operating conditions, the service life of the tuyeres varies from several days to several months. A detailed understanding of the tuyere failure mechanism is essential to achieve the extension of the service life of tuyeres. The former investigations of the failure mechanism reported different reasons for the tuyere destruction [4, 5]: cracking, wear and local burning. The cracking was primarily explained by presence of construction and material defects. The tuyere wear occurs continuously as a result of mechanical action of the charge materials particularly the coke chunks, circulating in the tuyere surrounding.

The most frequent type of the tuyeres failure is reported to be the burning through the tuyere wall caused by molten iron. Under conditions of an insufficient cooling or during the clogging of the furnace hearth, the copper temperature in the contact spot with hot metal is assumed to exceed its melting point (1083 °C) and the tuyere burns [6-9].

Various attempts have been made to increase the tuyere service life by modifying its shape [10] or by applying different refractory coatings [11, 12]. Despite these efforts, the problem of the tuyere failure has remained unsolved and there is no state of art protection technology. The understanding of the mechanism of this failure will contribute to the design of a tuyere ensuring a long-term performance.

Proposed concept of the tuyere failure mechanism

Before presenting the experimental results of the investigation, the concept of the tuyere failure mechanism obtained from our own research will be explained.

The study of the metallographic specimens of the failed tuyeres as well as the laboratory simulation experiments of the tuyeres destruction pointed out that the tuyere destruction occurs through a complicated mechanism. The mechanism includes two interactive stages, the stage of corrosion and the stage of melting.

The chlorine-containing compounds present in the blast furnace (e.g., metal chlorides, Cl_2 , HCl gas) are supposed to play an important role in inducing corrosion of the copper tuyeres. Volatile metal chlorides occur normally in the blast furnace gas, but sometimes they may condense on the material relatively close to the cold furnace wall and move down the wall to the lower part of the furnace. When they are transported to the hot blast they can be burned to Cl_2 or HCl which can provoke corrosion of tuyeres.

Also, it can be assumed that, due to the high pressure (4.5 – 5 bar) existing in the tuyere zone of a blast furnace the formation of an aqueous electrolyte on the tuyere surface is possible. The atmosphere of the blast furnace contains some amount of water vapour. The boiling point of water at a pressure of 5 bar is about 150 °C [13], indicating that water vapour inside the furnace may condense on the cold tuyere surface under certain conditions. Condensation of water can be facilitated by previous solidification of an iron or slag layer on the tuyere surface. The small gap existing between the solidified layer and the tuyere surface is a suitable site for water vapour condensation due to thermal insulation effect of the solidified material.

Subsequent dissolution of the corrosive gases (e.g., volatile metal chlorides, HCl, Cl_2 , SO_2 , SO_3 , NO_x) in the aqueous condensate results in the formation of an aggressive electrolyte that will attack copper. Additionally, the particles of hygroscopic salts (e.g. CaCl_2 , ZnCl_2) accidentally deposited on the tuyere surface can absorb water vapour from the furnace atmosphere and produce a corrosive medium. The assumed failure mechanism is schematically represented in Figure 1 for a case where a tuyere is coated with an INCONEL 625® layer. INCONEL 625® is a nickel-chromium-molybdenum alloy which is sometimes used as protective coating on tuyeres. However, metallographic examination of the destroyed tuyeres revealed that they endure a similar damage, regardless if they are coated with INCONEL 625® or not.

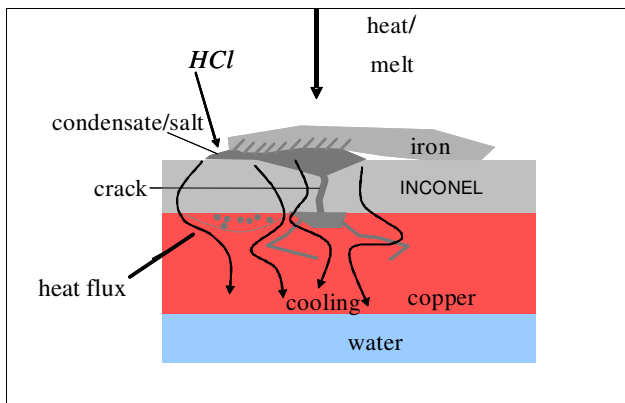


Figure 1: Schematic illustration of the tuyere failure mechanism

The tuyere failure begins with formation of a corrosive electrolyte (e.g., HCl dissolved in water condensate) in the gap between the tuyere surface and solidified iron droplet (Fig. 1). This acidic and corrosive solution attacks first the INCONEL 625® coating on the tuyere forming a channel which propagates to the copper. Cracks formed in the INCONEL 625® layer during the coating operation facilitate this process.

The corrosion process continues in the copper. The electrolyte reacts with impurities such as sulphides and oxides deposited at the grain boundaries forming the intergranular cracks. It is also possible that diffusion of the gases (e.g., hydrogen and/or chlorine) through the copper and their interaction with fine dispersed oxide and sulphide precipitates results in the formation of the micropores. The cracks and microporosity formed in the copper cause a significant decrease in copper thermal conductivity and deteriorate copper cooling within these regions. Due to continuous splashing of the hot iron and slag on the tuyere surface, the temperature of the copper rises, exceeds its melting point and local melting of the copper occurs. The liquid iron propagates through the tuyere wall reducing its thickness. Under certain thermal conditions a pocket of the steam can be formed on the inner tuyere wall. Simultaneously, the corrosion proceeds further through the solidified iron and copper.

The effects of permanent thermal load from above and reduced heat transfer due to steam beneath finally cause the rupture of the tuyere and the water flow into the furnace.

This concept of the failure mechanism resulted from the examinations which will be described in the following sections.

Examination of destroyed tuyeres

In order to get an overview of typical location of the failure sites and the failure extension, numerous destroyed tuyeres were visually examined. Observation of the destroyed blast furnace tuyeres showed that the failure areas are mostly located on the tip part of the tuyeres which is directly exposed to the furnace interior. In the majority of cases the defect areas are in the form of holes propagating through the tuyere wall and have a size of up to a few centimetres. (Fig. 2).



Figure 2: A tuyere showing defect in the form of small holes on its front part

The samples cut from the failure areas of destroyed tuyeres were metallographically examined (optical microscopy and scanning electron microscopy (SEM/EDX)). Also, elemental mapping was used to determine distribution and concentrations of the certain elements over the failure areas of tuyeres. Microscopic observations showed a few typical microstructure features of the destroyed regions: the presence of a layer of iron tightly adhering to copper, presence of channels, holes and copper inclusions in the iron as well as the presence of different defects in the copper in the vicinity of the copper/iron interface. The iron layer adhering to the copper consists of two sublayers: the first iron sublayer formed directly on the copper due to intensive cooling contains carbon chemically bonded to iron carbide (cementite, Fe_3C), while the second one, more distant from the copper/iron interface shows the presence of dispersed graphite flakes. The channels extending through the iron layer to the copper are most probably intersections of the cutting plane with the cracks present in the samples. They are partially filled with a grey phase and create sometimes cavities in the tuyere copper (Fig. 3).

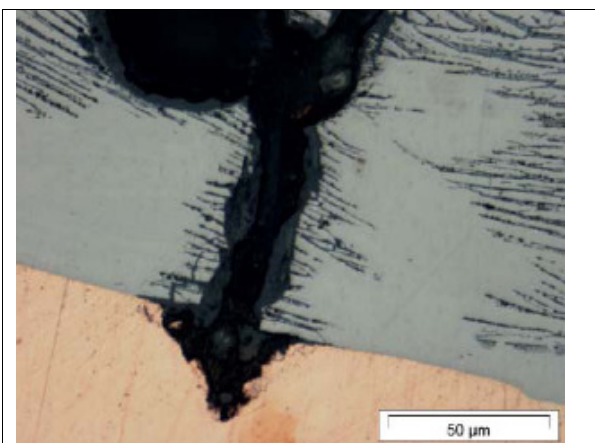


Figure 3: A channel extending through the iron layer to the copper

It seems that such cavities with rough walls are formed during a corrosion process in which the copper is dissolved and transported away with an electrolyte through the channel. As the corrosion process in the tuyere copper propagates, the cavities initiated at the copper/iron interface grow and may become as large as the one shown in Figure 4.

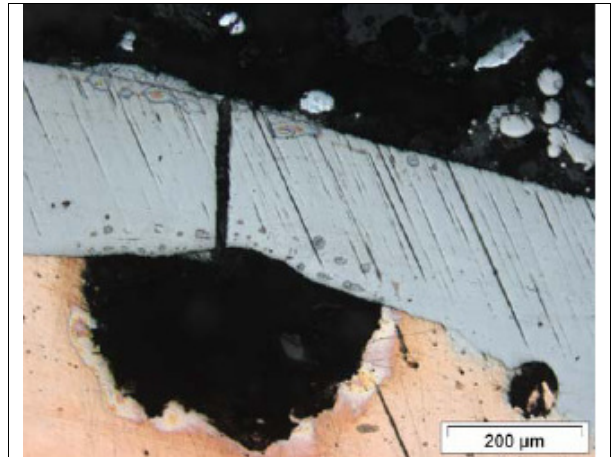


Figure 4: A large cavity in the tuyere copper

EDX analysis of the material filling the channels showed that it is an oxide phase composed mainly of Fe and O. Several other elements such as Cu, Zn, Si, Al, Ca, Mg, Al, K and S, were also detected in this material in the overall concentration of a few weight percent.

The needle-like structure of the iron visible in the surrounding of the channels is the result of an electrochemical reaction occurring between an electrolyte and the ferrite as less noble micro-constituent of iron [14]. The areas of corroded ferrite appear dark on the micrographs, while the more noble cementite appears as bright elongated grains (needles). This assumption was confirmed by metallographic observation of a tuyere sample exhibiting the needle-like structure in the surrounding of a channel in polished condition (Fig. 5a).

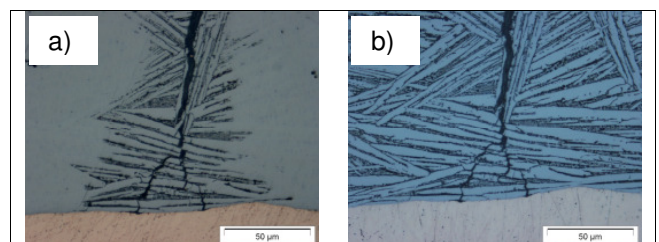


Figure 5: Iron microstructure in the surrounding of a channel: a) polished b) etched with 3% HNO_3

After etching with HNO_3 , the needle-like structure became visible over the whole iron surface due to the reaction between HNO_3 and ferrite (Fig. 5b). By subsequent polishing, the surface layer was removed and the needle-like structure of the iron was again visible only around the channel as shown in Figure 5a. This indicates that the iron revealing the needle-

like structure on the polished sample surface was already attacked with some electrolyte transported here through the channel (the crack in three-dimensions). The reaction between the electrolyte and ferrite in the iron occurred in the space surrounding the channel. The needle-like structure originated from this reaction can not be removed by polishing because it extends to some depth under the sample surface in the region adjacent to the crack. Another sign of corrosion in the samples of destroyed tuyeres are very small copper particles (from a few μm to tents of μm diameter) that have been discovered in the regions of dissolved ferrite in the iron layer. This copper could be brought there with some electrolyte in the form of copper ions and thereafter precipitated as metallic copper by cementation with ferrite.

Also, relatively large copper particles (with diameter of several tents to several hundreds μm) interspersed with graphite (Fig. 6) were found in the iron layer adhering to the tuyere copper.

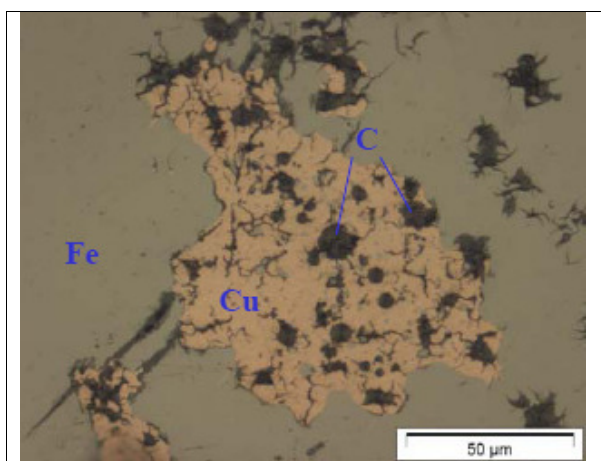


Figure 6: Copper inclusions containing graphite flakes found in the iron layer

Such type of copper inclusions is a consequence of the local tuyere melting by attack of molten iron, whereby an iron-copper-carbon melt is formed. According to Figure 6 one may get the impression that graphite was precipitated from copper. However that is not possible due to the negligible carbon solubility in copper [15]. As the Fe-Cu-C melt cools down, the precipitation of the carbon as graphite flakes from the melt takes place first. Then the copper-rich liquid phase precipitates on the graphite flakes. In the regions of the melt with larger amount of the copper-rich phase the adjacent droplets of the copper-rich liquid coalesce to form larger copper particles. The correctness of this explanation was proved by a laboratory experiment where liquid pig iron was poured on a non-cooled tuyere section. Metallographic examination of the samples cut from the attacked region of the copper revealed a very similar microstructure to that shown in Figure 6. This microstructural feature of the investigated tuyere

samples indicates that the melting of tuyere copper by hot iron is a stage of the failure mechanism. The copper in the vicinity of the copper/iron interface shows also signs of corrosion: cracks and porosity (Fig. 7 and Fig. 8). These defects in copper can significantly lower its thermal conductivity and cause local overheating resulting in copper melting in the affected area.

Figure 7 shows a polished tuyere sample containing cracks of several millimeters in length in the copper near the copper/iron interface. Observation of the etched sample revealed that the cracks propagation occurs along the grain boundaries due to intergranular corrosion. This defect can be caused by local attack of an electrolyte at the copper grain boundaries containing less noble precipitates such as oxides and sulphides. The crack tip at a high magnification is presented at the small picture in the lower left corner of Figure 7. It shows the path of the further development of the crack through the copper and gives clear evidence of corrosion process. The dark-grey phase visible on the crack walls is likely a mixture of dried electrolyte residues and corrosion products. Another explanation for the cracks is that hydrogen diffusing through the copper reacts with the oxides at the grain boundaries forming water under a high pressure.

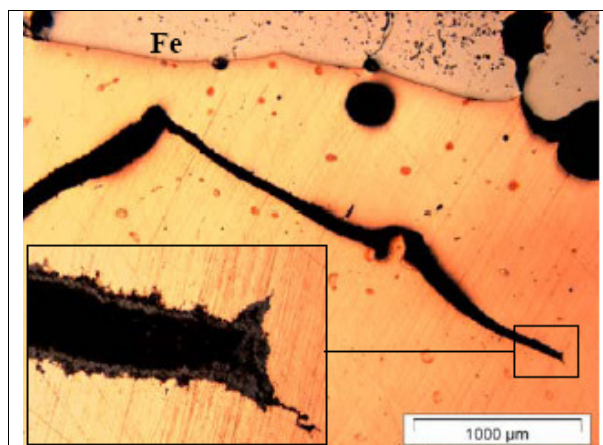


Figure 7: Cracks propagation in tuyere copper

Optical photomicrograph presented in Figure 8a reveals copper microporosity in a zone extending parallel to the interface copper/iron. The area of porous copper marked by the rectangle in Figure 8a is shown enlarged in Figure 8b. As can be seen in Figure 8b, the copper porosity spreads across the entire copper grains and exhibits orientation depending on the crystal grain orientation. The porosity can be attributed to a chemical reaction, which occurred between diffusing species (e.g. hydrogen and/or chlorine) and small precipitates (e.g. oxides and sulphides) dispersed along dislocations lines in copper. Figure 8c shows progress of local melting into the zone of porous copper induced by molten iron. The dark areas visible in the iron layer indicate the occurrence of corrosion.

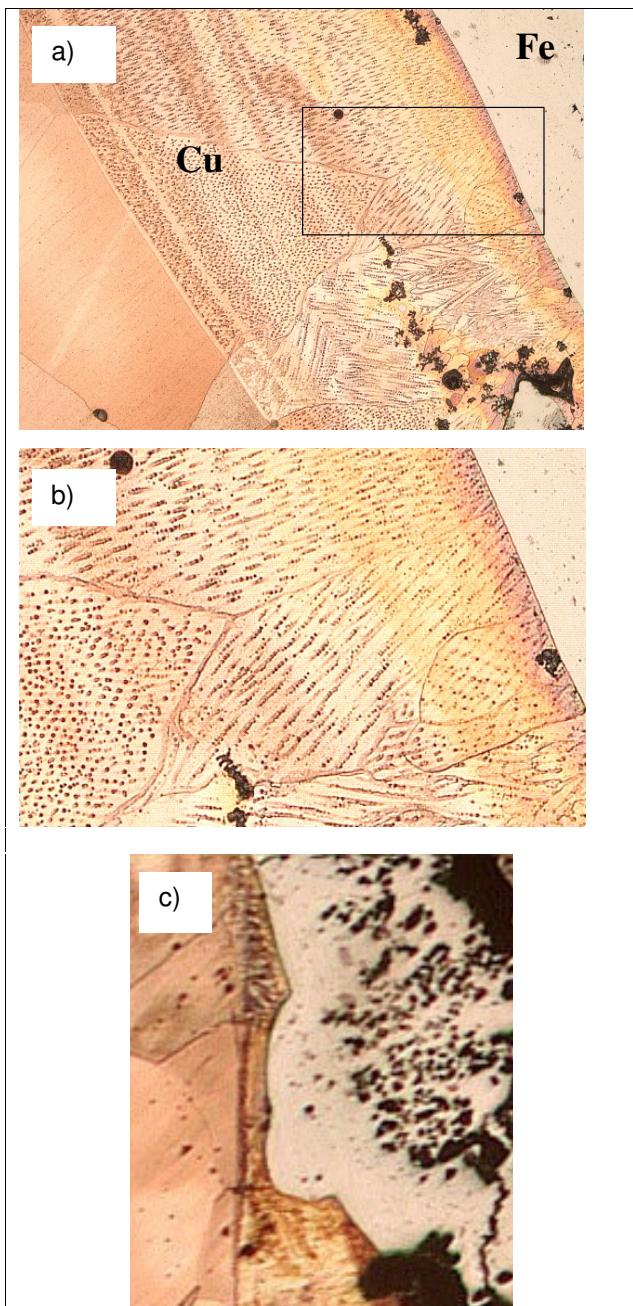


Figure 8: Microporosity in tuyere copper

The important role of chlorine in the failure mechanism of tuyeres was confirmed by ESMA analysis of a sample of a destroyed tuyere. The mapping area was chosen to include a channel going through the iron layer and forming a cavity at the copper/iron interface. Mappings of the elemental distribution were done for Cu, Fe, Si, S, Cl, Zn, K and Na. Chlorine and alkalis showed similar distribution within the analyzed area. They are mostly present on the channel wall and at the edges of the cavity in the copper as show the elemental maps for chlorine and potassium (Fig. 9). The coincidence of the distributions of K, Na and Cl indicates the presence of KCl and NaCl. But there are some areas in the chlorine map (the upper left corner of the chlorine

map and the interface copper/iron) where a high observed chlorine concentration (1.8 – 2.3 wt. %) is not correlated with especially high concentrations of alkalis. It seems that chlorine has higher mobility than the alkali metals in the attacked regions of tuyeres, which can be explained by simultaneous chloride transport by both metal chlorides and HCl, whereby the latter one spreads more easily.

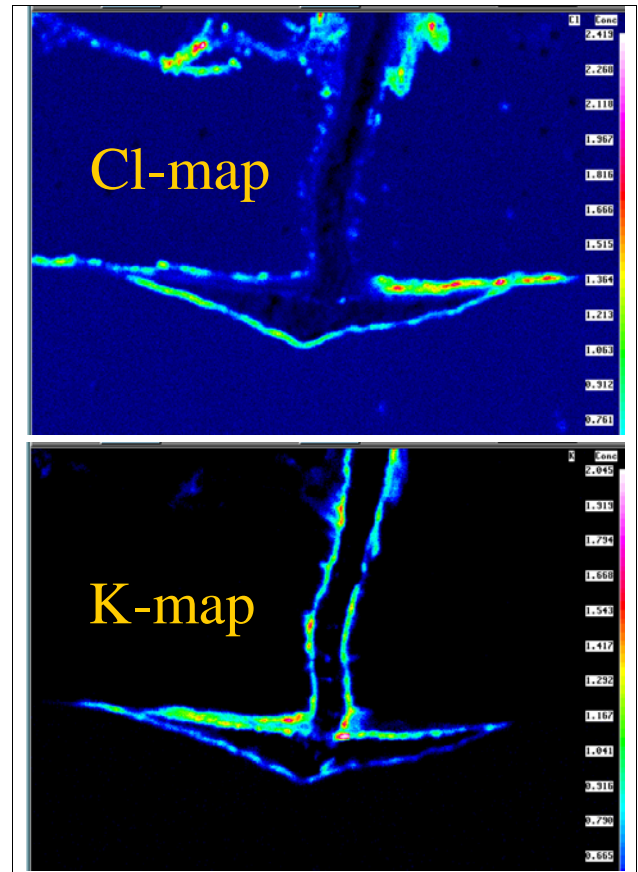


Figure 9: Elemental maps of Cl and K in a failure site

Summing up, the metallographic investigation of destroyed tuyeres provides evidence of a complex mechanism leading to the tuyeres destruction. Some of the defects found in the investigated tuyere samples (needle-like structure of the iron, presence of small copper particles between cementite needles, intergranular cracks and microporosity in copper) are evidence of corrosion, while some other (copper particles interspersed with graphite) are consequence of local melting of the tuyere copper. Anodic corrosion of copper in the presence of cementite as an important aspect of the tuyere failure mechanism was investigated by a laboratory experiment described in the following.

Influence of cementite on corrosion behaviour of copper in an aqueous chloride media

It is well known that galvanic coupling between cementite and ferrite can significantly affect corrosion of steels and other ferrous alloys that contain carbon [15], but effect of cementite on electrochemical behaviour of copper has not been investigated until now.

Metallographic examination of the tuyere failure sites showed that there is always an iron layer containing a substantial amount of cementite in contact with copper. In the presence of an electrolyte, galvanic coupling between copper and cementite can lead to an accelerated copper dissolution. Therefore, the effect of the cementite phase contained in iron on the copper electrochemical behaviour was investigated. A charge of 400 g iron was remelted in an induction furnace and poured in a thick-walled copper mould to ensure a high cooling rate which promotes cementite formation. A sample cut from the iron plate produced in such a way revealed the presence of a substantial amount of cementite in the microstructure. For that reason, this rapidly solidified iron is suitable for use in the experiment investigating the influence of cementite on the copper corrosion.

Two test samples (galvanic couples) were prepared for the experiment. A piece of tuyere copper and a piece of the cementite-rich iron, both in rectangular form, were joined by tungsten inert gas welding. For the purpose of having a reference, another couple was prepared in the same way, but composed of tuyere copper and Armco iron (nearly pure iron containing ferrite and no cementite). The copper and iron pieces were weighed before being welded as well as the couples obtained after welding to enable later the determination of their weight loss during the immersion test. The both galvanic couples were tested in HCl solutions under same conditions: 270 mL 0.5 M HCl (initial concentration) at 45 °C, stirred with a magnetic stirrer. The weight loss of the samples immersed in the HCl solutions was determined each 24 hours.

After initial dissolution of the surface oxide film formed during the welding, no significant changes in the appearance of the copper piece coupled with Armco iron were observed. The copper seemed to be resistant to the corrosion attack, while at the same time, the Armco iron piece suffered a considerable corrosion. After 12 days of immersion the bond between the copper and Armco iron pieces was broken due to the dissolution of the welded joint. The pieces were taken out of the solution, rinsed with distilled water, dried and weighed. The total weight loss of the copper piece coupled to Armco iron after 12 days of immersion in HCl solution was only 1.7 wt. % of its initial weight, while during the same period of time, the Armco iron piece corroded severely and lost 40.7 wt. % of its initial weight. Being the less noble

member of the galvanic couple, the Armco iron corrodes providing cathodic protection to the copper. The galvanic couple consisting of tuyere copper and rapidly solidified iron exhibited quite different dissolution behaviour in HCl solution. During the first 8 days of immersion, except for the initial dissolution of the surface oxide film, the copper piece did not show any observable changes in the appearance. Simultaneously an intensive formation of the hydrogen bubbles on the iron indicated the dissolution of its ferrite phase. However, after this period, a rapid dissolution of the copper began which was observed by the diminution of the copper piece size and subsequent copper deposition from the solution onto the surface of the iron piece in the form of fine particles (Fig. 10). After 15 days the experiment had to be stopped due to breakdown of the welded joint. At that moment the whole surface of the iron piece was covered with fine copper particles (Fig. 10b).

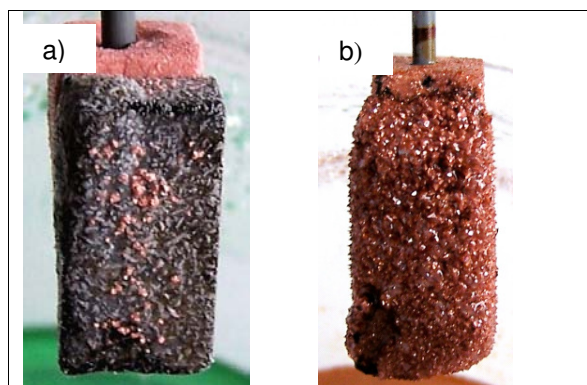


Figure 10: Deposition of copper from HCl solution on the cementite-rich iron: a) after 12 days and b) after 15 days of immersion

This visual observation of the tuyere copper-rapidly solidified pig iron couple is in accordance with its weight loss-time curve presented in Figure 11, where a significant increase in the weight loss after 8 days indicates the initiation of the copper dissolution. Thus, the dissolution curve can be divided into two stages. The first stage corresponds to the ferrite dissolution from the rapidly solidified iron. The second stage beginning around the eighth day of immersion involves an intensive copper dissolution, even though a considerable amount of copper precipitates again from the solution on the iron part of the sample.

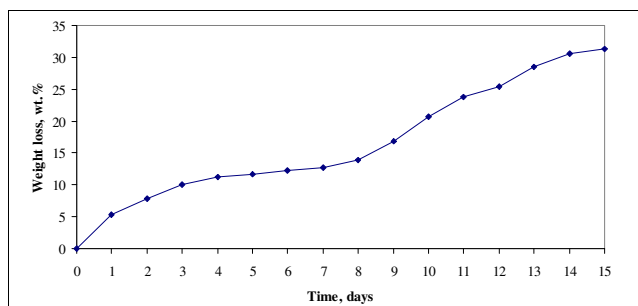


Figure 11: Weight loss-time curve for the couple consisting of tuyere copper and rapidly solidified iron in 0.5M HCl

The total weight loss of the detached copper piece after 15 days of exposure to the HCl solution was 20.6 wt.% of the initial weight, which is significantly higher than that of the copper piece coupled with Armco iron, 1.7 wt.% after 12 days.

The experimental results indicate that copper suffers increased corrosion upon coupling to the cementite-rich iron in HCl solution. After the ferrite phase has been selectively dissolved, the relatively noble cementite remained in the iron causes an accelerated corrosion of the copper. Besides this, the large surface of the cementite lamellae provides a large cathodic area coupled to relatively a small surface of the less noble tuyere copper which results in a much more rapid dissolution of the copper. The copper ions accumulate in the solution, while the released electrons are consumed by different cathodic reactions proceeding at cementite rich sites. In the later phase of the test when the concentration of the dissolved copper in the solution is substantially high, copper ions are reduced giving pure copper deposits on the cementite surface. It can be assumed that the tuyere copper containing impurities is less noble and therefore has a more negative redox potential than pure copper that is being deposited on cementite lamellae.

Summing up, this experiment showed that the iron containing cementite does not act as a sacrificial anode for copper. In contrast, it enhances copper corrosion. A rapid copper dissolution begins after the less noble ferrite from the iron structure has been dissolved. Under these conditions, the copper becomes anodic with respect to the cementite remained in the iron. A quite similar situation exists on a tuyere where copper and cementite contained in the iron solidified on the tuyere surface are in contact with an electrolyte (see Fig. 3).

Conclusions

The results obtained in this investigation indicate a complex failure mechanism of blast furnace tuyeres consisting of two interacting stages: corrosion and local melting of tuyeres. The corrosion is caused by the attack of aggressive chemicals present in the blast furnace. Chlorine-containing compounds are

most likely responsible for the corrosion attack. Chlorine circulates and accumulates in the blast furnace, thus increasing its concentration within the furnace, whereby the corrosion on tuyeres becomes more likely. Presence of chlorine in significant concentrations in the damaged regions of tuyeres was evidenced by ESMA analysis of the tuyeres samples.

A high pressure of about 5 bar existing in the tuyere zone of a blast furnace can cause some of the water vapour present in the furnace to condense on the cold tuyere surface. Subsequent dissolution of corrosive gases such as volatile metal chlorides, Cl_2 , HCl or sulphur oxides in this water condensate results in the formation of a corrosive solution attacking the tuyere. The zones on the tuyere surface covered with solidified iron are especially favourable for condensate formation due to the thermal insulation effect of the solidified iron. The corrosive electrolyte can also be formed at locations on the tuyere surface where particles of hygroscopic salts (e.g., CaCl_2 , ZnCl_2) are present.

The reaction between these corrosive agents and impurities present in the tuyere copper, as precipitates at the grain boundaries or fine dispersed impurities within the copper grains results in the generation of intergranular cracks and microporosity. The cracks and microporosity originated from the corrosive attack in the tuyere copper cause a significant decrease in the effective thermal conductivity of the copper and consequently a weak cooling of the affected area. This results in an increase in temperature and finally local melting of the tuyere, particularly upon the contact with hot metal.

It was found that cementite present in the iron solidified on the tuyere surface plays a remarkable role in the corrosion stage of the failure. Namely, galvanic coupling between copper and cementite in an acidic chloride containing electrolyte leads to an increased rate of the copper dissolution.

Based on the results of this investigation, the future work will be focused on development and testing of a protective coating for tuyeres. The coating should provide a good corrosion and wear protection. The coating material has to be especially effective against possible galvanic coupling between the tuyere surface and cementite contained in iron.

References

- [1] Gudenau, H.W.; Johann, H.P.; Meimeth, S.: Entfernung von Alkalien aus dem Hochofen; Stahl und Eisen 116, 1996, No. 9, P. 89 – 96
- [2] Turkdogan, E.T.: Physical Chemistry of High Temperature Technology; Academic Press, 1980, P.
- [3] Lectard, E.; Hess, E.; Lin, R.: Behaviour of chlorine and alkalis in the blast furnace and

- effect on sinter properties during reduction;
Revue de Metallurgie – CIT, 2004, P. 31 – 38
- [4] Bechmann, H.; Berner, K.; Esfeld, G.: Über den Verschleiß von Blasformen am Hochofen, Teil I.: Ursachen der Blasformschäden; Stahl und Eisen, 1970, No. 10, P. 508-515
- [5] Sagaydak, I.I.; Galemin, I.M.; Shparber, L.Ya.; Karshin, V.P.: Durability of air and slag tuyeres; Metallurgist, 1964, No. 4, P. 155-157
- [6] Boris, I.I.; Andronov, V.N.; Buklan, I.Z.: Reasons for massive burnout of tuyeres; Metallurgist, 1968, No. 12, P. 639–640
- [7] Ayukov, A.S.: Burning of tuyeres; Metallurgist, 1963, No. 1, P. 10-11
- [8] Ragin, B.I.: The construction of blast-furnace tuyeres; Metallurgist, 1965, No. 9, P. 510–512
- [9] Donskov, D.E.; Donskov, E.G.; Kostenko, G.P.; Listopadov, V.S.; Otorvin, P.I.: Reducing air-tuyere failure; Steel in Translation, 2006, No. 1, P. 12–18
- [10] Krasavtsev, I.N.; Skladanovskii, E.N.; Spirin, A.M.; Stepanov, V.V.: Melting foundry iron with sloped tuyeres; Metallurgist, 1973, No. 11, P. 794–796
- [11] Gudenau, H.W.; Jokiel, P.; Koerfer, M.: Möglichkeit zur Verlängerung der Standzeit von Hochofenblasformen durch eine thermisch gespritzte Schutzschicht aus Picrochromit; Radex-Rundschau, Heft 1, 1990, P. 213–226
- [12] Ohmae, Y.: Surface-coated blast furnace tuyere made of copper or copper alloy and method of surface-coating the same; US Patent No. 4,139,673 (February 1979)
- [13] http://www.engineeringtoolbox.com/boiling-point-water-d_926.html
- [14] Shepelev, Yu.S.; Rudenko, L.F.: Mechanism of gray cast iron corrosion; Materials science, 1978, No. 1, P. 86–87
- [15] Marques, M.T.; Correia, J.B.; Conde, O.: Carbon solubility in nanostructured copper; Scripta Materialia, 2004, No. 7, P. 963–967