

The Fracture Mechanisms of an Austenitic Heat Resisting Steel in Copper Converter Atmosphere

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Abstract

The openings of Copper converter in Sarcheshmeh Copper Complex in Iran is made of a heat resisting austenitic steel (Fe-25Cr-12Ni) and many failures have been reported. Understanding the failure mechanism of the alloy helps to develop better alloys for similar complex environments. Samples of as-cast alloy and those taken from failed ones were examined. Optical Microscopy (OM), X-Ray Diffraction (XRD) and Scanning Electron Microscopy (SEM) have been applied to examine the alloy and oxide scales. Investigations show that microscopic structure and operational conditions are parameters which affect the fracture of the alloy. The existence of SO₂ in the environment increases the reaction rate and formation of sulphides comes near the surface and around the grain boundaries. The sulphides decrease the oxidation resistance of the alloy.

Keywords: Heat resisting steel, Fracture mechanism, Sulphidation, Corrosion resistance, Sensitization

Introduction

In Sarcheshmeh Copper Complex, the conversion of matte to blister copper is done in a converter and its opening is exposed to 800-1050°C. This opening is made from four plates. Two of these plates in the upper and lower sides have been marked "F" and the other two plates in the left and right hand sides have been named "side" as shown in figure 1.

The successful application of alloys in corrosive atmospheres at elevated temperatures generally depends on their ability to form a protective scale¹. Austenitic heat resisting steels are widely used at elevated temperatures when ferritic or martensitic steels do not provide adequate corrosion resistance and/or sufficient strength at these temperatures². The alloying elements in these steels have the most effect in their microstructure^{3, 4}. The composition of the alloys should be selected so that no brittle phases form in the structure at high temperatures^{3, 4}.

Sensitization is a disastrous effect that occurs in the range of 500-1000°C and increases with carbon content⁵. It occurs when carbon diffuses to grain boundaries and forms chromium carbides so that grain boundary corrosion occurs.

The oxidation resistance of heat resisting steels depends on the formation of Cr₂O₃ layer on the surface. High Pilling Bedworth Ratio (P.B.R) which produces compression stresses during the growth and volatilization at high temperatures is a disadvantage of this layer⁶.

Considering that this alloy exposes to the molten metal or splashing, the copper can diffuse in the metal, which causes mechanical failure.

In this paper the fracture mechanism of an austenitic heat resisting steel which fails after 120 cycles (1000 hours) in Copper Converter atmosphere is investigated.



Fig. 1. The openings of Sarcheshmeh Copper Converter.

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Experimental Techniques

Optical Emission Spectroscopy (OES) analysis was carried out to determine the chemical composition as shown in Table 1. This alloy is made by induction melting and casting. Test specimens

Table 1. Alloy composition (wt. %).

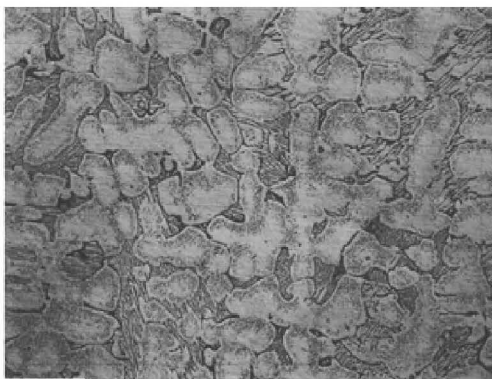
Ni	Cr	Si	Mo	S	P	Mn	C	Fe
10.2	24.7	1.80	0.78	0.005	0.024	1.06	0.25	Bal.

were cut from the as-cast alloy and failed opening. The finished dimensions of the test specimens were 15×15×10 mm. The test specimens were degreased in NaOH solution, then polished with 6µm alumina powder. They were etched with 5 gr FeCl₃, 2 cc HCl and 95 cc alcohol solution.

To characterize the structure and composition of corrosion products, Optical Microscopy (OM), X-Ray Diffraction (XRD) and Scanning Electron Microscopy (SEM) have been employed.

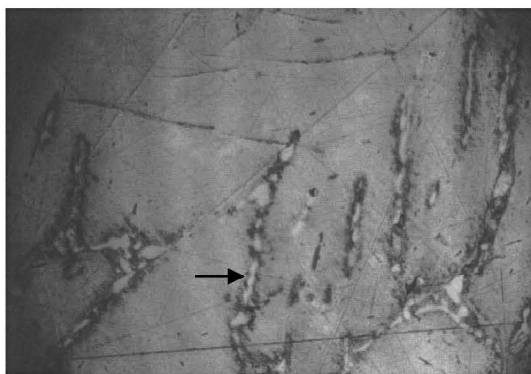
Results

Figure 2 shows the microstructure of the as-cast alloy. The alloy has duplex structure of austenite and ferrite. Sigma phase forms in austenite matrix and grain boundaries (Figures 3 and 4). This phase can be seen as light regions in austenitic matrix.



100 µm

Fig. 2. The structure of as received Fe-10Ni-25Cr.



100 µm

Fig. 3. Formation of sigma phase in austenitic matrix and grain boundaries after 120 cycles.

Figure 5 show continuous carbides formed in grain boundaries. Exposure of the alloy at an elevated

temperature for a long time caused grain growth. At a high temperature, carbon diffusion to the grain boundaries increases so that a carbide network forms at these regions⁷. At about 1050°C, sensitization occurs in some of the specimens. Carbide network, which formed in the grain boundaries, is the cause of sensitization (Figures 6 and 7). The eutectic chromium carbide formation under Cr₂O₃ layer and its coarsening above 1000°C causes depletion of chromium, and internal oxidation occurs (Figures 8 and 9). The matrix depleted from chromium and severe oxidation occurs (Figure 8).

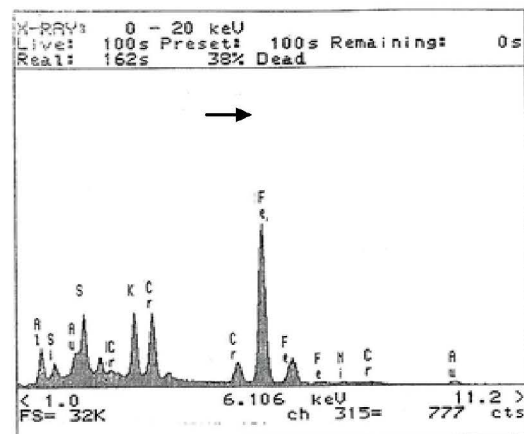
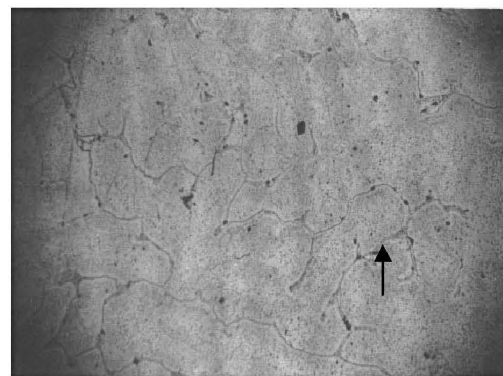


Fig. 4. Point analysis of the alloy after exposure to the environment after 120 cycles.



100 µm

Fig. 5. Sensitization occurred in the specimens after 120 cycles.

SO₂ diffuses through pores and microcracks in the oxide layer and increases the rate of reactions (figure 10). The molten sulphides diffuse through grain boundaries and form diffusion channels, and internal oxidation increases with sulphidation

(Figure 11). Diffusion of alloying elements such as iron and nickel through the chromium oxide forms external sulphides such as Cr_2S_3 , Cr_3S_4 , $Fe_{1-x}S$, etc. (Figure 12).



Fig. 6. Coarsening of carbides at grain boundaries after 120 cycles.

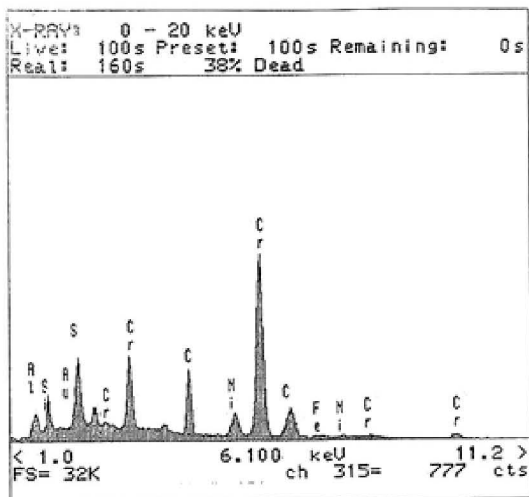


Fig. 7. Point analysis of the alloy after exposure to environment after 120 cycles.

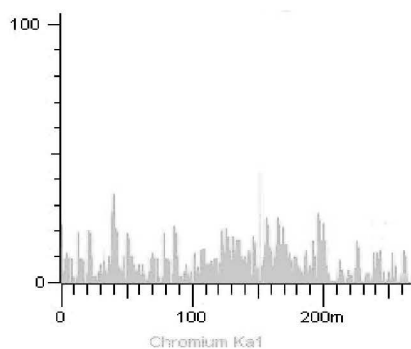


Fig. 8. Chromium depletion under the surface after 120 cycles.

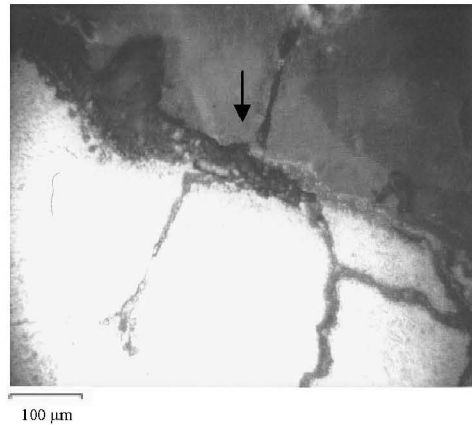


Fig. 9. Eutectic chromium carbides are indicated by arrow after 120 cycles.

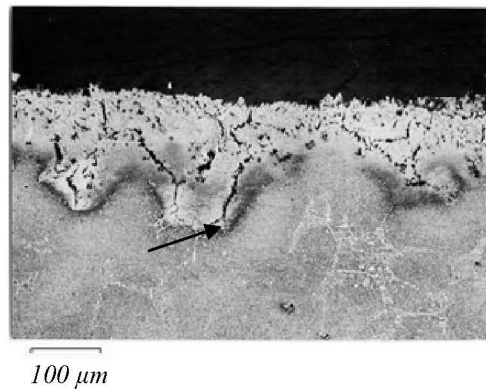


Fig. 10. Diffusion through microcracks after 120 cycles.

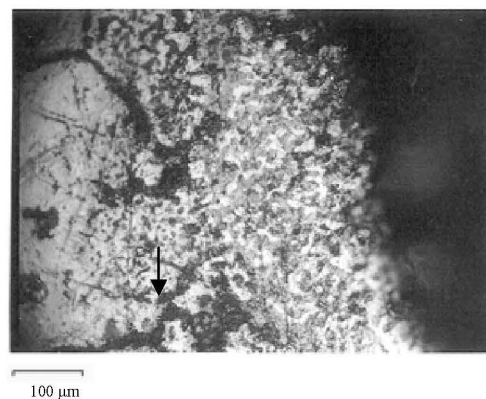


Fig. 11. Internal oxidation due to chromium depletion under the surface.

Continuous and thick carbides along grain boundaries will be formed. This causes copper diffusion through grain boundaries under the surface. Grains separation occurs due to an operational impact and development of cracks on the surface (Figures 13 and 14).

of this network can embrittle the alloy. However, it is necessary to reduce the carbon content of the alloy to increase corrosion resistance of grain boundaries by controlling the carbon content so that it does not exceed 0.08%. The sensitization can cause the subsurface oxidation. The eutectic chromium carbide formation under Cr_2O_3 layer and its coarsening above 1000°C causes depletion of chromium, and the internal oxidation occurs (Figures 8 and 9).

The other mechanism which affects the corrosion rate is sulphur in the environment. SO_2 increases the rate of reactions. It is believed that SO_2 diffuses through pores and microcracks in the oxide layer (Figure 10), decomposes and reacts with the surface to form iron and chromium sulphides^{8, 9)}. Sulphur concentration, due to grain boundaries diffusion, increases internal sulphidation near the grain boundaries. The operational temperature of steels and precipitation of FeS at the grain boundaries causes hot shortness and metal damage^{10, 11)}. Sulphide components are absolutely non stoichiometry. Anions and cations transport move easily through these regions, so they decrease the oxidation resistance of the alloy⁸⁾.

For the sulphidation resistance, alloys are needed to produce a compact and adherent barrier between matrix and atmosphere and protect them in the long run¹²⁾. The diffusion of sulphur components to the grain boundaries and the expansion due to the reactions in this region cause cracks in the scale^{13, 16)}. The alloying elements which produce stable sulphides can diffuse through oxide scale and form sulphides on the oxide layer^{8, 12)}. However, the corrosion rate increases because some of eutectic sulphides may melt (The melting point of iron sulphides is 985°C and that of mixed sulphides of iron/nickel is less than this amount). The formation of molten phase is disastrous because anions and cations transport through molten phase increases. If the molten phase forms in the metal/scale interface, the adherences of metal/scale is damaged¹⁵⁾. It results in the formation of diffusion channels through molten sulphides; and therefore, internal oxidation increases (Figure 11).

In the severe sulphidation and scale fracture conditions, the alloying elements such as iron and nickel diffuse through the chromium oxide and react with the environment to form external sulphides such as Cr_2S_3 , Cr_3S_4 , Fe_{1-x}S , etc.^{8, 17)} (Figure 12). Iron and chromium sulphides are formed inside the oxide layer and cover it completely after a long time.

As the diffusion rate of Fe^{2+} in the spinel is three times as much as that in Cr_2O_3 ^{19, 20)}, the spinels growth is increased and rapid diffusion paths are produced. By increasing the interface between spinels and Cr_2O_3 , the rate of oxidation/sulphidation increases^{15, 20)}. In primary stages of sulphidation, fine particles of sulphides formed under the surface and chromium will be more depleted in this region. After the fracture of Cr_2O_3 layer, chromium should diffuse

to the surface to form new oxide in the surface, but as the chromium content under the surface decreases to less than the critical chromium concentration for external Cr_2O_3 formation (N_{Cr}^*) and as the diffusion rate of chromium in austenitic steels is much lower than ferritic steels^{12, 15, 20)}, Cr_2O_3 is not formed on the surface. Due to chromium depletion, Fe concentration in the matrix surface increases. The high concentration gradient of Fe causes the formation of sulphides enriched by iron in this region^{12, 15)}. However, the low concentration of chromium and low rate of chromium diffusion are two factors which cause internal sulphidation.

The other factor which affects the steels fracture is copper diffusion in the steel that forms a layer under the surface. Principally, copper does not have a role in oxidation resistance because it doesn't enter the oxide structure but it decreases the mechanical properties of steels. As the operational temperature of this steel is about the melting point of copper, the possibility of melting the copper in the grain boundaries and hot shortness exists so that the grain boundaries are covered by a molten layer. By applying stresses to separate cold spots of molten metal, grains separate and cracks appear on the surface (Figures 13 and 14).

The other parameter in damaging the steel is Cr_2O_3 volatilization. When volatilized corrosion products form at a high temperature, the corrosion rate increases. At high pressure of O_2 and high rates of gas flow in scale/gas interface, Cr_2O_3 scale volatilize according to the below equation⁶⁾:



Above 800K , CrO_3 is in unstable gaseous form. Oxide volatilizes directly at 1000°C or more. Above 970°C , gaseous Cr in the scale-alloy interface has high pressure and chromium can volatilize by diffusing through cracks, pores and defects of oxide film, and short circuit diffusion can occur. Gaseous chromium in the oxide can react with the oxygen inside, on the surface or outside the film and form Cr_2O_3 or $\text{CrO}_3 (\text{g})$. In an atmosphere of sufficient oxygen, $\text{CrO}_3 (\text{g})$ is the only possible gaseous component which forms outside the oxide surface²²⁾. As the pressure and rate of exhausted gases of converter is too high, the thinning of the film is high or extremely high. This phenomenon is seen in the worked specimens and thickness of the parts is reduced. This increases the oxidation rate and has a main role in internal oxidation.

Conclusions

- 1- The existence of SO_2 in the environment increases the reaction and formation of sulphides near the surface and around the grain boundaries.
- 2- The high concentration of chromium in grain boundaries and sulphur content due to grain

boundaries diffusion increase internal sulphidation around grain boundaries.

- 3- Melting of eutectic sulphides causes diffusion through grain boundaries.
- 4- The diffusion of copper and formation of sub layer decrease the mechanical properties and separation of grains.

Acknowledgments

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