The Effect of Carbon, Titanium and Rem on Oxidation Resistance of Cr-Al Steels

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Abstract – The aim of the work is to determine the influence of carbon, titanium and REM (Rare Earth Metals) on oxidation resistance of Cr-Al steels. The negative impact of high concentration of carbon on performance characteristics of steels under examination has been established. To provide the target time of service the concentration of chrome, aluminium, carbon and titan is recommended. It has been found, that small additions of REM substantially improve the quality of coupling of oxide films with the surface of the basis of metal. The exceedence of the set number results in early destruction of protective oxide layers and decrease of pieces’ service time. The studies of oxide films have examined the possibilities of changing the compositions and structure of phases of oxides in the system, that confirms the fact that at high temperatures in an oxidizing environment the stable phases of oxides are rhombohedral phases, rather than spinel structures. By results of research, a mathematical model, which allows to forecast performance characteristics of pieces depending on titan and carbon content, was calculated.

Keywords – Carbon, Titanium, REM (Rare Earth Metals), Oxide Films, Oxidation Resistance, Cr-Al Steel, Structure

INTRODUCTION

On the durability of moulded parts, which operate in conditions of high temperatures, the interaction processes of these parts with working environment have exceptional influence. The most common type of interaction is oxidation. Oxidation processes in terms of thermal resistance for Fe-based alloys play a huge role.

It is known [1-5] that the resistance of steel to gas corrosion under high temperatures is defined by the concentration of alloying elements in a solid solution that during the oxidation can form a protective oxide layer on the surface. Unfortunately, the effect of the same elements on oxidation resistance of steels of different chemical composition is different and depends greatly on the content of other elements. That is why this paper attempts to identify oxidation resistance of Fe-based alloys with a wide range of carbon, titanium and REM (Rare-earth metals) concentrations, maintaining regular content of other elements (chromium, aluminum, manganese and silicon) as much as possible. The content of phosphorus and sulfur was kept at the level of 0.020-0.025%.

The authors [6] established that with the increase of carbon content in thermal-resistant steels their oxidation resistance decreases due to the reduction of Cr concentration in an alloyed ferrite as Cr was used to form carbides. Thus, the quantity of chromium ions, which diffuse to the surface of the piece and form a protective oxide film Cr₂O₃ is reduced. As a result, general protective properties of the oxide film become worse even in the condition of relatively high (1.5-2.0%) concentration of aluminum in a steel.

On the other hand, it must be taken into account that the rise of C content in steels leads to the increase of their basic characteristic – practical fluidity – and in some way to the improvement of mechanical properties. It is very important for a highly alloyed steel with a coarse-grained structure.

The analysis of technical literature on the matter has established that harmful effect of C on oxidation resistance of heat-resistant steels can be partially or fully neutralized by adding to the liquid-alloy active carbide-forming elements that have a greater affinity for carbon than chrome does.

The studies of thermodynamic properties of chemical elements have established that the most promising for this is titanium. It forms a very strong and refractory carbide TiC (T melting = 3140°C). Taking into account the fact, that titanium in addition to carbides actively forms nitrides and oxides, the determination of its optimal concentration in Cr-Al steels is the matter of current interest.

PROBLEM STATEMENT

The following tasks were formulated by the authors of the paper for solving this problem:

- To examine the effect of carbon and titanium on oxidation resistance of Cr-Al steels in conditions of overheated air at a temperature of 1200°C;
- To explore the impact of REM (rare earth metals) on special properties of heat-resistant steels with high content of Cr and Al;
- To explain the mechanism of oxidation of heat-resistant steels and the impact of main alloying elements on this process;
- To establish the dependence of optimal content of Ti knowing the content of C to get high oxidation resistance of Cr-Al steels.

**EXPERIMENTAL DATA**

The common effect of C in the range of concentrations 0.08 to 0.81% and Ti - to 0.63% - on oxidation resistance of the Cr-Al steel, which contain 30% Cr and 2% Al has been studied. Samples with a diameter of 10 mm and a length of 20 made of a billet in the form of bars with a diameter of 15 mm, obtained while studying the technological properties of the same steels were used for experiments. The changes in the content of oxides in an oxide scale of 30Cr30Al2 steel are shown in Fig. 1.

The favorable effect of Ti on oxidation resistance can be explained by the fact that in addition to the release of a part of Cr, which would have formed carbides, the formation of an oxide scale with the involvement of titanium oxides occurs. Such oxide film has high protective properties. Furthermore, alloying of steel with titanium reduces Fe diffusibility in a ferrite and decreases the number of its oxides in an oxide scale that is formed on the surface of the piece. This is confirmed by a microchemical analysis of oxide films: with a Ti content 0.25% there were found 0.5-0.6% of its oxide in steel, and iron oxides content, compared to the oxide scale, which is formed on samples of steel without titanium decreased from 2.35-2.60 to 1.60-1.75%.

For Cr-Al steel with an average carbon content (0.30-0.40%) optimal addition of titanium can be regarded as 0.25-0.45%. Generally speaking, optimal titanium content, which provides maximum heat resistance of Cr-Al steels, depends on the carbon concentration and is determined from the relation:

\[ \% \text{Ti} = (1,3-1,5) \% \text{C} \]

After the increase of titanium content in steel its quantity in oxide films grows and alloy’s oxidation resistance decreases.

Oxidation resistance of steels, where carbon content changed from 0.08 to 0.88% has been studied. Researches have been conducted at temperatures 1200 and 1300°C during 100 and 500 hours. The results of changes in oxidation resistance of steels at the temperature of 1200°C is shown in Fig. 2.

It has been established, that with the increase of carbon content in steel its oxidation resistance decreases and mass loss increases. This is due to the fact, that carbon promotes the formation of a larger number of chromium carbides, and solid solution - alloyed ferrite – is depleted by chromium. A steel structure becomes nonhomogeneous, the composition of oxide scale changes, the number of Cr₂O₃ in it reduces and its protective properties decrease.

However, it should be noted that with the carbon content of 0.25-0.30% oxidation resistance of steel remains almost stable because Cr rate in the formation of carbides are rather small, and the composition of the protective oxide film remains unchanged. With the increase of carbon to 0.35-0.45% a less dense oxide scale is formed on the sample’s surface. It is easily exfoliated, especially in places, where carbide groups exit to the surface and damage the oxide scale homogeneity, reduce the strength of its grip with the metal surface and decrease the level of protection properties of the oxide scale.

The same dependencies as for oxidation resistance of steels with high chromium and aluminum content, but with higher mass losses of samples have been obtained after testing at the temperature of 1300°C.
Based on the results of the research, it was established that with the increase of the test temperature oxidation resistance of Cr-Al steels changes in some way, but it still remains quite high. From such steels it is possible to produce moulded parts that will work reliably for a long time at temperatures up to 1300°C, if the titanium content will be within 0.2-0.4%, and carbon - in the range 0.25-0.30%.

As indicated earlier, titanium is a stronger carbide-forming element than chromium and therefore it should neutralize the harmful effect of carbon decreasing the number of chromium tied up in carbides. The effect of titanium on oxidation resistance was studied in a range of its concentration in Cr-Al steel up to 2%. The results of studies are shown in Fig. 3.

![Graph showing the effect of titanium on oxidation resistance of Cr-Al steel at 1200°C](image)

1 – samples’ holding time 100 hours; 2 – samples’ holding time 500 hours

Fig. 3. The Effect of titanium on oxidation resistance of Cr-Al steel 30Cr30Al2Ti at the temperature of 1200°C

It was determined that increasing the titanium concentration in Cr-Al steels to 0.3-0.4% significantly reduces the mass loss of metal at the temperature of 1200°C. This is due to the fact, that in addition to the release of chromium, previously tied up in carbides, after the steel has been alloyed with titanium protective properties of the film were improved due to the formation of complex spinels with the participation of titanium.

This conclusion is agreed upon with the decrease in the rate of oxidation in long – term tests that can be found in comparing the weight loss by samples made of steel without titanium and with titanium during 100 and 500 hours.

With the content more than 0.5-0.6% of titanium in the steel a large number of titanium carbides located in separate colonies appear in the structure.

The heterogeneity of steel has a negative impact on its special properties, and oxidation resistance in particular. Thus, the optimal content of titanium in Cr-Al steels with 0.30-0.35% of carbon is determined by the required temperature and duration of the product’s service life and must be within 0.2-0.5%. For example, If the steel contains 0.25-0.35% titanium, it looks like homogeneous and coarse-grained structure. This steel doesn’t have a tendency for intensive grain growth during prolonged exposure to high temperatures.

Rare earth metals (REM) are known as active desoxidants, degasifiers, dephosphorizers of steel. In addition, they can strengthen and densify an oxide film, making it more resistant to peeling processes during changes in temperature of the surface of the product. Since REM significantly improve casting and mechanical properties of Cr-Al steels and if taking into consideration different interpretations given in the technical literature for their effect on heat resistance of steels, we studied their effect on basic operational characteristic – oxidation resistance – of the steel 30Cr30Al2Ti with a small difference in chromium content. Rare earth metals in the form of 1.0% ferrocerium were added as per calculation. The results of the research are shown in Fig. 4.

![Graph showing the effect of REM on oxidation resistance of Cr-Al steels at 1200°C](image)

1 – samples’ holding time 100 hours; 2 – samples’ holding time 500 hours;
a – the steel contains 0.30% of carbon, 28.20% of chromium and 1.95% of aluminum;
b – the steel contains 0.25% of carbon, 31.50% of chromium and 2.05% of aluminum

Fig. 4. The effect of REM on oxidation resistance of Cr-Al steels at the temperature of 1200°C
It was established that 0.30-0.35% of REM addition slightly improves oxidation resistance of steels while for a steel with higher chromium content such improvement remains until the addition of 0.45% of REM. Further increase in REM concentration leads to the dramatic deterioration of oxidation resistance and with 1.0% of REM content this characteristic is almost twice as worse than in a steel without REM.

By the visual analysis of the surface of samples containing different amounts of REM, it was established that in the environment of overheated air at the temperature of 1200°C a dense light film appears on the samples with a low content (0.25%) of REM.

With the increase in concentration of REM a film is getting darker as a result of its depletion with oxides of aluminum and formation of fine (for steels containing 0.3..0.6 % of REM) and large and small pits (Fig. 5).

Such effect of REM can be explained by a large volume of their atoms and also by phases formed with the involvement of REM, which dramatically slow down and in some places block some parts of the surface on which the formation of fine pits is possible.

The research results make it possible to conclude that the increase of REM addition to more than 0.3% reduces the content of Al2O3 in the oxide, which in turn affects the reduction of the protective properties of the oxide film and leads to reduced oxidation resistance. Such effect of REM can be explained by a large volume of atoms, which fill the cavity of a crystal grating of oxides and in this way prevent the diffusion of aluminum to the surface of the sample. With REM content more than 0.6% on the border metal-oxide the oxide CeO2 is formed, which increasingly prevents the diffusion of aluminum to the surface of the oxide-gas environment.

Color change with the increased content of REM makes it possible to determine the decrease in the number of Al2O3 in the oxide scale and appearance of chromium oxide in it and even iron.

Increasing the concentration of REM from 0.25 to 1.0% promotes the coarsening of ferrite grain (Fig. 6, a, b) and thickening of the grain boundaries. When the REM content exceeds 0.5%, it reduces mechanical properties.

Separation of REM compounds at the grain boundaries leads to the serious deterioration in oxidation resistance as a result of intercrystalline corrosion development (Fig. 6 d and Fig. 7, b). Metal oxidation starts at the point of the sample, where grains’ boundary or grating defects are located. Further oxidation of the sample happens into the depth of the sample along grain boundaries with the formation of numerous large and fine pits (Fig. 6, d).

The zone of internal oxidation is caused by oxygen diffusion into the depth of metal and alloying elements - in the opposite direction to the interaction with oxygen.

An internal oxide layer doesn’t create the resistance to diffusion of oxygen. Increasing of external layer of the oxide scale slows down the development of the layer of internal oxidation [7].

Selection of thin particles of oxide in the metal phase during internal oxidation leads to surface strengthening of alloy, complicate the recrystallization process and growth of metal’s crystals. An oxide scale on the surface of the sample increases the grip with the alloy and in this way promotes the improvement of heat resistance of the alloy during temperature changes of the product. Especially effective in this area are cerium and yttrium after their addition to Cr-Al steels [3, 7].

Thus, it was established that Cr-Al steels based on casting and mechanical properties would be preferable to treat with REM in the quantity of 0.15-0.25% as further increase their content significantly reduces oxidation resistance of steels.
1 – steel containing 0.2% of REM; 2 – steel containing 1.0% of REM; a, b – general microstructure of the steel before oxidation; c, d – steel microstructure of the periphery of the sample after oxidation

Fig. 6. The effect of REM on the microstructure of steel 30Cr30Al2Ti before and after oxidation

Fig. 7. The formation of intercrystalline corrosion during the test of Cr-Al steel 30Cr30Al2Ti (test conditions: temperature - 1200°C, duration – 100 hours)

Fig. 8 shows the results of oxidation resistance investigation of 30Cr30Al2Ti steel treated with 0.25% of REM, depending on the content of titanium. It was defined, that steel treated with REM has higher oxidation resistance when compared to steel without REM. So, to assure high oxidation resistance and taking into consideration satisfactory casting and high mechanical properties, the steel should contain 0.25-0.35% of carbon, 25-32% of chromium, 1.5-3.5% of aluminum, 0.30-0.45% of titanium and 0.15-0.25% of REM (on the basis).

Fig. 8. The change of oxidation resistance of 30Cr30Al2Ti steel due to combined effect of titanium and REM at the temperature of 1200°C

1 – without REM additives; 2 – with the addition of 0.25% REM

Bases on the analysis of titanium impact on the complex of casting, mechanical and special properties of heat-resistant Cr-Al steels it becomes possible to offer the next mechanism of its impact on the characteristics of this class of steels. Titan (up 1%) is dissolved partially in Cr-Al ferrite, promotes the dispersion hardening and reacts with the carbon and nitrogen, forming fine carbides and nitrides with high melting point, which are very similar to each
other in their properties, and so they are called carbonitrides.

Grain refining and ferrite strengthening due to the formation of a large number of grains of crystallization with high melting point and dispersion hardening lead to increasing the strength of steels. However, with 25-30% of chromium in the steel there is an area of thermodynamic instability of the carbide phase. This instability is that balance between chromium and titanium carbides is damaged, while passing through a certain temperature range (600-900°C). At the same time the transition TiC → CrC takes place, which is accompanied by weakening of interphase boundaries similar to carbide transformation Cr₂C₆ → Cr₃C₄, which significantly reduces the strength and ductility of the metal.

If the steel has a content of chromium 25-30% and 0.3% of carbon, a zone of instability of carbides is within 0.1-0.2% of titanium [4, 8].

With the increasing in concentration of carbon, this zone shifts towards lower content of titanium (0.05-0.1% with 0.6% of carbon) and higher temperatures. If the carbon content is less than 0.1%, this area is not detected, as such steels have a small number of carbides. However, in terms of thermodynamics, the required concentration of titanium in low carbon steels should be higher than in middle/high carbon steels.

Middle carbon steels, which are the most sensitive to described type of structural damage form the basis of industrial heat-resistant alloys. Based on the research results it was determined, that the content of titanium in these steels should be at the level of 0.4-0.5%. Under such condition there is no carbide transformations in steels and dispersion strengthening effect is used at its maximum efficiency.

While metal is heated, temperature variations increase the speed of oxidation of the metal. In the oxide film thermal tensions and cracks are formed and it starts to flake off the metal.

If the oxidation is limited by the chemical reaction of the metal, the corrosion rate increases proportionally to the square root of the pressure of oxygen. If the reaction rate is determined by the diffusion process in a protective film, there is no clear dependence on the gas pressure [4, 5, 7].

At present, there are three the most grounded theories of alloying contributing to heat resistance. They are not opposites but complement each other.

It is necessary to ensure the resistance of the oxide of the alloying component in the presence of the base metal. In this case the oxide of the component should be more resistant than the oxide of the base metal. If this condition is not met, the oxide of the alloying elements will be recovered by the base metal.

Al₂O₃, Cr₂O₃ and SiO₂ confirm the rule formulated above. Moreover, if first the mixed oxide is formed, further in terms of thermodynamic equilibrium, it transforms into a clean oxide of the alloying component.

\[ 3\text{FeO} + 2\text{Al} = \text{Al}_2\text{O}_3 + 3\text{Fe} \]

The size of ions of the alloying element must be less than the size of the ion of the base metal [4, 7]. This facilitates the diffusion of the alloying element to the surface of the product, on which a protective film is formed.

The alloying component and base metal must form a solid solution for a given alloy composition. Only under this condition a complete film of the oxide of the alloying component over the entire surface of the product can be provided. This theory of alloying contributing to heat resistance is confirmed by a number of practical data.

Radiographic studies have established a regular link between the decreasing the parameters of the crystal gratings and the effect of thermal resistance increasing. It is clear, that the introduction in the spinel’s structure new cations with a smaller ionic radius decreases the grating’s parameters and complicates the diffusion of oxygen ions and the base metal.

To simplify the various reactions the author of the work [4] introduced two categories between two solid crystalline compounds that can form oxides:

Examples of combination reactions can include the formation of oxides with oxygen, sulfur, carbon, when a diffusion layer of oxide, coupled with the surface of the metal and which separates it from the reaction, appears.

Nowadays, there is no complete theory explaining such processes as a result of their complexity. During the oxidation process two oxides are formed, which can form a solid solution or a double oxide. The easiest way is to obtain a solid solution on condition that ionic radius are close. The solid solution can be complete mutual solubility (Fe₂O₃ – Cr₂O₃) or partial solubility (Al₂O₃ – Fe₂O₃, Al₂O₃ – Cr₂O₃, Fe₂O₃ – Mn₂O₃)

The formation of the double oxide becomes possible, when one oxide is acid (Fe₂O₃, Cr₂O₃, Al₂O₃, TiO₂) and the other is main (FeO), or the interaction between an acid oxide of trivalent metal and basic oxide of bivalent metal with formation of spinel compounds occurs. Numerous studies of authors [2, 4, 7] provide an opportunity to consider spinels as a cubic close packing of oxygen ions in tetrahedral and octahedral cavities of which divalent and trivalent ions are located. The mechanism of diffusion of cations hasn’t been fully understood yet.

The study of oxides under appropriate thermodynamic conditions give the possibility to install the following reactions, in which the oxidation of chromium steels occurs:

1. The oxidation of the alloy elements:
   \[ \text{Fe} + \text{O}_2 \rightarrow \text{FeO} \rightarrow \text{Fe}_2\text{O}_4 \rightarrow \text{Fe}_2\text{O}_3 \]
   \[ \text{Cr} + \text{O}_2 \rightarrow \text{Cr}_2\text{O}_3 \]

2. The reaction in the solid state:
   - The interaction between oxides:
     \[ \text{FeO} + \text{Cr}_2\text{O}_3 \rightarrow \text{FeCr}_2\text{O}_4 \rightarrow \text{ferrum chrome} \]
     \[ \text{FeCr}_2\text{O}_4 + \text{Fe}_2\text{O}_4 \rightarrow \text{Fe(Fe, Cr)}_2\text{O}_4 \rightarrow \text{spinel solid liquid} \]
Fe₂O₃ + Cr₂O₃ → (Fe, Cr)₂O₃ – rhombohedral solid liqui.

- Diffusion of oxygen:
  FeO + O → Fe₂O₄ → Fe₂O₃;
  2Fe(Fe, Cr)₂O₄ + 1/2O₂ → 3(Fe, Cr)₂O₃;
- Diffusion of metal:
  4(Fe, Cr)₂O₃ + (Fe, Cr) → 3Fe(Fe, Cr)₂O₄

Fe₂O₃ + Fe → 3FeO
  ↓  ↑
Fe₄O₁₂
Fe₄O₇ + Cr → 2Fe₂Cr₂O₇
  ↓  ↑
Fe₅O₉ → FeO

Thus, due to our studies and researches, done by authors of papers [4, 7], the possibilities of changes in the compositions and structures of oxide phases in the system were established. This allows to conclude that under high temperatures in the oxidizing environment stable oxide phases are rhombohedral phases, not spinel structure. It means that recovery of ferrum oxide with chromium is the reaction, which is thermodynamically probable, but very slow.

This research was carried out using a complete factorial experiment, when the increase in mass of the sample during the oxidation (q) is the optimization parameter (y) of two variable controlled factors: X₁ (% C) and X₂ (% Ti):

\[ y(q) \rightarrow X_1 (%C); X_2 (%Ti) \]

Other factors, affecting the oxidation resistance (chemical composition, temperature, composition of gas atmosphere) were remained the same. Carbon and titanium content were changed within 0.13-0.73 and 0.08-0.70 respectively. The content of the main components of steel was on the level 26% of chromium and 2.9% of aluminum.

The obtained dependence enables to determine the optimal content of titanium for achievement of high oxidation resistance with a known content of carbon

\[ q = 2.855 + 0.855x_1 + 0.228x_2 - 0.408x_1x_2 + 0.272x_1^2 + 0.602x_2^2 \]

CONCLUSIONS

1. To ensure high level of oxidation resistance the content of titanium in Cr-Al steels should be within 0.25-0.45% with the carbon concentration of 0.30-0.40%.
2. To maintain a high level of casting and mechanical characteristics and increase of oxidation resistance, Cr-Al steel should be treated additionally with 0.15-0.25% of REM (with additive).
3. The mechanism of oxidation of chromium, which explains the changes in composition and structures of oxide phases in the system, because of which oxidation resistance of steels with high chromium content varies, was established.
4. The dependence, which allows to determine the optimal content of titanium for achievement of high oxidation resistance of Cr-Al steels with a known content of carbon in them, was obtained.

REFERENCES