# Oxidation and decarburisation of high-carbon-chromium steel under charcoal protection during spheroidising

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High-carbon-chromium bearing steel is often annealed in a sealed pot with a small amount of charcoal without physically contacting it. The charcoal is supposed to provide non-contact protection by simultaneously preventing oxidation and decarburisation during spheroidising. However, the actual effects of charcoal have not been thoroughly studied previously. In this paper, the effect of the non-contact charcoal protection is investigated. It remarkably reduces oxidation, but significantly increases decarburisation, compared with ambient air annealing. The oxide and decarburised layers with the non-contact charcoal protection are thicker than those after annealing in a sealed pot without charcoal protection and in ambient air. Experimental results have been analysed based on thermodynamics, and an improved spheroidising process for the bearing steel is suggested.

Keywords: Annealing, Oxidation, Decarburisation, Charcoal, Non-contact protection

## Introduction

Steel processed at elevated temperatures suffers from oxidation and decarburisation, which in most cases occur simultaneously (except in a strictly controlled atmosphere). Decarburisation changes the surface mechanical properties of materials.[1] Oxidation can cause material mass loss. Decarburised and oxidised layers are usually cleaned from the surfaces by chemical etching and machining.

Oxidation and decarburisation of some steels at relatively high temperatures have been extensively investigated. Hajduga and Kucera[2] measured the surface carbon concentration curves for Fe–Cr–C steels in air at 900, 1000 and 1200°C. Adamaszek et al.[3] investigated the decarburisation and the hardness changes of carbon steels during annealing in air at temperatures between 900 and 1200°C. Gong et al.[4] investigated the equilibrium internal oxidation of CMnSi TRIP steel at intercritical annealing temperature of 870°C, in a $N_2 + 10\%H_2$ atmosphere with a $+3°C$ dew point, and reported that the intercritical annealing resulted in the formation of three types of isolated particles on the surface, i.e. crystalline MnO oxide particles, crystalline $xMnO.SiO_2$ $(1 \leq x \leq 4)$ and amorphous $\alpha$-$xMnO.SiO_2$ $(0 < x < 0.9)$ oxide particles. A thin film of crystalline $xMnO.SiO_2$ $(1 \leq x \leq 2)$ was present between these parti-

cles, and thin discontinuous transition oxide layers were formed between the MnO particles and the Fe matrix. Wen et al.[5] studied effect of heating temperature on decarburisation of spring steel. Their results show that there was a minimum value in decarburisation depth in the temperature range of 900–1000°C, and the characteristics of oxidation and decarburisation of steels under different heating conditions varied. Oxidation and decarburisation of bearing steel during spheroidising annealing at relatively low temperatures have not been rigorously researched.

In developing countries spheroidising annealing of the bearing steel is usually carried out in air, or in a sealed pot with a small amount of charcoal. When the bearing steel is annealed in a sealed pot with charcoal, the charcoal consumes oxygen from the air sealed in the pot, which supposedly prevents both oxidation and decarburisation of the bearing steel. Since charcoal scarcely contacts the bearing steel due to its small amount, the process is called non-contact charcoal protection.

Non-contact charcoal protection is widely used during annealing of the bearing steel. However, whether both oxidation and decarburisation are prevented simultaneously, has not been carefully investigated and analysed. In this paper, oxidation and decarburisation of high-carbon-chromium bearing steel spheroidising annealed under non-contact charcoal protection were investigated, and compared with those processes either without charcoal protection in pots, or in ambient air. Experimental results were analysed based on thermodynamics.

## Experimental

The material employed was a high-carbon-chromium bearing steel (0·95–1·05 wt-%C, 1·4–1·65 wt-%Cr) wire

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rod 10 mm in diameter. Twelve specimens with a length of 15 mm were cut from the wire rod. The surface decarburised layer formed during hot rolling was cleaned off before testing. Several mini-muffle pots of heat-resistant steel were used as the sealed pots for spheroidising annealing. A groove was machined at the edge of the opening of the muffle pot body, and asbestos cord was stuffed in the groove for better sealing. The pot cover was bolted to the pot body. The internal dimensions of the muffle pot are $\Phi 60 \times 60$ mm. All muffle pots, charcoal and asbestos cord were dried before testing.

The 12 specimens were divided into three groups (four specimens per group). In each group, three specimens were annealed in three muffle pots, and the fourth specimen was annealed in ambient air. The first specimen with 3 g of charcoal powder was sealed in the first muffle pot, and the charcoal did not contact the specimen (non-contact charcoal protection). In the second muffle pot, only the specimen was sealed in without charcoal. In the third muffle pot, a specimen buried in charcoal powder (contact charcoal protection) was sealed in the pot. The three sealed muffle pots and a remaining specimen were simultaneously placed into a resistance furnace for spheroidising annealing at 790°C for 8 h, and then cooled to 650°C in the furnace at a cooling rate of about $0.8°C\ s^{-1}$. Finally, they were cooled to room temperature in air. Each experiment was repeated three times, i.e. the specimens from all three groups were tested. The metallographic observation and the measurements of the thickness of the decarburised layer were carried out by using an OLYMPUS PMG3 optical microscope.

## Results and discussion

### Analysis of charcoal amount

The assumption of the non-contact charcoal protection is that charcoal would react with oxygen in the sealed pot to generate carbon monoxide, and if oxygen in the sealed pot reacts completely with the charcoal, the oxidation and decarburisation will not occur. According to this assumption, the weight of charcoal used in production and the experiment can be calculated by estimating its volume. For example, a muffle pot with the internal dimensions of $\Phi 1400 \times 1800$ mm is used for spheroidising annealing of 2000 kg of high-carbon-chromium bearing steel wire rod, the volumes of the muffle pot and the steel wire rod are 2796 and 256 L, respectively. The residual volume in the muffle pot is occupied by air, and therefore the volume of $O_2$ in the sealed air is 528 L, and $O_2$ mole number is 23·6 mol. In fact, the sealing method used in the production and this experiment cannot keep a very high positive pressure in the muffle pot during heating, and some of air sealed in the muffle pot will escape during heating. Charcoal weighing 0·57 kg is needed to consume $O_2$ sealed in the muffle pot, without accounting for the $O_2$ loss during heating. In commercial production, about 1·5 kg of charcoal is placed in the muffle pot in order to make sure that there is enough charcoal.

In this paper, the volume of the mini-muffle pot is $169.6 \times 10^{-3}$ L, and the volume of the specimen is $2 \times 10^{-3}$ L. Therefore, the volume of air sealed in the muffle pot is $167.6 \times 10^{-3}$ L, the volume of $O_2$ is $35.2 \times 10^{-3}$ L and the mole number of $O_2$ is $1.6 \times 10^{-3}$ mol at 25°C. The calculated consumption of charcoal is 0·4 g, without accounting for $O_2$ loss during heating. To ensure charcoal protective effects, the weight of charcoal used in the experiments was 3 g.

### Oxidation and decarburisation

Three groups of experiments yielded almost the same results, with a minimal scatter between the groups. The thickness of the oxide layer and the fully decarburised layer for different annealing conditions are shown in Table 1.

There is neither oxidation, nor decarburisation on the surface of the specimen annealed under the contact charcoal protection. The thickness of the oxide layer of the specimen annealed in air is 15 μm higher than that of the specimen annealed in the muffle pot without charcoal protection, but there is no difference in the thickness of the decarburised layers between the two specimens.

Compared with the non-contact charcoal protection, the specimen in the muffle pot without charcoal protection was seriously oxidised, but with only slight decarburisation. Based on the macroscopic and microscopic observation, its oxide and decarburised layers can be divided into four layers of the following sequence from the surface to the inside: the incompact and caducous oxide layer with an average thickness of 123 μm, the combinative oxide layer with a thickness of only a few micrometres (was taken as 0 μm in Table 1 because of its small thickness), the fully decarburised layer (ferrite) with an average thickness of 75 μm, and the semi-decarburised layer (ferrite/pearlite mixed layer) with an average thickness of 65 μm. The total thickness of the oxide layer and the fully decarburised layer is about 198 μm. However, the specimen with the non-contact charcoal protection exhibited slight oxidation, but very serious decarburisation. The incompact and caducous oxide layer was not found on the specimen surface, and the combinative oxide coating was only a few micrometres thick (also ignored in this paper). The fully decarburised layer is very thick, about 225 μm.

Among all the decarburised specimens, the thickness of the semi-decarburised layers is approximately the

**Table 1 Thickness of oxide layer and fully decarburised layer for different annealing conditions (average of three groups)**

| | Thickness/μm | | |
| --- | --- | --- | --- |
| Annealing conditions | Oxide layer | Fully decarburised layer | Combined |
| Contact charcoal protection | 0 | 0 | 0 |
| Non-contact charcoal protection | 0 | 225 | 225 |
| No charcoal protection | 123 | 75 | 198 |
| In ambient air | 138 | 75 | 213 |
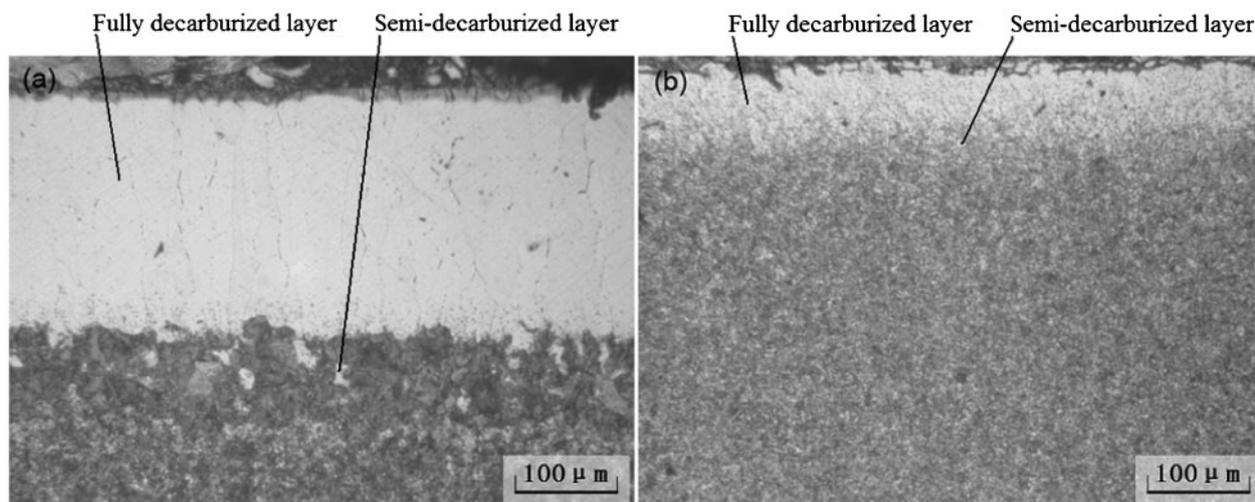
1 **Cross-sectional optical micrographs of decarburised layer of specimens annealed in muffle pots *a* with non-contact charcoal protection and *b* without charcoal protection**

same. The total thickness of the oxide layer and the fully decarburised layer of the specimen with the non-contact charcoal protection is obviously thicker than that of the specimen annealed in the muffle pot without charcoal protection. Figure 1 shows optical images of the decarburised layers of the specimens annealed in the muffle pots with the non-contact charcoal protection (Fig. 1a), and without charcoal protection (Fig. 1b), respectively. The non-contact charcoal protection is very efficient in oxidation prevention, but is useless to prevent decarburisation.

Figure 2 shows a version of an Ellingham diagram.[6] $\Delta G$ is standard Gibbs free energy change and equals to $RT\ln Po_2$, where $R$ is the gas constant, $T$ is the absolute temperature, and $Po_2$ is the equilibrium oxygen partial pressure. According to Fig. 2, at 570°C the standard Gibbs free energy change of the chemical reaction $(3/2)Fe+O_2=(1/2)Fe_3O_4$ is roughly equal to that of the chemical reaction $2Fe+O_2=2FeO$. When temperature is below 570°C, the main iron oxide is $Fe_3O_4$; when temperature is above 570°C, the main iron oxide is FeO. The standard Gibbs free energy change $\Delta G$ for $2Fe+O_2=2FeO$ is determined as $-386$ kJ mol$(O_2)^{-1}$ (per mole $O_2$) at 790°C, and the corresponding equilibrium oxygen partial pressure $Po_2$ is $1\cdot1\times10^{-19}$. In addition, the standard Gibbs free energy change $\Delta G$ of $2C+O_2=2CO$ is determined as $-409$ kJ mol$(O_2)^{-1}$ at 790°C, and the corresponding equilibrium oxygen partial pressure $Po_2$ is $7\cdot8\times10^{-21}$. Therefore, if the oxygen partial pressure is below $1\cdot1\times10^{-19}$, the oxidation will not occur, and if the oxygen partial pressure is below $7\cdot8\times10^{-21}$, the decarburisation will not occur.

The specimens annealed in air, or in a sealed pot, without the charcoal protection, have sufficient oxygen supply, and oxygen partial pressure is much higher than the equilibrium oxygen partial pressure of FeO and CO. Thus, oxidation and decarburisation can be simultaneously carried out on the surface. On the surface, the oxidation rate is lower than the decarburisation rate. (If the oxidation rate was higher than the decarburisation rate, decarburised layer would not exist.) As mentioned earlier, the decarburised layer is very thin because of the following reasons. First, the outermost decarburised layer is later oxidised, transforming into the oxide layer.

Second, the contact of oxygen with carbon is blocked with the increasing oxide layer thickness. Therefore, the oxide layer takes up a great portion of the total thickness of the oxide and the fully decarburised layers. The proportions of the oxide layer are about 62% in ambient air and 65% in a sealed pot.

Under the charcoal contact protection, since the specimen is buried in the charcoal powder, oxygen cannot directly contact the specimen surface, and oxygen is completely consumed when it passes through the charcoal powder. Therefore, metal oxidation and decarburisation do not happen under this condition.

Under the non-contact charcoal protection, most of oxygen is consumed by charcoal. The average oxygen partial pressure is very low, but the atmosphere uniformity in the muffle pot is poor. Oxygen partial pressure near the specimen is higher than near charcoal. Although the muffle pot containing the specimen was placed into the furnace at 790°C, it took some time to raise the specimen's temperature up to 790°C. During the temperature elevating process the reaction rate between charcoal and oxygen is low due to the low temperature and the oxygen partial pressure near the specimen is high, therefore oxidation and decarburisation can happen simultaneously. Moreover, the oxidation occurs more easily when the temperature is below 700°C. During soaking at 790°C, charcoal burns and consumes a large amount of the oxygen, so the oxygen partial pressure near the charcoal reaches the equilibrium oxygen partial pressure of $7\cdot8\times10^{-21}$ of the chemical reaction $2C+O_2=2CO$. However, because the atmosphere in the muffle pot is inhomogeneous, which can be inferred from the experimental results, then the oxygen partial pressure near the specimen ought to be higher than $7\cdot8\times10^{-21}$, and lower than $1\cdot1\times10^{-19}$, therefore oxidation stops, and decarburisation continues to happen. Therefore oxidation is low, but decarburisation is significantly increased under the non-contact charcoal protection.

## Appropriate annealing process

For the high-carbon-chromium bearing steel, it is uneconomic to employ contact charcoal protection. Our results indicate that the decarburised layer of the
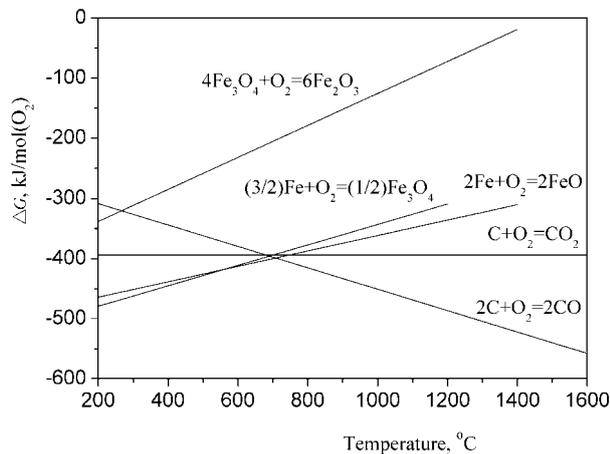
**2 Ellingham diagram[6]**

specimen annealed with the non-contact charcoal protection is thicker than of the specimens annealed in the muffle pot without charcoal protection, or in air. Annealed high-carbon-chromium bearing steel workpieces often require no decarburisation, or slight decarburisation, before entering into the next operation. In commercial production, the outmost incompact and caducous oxide layer, which accounts for 95% of the oxide layers total thickness, is easily removed by knocking, while the inner combinative oxide and the decarburised layers are removed by acid pickling. Without protection, the thick incompact and caducous oxide layer can be removed by knocking, and the decarburised layer is thin. This means less acid consumption is required, and the size reduction of the workpieces becomes less. Therefore, compared with the annealing process under the non-contact protection, the annealing process without protection can save tons of charcoal and acid in commercial production.

Because there are no significant differences in the thicknesses of the oxide and the decarburised layers between the specimens annealed in a sealed pot without the charcoal protection, or in air, if the controlled atmosphere furnace is unavailable, the bearing steel ought to be directly annealed in air. In this way charcoal and the heat-resistant steel pots are not needed and the

acid can be saved, so that energy consumption is reduced and the environment is better protected, and subsequently immense economic benefits for the industry may be achieved.

## Conclusions

The non-contact charcoal protection during spheroidising reduces oxidation remarkably, but increases significantly decarburisation compared with annealed in ambient air. The total thickness of the oxide and the decarburised layers of the specimen annealed in a sealed pot with the non-contact charcoal protection is higher than that of the specimens annealed in air and in the sealed pot without the charcoal protection. The specimens annealed in air or in a sealed pot without the charcoal protection have almost the same total thicknesses of the oxide and the decarburised layers.

This work suggests that, if the controlled atmosphere furnace is unavailable, the bearing steel ought to be directly annealed in ambient air to achieve immense economic and environmental benefits in commercial production.

## Acknowledgements

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