SURFACE OXIDATION AS A WAY OF INTENSIFY OF COATING Fe-C ALLOYS WITH COPPER

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Abstract
The paper concerns effects obtained as the result of cast iron coating with copper using different methods. Authors studied the influence of the high-temperature oxidation, as the preliminary stage previous to coating with copper on the change of surface layer structure as well as subsurface layer of cast iron with flake graphite. Received effects were compared to these obtained during cast iron coating in liquid copper without preliminary thermal processing, as well as coating with copper during turning. As the consequence of conducted high-temperature oxidation in subsurface layer of cast iron pores have been created, that in result of coating in liquid copper were filled with new phase and in this way the new zone with different properties was obtained. It was additionally stated that the cast iron layer enriched in copper is considerably thicker than layers got with application of other methods.

1. INTRODUCTION
The investigations of high-temperature corrosive resistance of cast iron have been led for tens years and they concern different aspects of this problem. The presented in literature results usually describe the structure of cast iron scale layer or analyze the influence of different factors (the chemical composition of cast iron, shape of graphite, etc.) on oxidation mechanism [1-6]. The investigation of different grades of cast iron: with flake graphite, white, nodular and ductile showed that the oxidation kinetics and the scale layer morphology depend closely on size and distribution of flake graphite. With temperature increasing the process of oxidation accelerate, the scale layer porosity enlarges and the scale layer adhesiveness to metal core gets smaller [5].

It in present work authors decided to look at the high-temperature oxidation process from the point of view its influence on effects got during cast iron coating with copper.

As the result of copperizing some usable properties of iron alloys decrease [7]. From the other side the copper layer, even if it is not too thick - from 5 to 20 µm, makes more easy of next layers coating (chromium or nickel) [8]. Moreover, the coated layer of copper enlarges the corrosion resistance of Fe-C alloys in acid medium about thousands percentage.

The aim of cast iron coating with copper is mainly the enlargement of adhesiveness and lifetime of nickel or chromic coats. The layer of copper can sometimes be applied as self-contain coat in case of imitation of copper alloys [9].

Introducing the new material into the pores' place created as the result of high temperature oxidation in surface layer of cast iron may lead to: enlargement of thickness of subsurface cast iron layer enriched in copper; obtaining composite surface layer with specific proprieties without necessity of expensive gear application.
The aim of begun investigations is to practical verify and confirm the mechanism of oxidation of cast iron containing the different graphite shape: flake, coral, vermicular and nodular as well as evaluation of the influence of high-temperature processing on following additional treatment, i.e. copperizing.

2. METHOD OF INVESTIGATION

During the investigations cast iron with flake graphite melted in induction furnace of medium frequency was applied (3,3% C; 1,7% Si; 0,5% Mn; 0,06% P; 0,06% S). Liquid metal was cast to sand mould with dimensions φ30x300mm. From such cast rolls from their bottom part samples were turned φ=11-19mm and length l=110-200mm. Samples were oxidized in silite furnace PKS 600/25. The experiment was led in five different temperatures - 850, 900, 950, 1000 and 1050°C. Samples have been taken out from the furnace separately after: 4, 6, 8, 10 and 12 hours. After cooling dawn samples were exactly measured, weighed, and metallographic specimens were prepared to observe surface perpendicular to sample’s axis.

The scale layer was removed in two stage procedure: mechanically by sandblasting as well as chemically by dipping in solution of oxalic acid. After scale layer removal the copperizing in liquid copper with temperature 1100°C has carried out, in crucible with capacity 70 kg. Samples were kept in liquid metal from 2 up to 25s. The plunged part of samples was about 70% the total length. Samples appearance after coating with copper is presented at Fig. 1.

Fig. 1. The view of samples after copperizing in time 2-25 s - the surface of samples (upper - the time of copperizing 20s, bottom - the time of copperizing 10s).

To optical observation microscope "NEOPHOT 2" as well as “Axiovert A -100” were applied, whereas further examination was made with application of scanning microscope “Jeol J 7” and X-ray analyzer “JCA – JEOL”. The sample’s surface quality was described additionally by roughness measurements made after scale layer removal.

3. RESULTS OF INVESTIGATIONS AND THEIR ANALYSIS

The thickness of copper layer created on surface of cast-iron samples grows with increasing of immersing time in liquid copper. In case of short times holding < 10s, the produced surface layer characterizes with large smoothness. For time longer than 10s holding, surface of coated layer is non-uniform and shows numerous emptinesses and niche.
As the copperizing effect in case of samples from grey cast iron not subjected the preliminary high-temperature oxidation, after longer time of holding (t > 20s), the subsurface ferritic layer was observed followed from the heat treatment to which samples were subjected.

The obtained results were compared to effects of copperizing of cast iron samples not subjected oxidation as well as the effects of coating with copper the cast iron during turning [9]. For every copperizing method the measurement of concentration change N(Cu) and the N(Fe) in surface layer of samples has been conducted.

As the result of copperizing during turning the layer with thickness 1µm has been created, that has partly diffusive character. The essential meaning has here the fact that coating is executed directly in moment of uncovering very clean surface. Additionally this operation is combined with relatively high temperature (ab. 800 °C) existing in place of turning tool contact with sample surface.

In the case of short time coating with copper in liquid bath (t = 2s) the evaluation of reciprocal enriching Cu⇔Fe was no possible. Starting from copperizing time t=4s the mutual penetration Cu⇔Fe was stated. At the Fig. 2 results of Cu and Fe concentration measurements are presented with reference to sample copperized within 10s. The asymmetry of concentration curves at the Cu/Fe surface (x = 0) proves, that during this kind of copperizing except Cu and Fe diffusion samples dissolving in copper bath is also running. The dissolved part of samples is replenished the similar quantity of Cu.

The copperizing effect of cast iron that was subjected previously to high-temperature oxidation differs from results obtained without such processing. The cast iron oxidation causes except scale layer growth (scale layer is removed by sandblasting and chemical etching) the formation in cast iron subsurface zone without graphite which thickness achieves even 1,6 mm. So, the observed cast iron structure can be generally divided on three layers (scale layer, porous layer, core structure). Also in this case we observe the metallic structure change from pearlitic to ferritic.

The thickness of porous layer increase with temperature and oxidation time increasing. To obtain more detailed information regarding the oxidation mechanism -
the graphite removal as well as the silicon influence in studied process the investigation with use of X-ray analyzer was applied.

Fig. 3. The RTG analyses; the analyzed structure with line of measurement; b – results of analyses.

At Fig. 3. the linear qualitative analysis of subsurface layer for six basic elements (C, O₂, Si, Cr, Mn, Fe) is presented. Visible is, that although graphite precipitations became almost completely removed some graphite remainders exist in formed niches. The silicon content is significantly higher at interfacial surface graphite – metallic matrix and probably SiO₂ layer is created there which prevents the more far corrosion of metal matrix. The mechanism of pores creation in cast iron with flake graphite together with coating effect with copper is presented at Fig. 4 [11].

Fig. 4. Mechanism of oxidation and copperizing of cast iron with flake graphite: a - the appearance of subsurface layer, magn. x100; b – the drawing of preliminary oxidation process as well as the copperizing [10].

The copperizing of samples where the scale layer was removed leads to existing pores' fulfillment with new phaze enriched in copper. Depth of this zone depends on pores' size, time and temperature coating and it can get up to tens micrometers. The schematic and real effect of oxidation process of cast iron with following coating with copper is presented at Fig 4. At Fig. 2 the concentration distribution N(Cu) and N(Fe) in subsurface layer after copperizing without oxidation is presented, on the chart the change of copper concentration in cast iron got after coating with copper within 10s with previous oxidation was plotted.
4. CONCLUSIONS
1. As a result of high-temperature oxidation of cast iron previous to the copperizing the graphite participations are almost completely removed, however inside the formed niches some graphite remainders left. The silicon content is essentially higher at interfacial surface: graphite – metallic matrix and probably SiO₂ layer is created there which prevents the more far corrosion of metal matrix.

2. Layer of copper created on samples surface as the result the copperizing in liquid copper has typically diffusive character. Thickness of the layer obtained in this way is a dozen or so time higher then layer thickness resulting from copperizing during turning.

3. Time of copperizing in liquid copper should be individually chosen in dependence on parameters describing every sample (dimensions, mass, wall thickness). The overcrossing the optimum time of copperizing causes, that the obtained Cu layer is not smooth and contains the numerous emptinesses and the cavities, the surface of Fe-C alloy shows high differentiation. The shorter time of coating decrease thickness of received diffusive layer and in effect decrease awaited usage proprieties. In case of studied samples with dimensions φ = 19, l = 200 mm the optimum time of coating is 10s.

4. The application of high-temperature oxidation before cast iron copperizing makes possible the producing the new cast iron layer - consisting from "after - graphite" pores fulfilled with phaze enriched in copper with thickness about 35µm. It was stated additionally, that such treatment intensifies the copperizing effect. The recorded Cu concentration distribution in cast iron shows except considerably higher copper contents also higher thickness of subsurface layer enriched in this element.

5. The presented methods of copperizing can be applied with success to production the protective layers on iron carbon alloys.
Literature