’Contiblu‘ - a new process for continuous steam treatment.

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1 Abstract

The steam treating furnace ’Contiblu‘ offers continuous operation without the need for a boiler. Burning natural gas or propane generates carbon dioxide and steam - this protective atmosphere is directly used for oxidizing the PM parts.

’Contiblu‘ process is a multifunctional gas heating system which couples protective gas generation, afterburning of flue gases and furnace heating. This results in a very low energy consumption and an enormous cost benefit for the PM customer. In this furnace design unburnt hydrocarbons (oil and emulsion residues) are afterburnt in the furnace with the resulting heat being used for furnace heating. Exhaust gases do not need to be scrubbed. The process is completly PC controlled and network logged.

2 The Process and the Theory

The process of providing ferrous materials with a blue, rust-protecting iron oxide layer was proposed as early as 1877 by F.S. Barff in the USA.

In contrast to solid iron parts such as sheets, drills etc. the steam-treatment of sintered iron parts changes during this procedure not only the surface but also the structure of the parts in a remarkable way. Steamed or blued sintered iron parts achieve greater hardness, become more resistant to mechanical wear and receive an anti-corrosive coat.

2.1 The chemical process

The chemical process of iron blueing in the presence of water vapour runs above 300°C according to the following reaction:

$$3Fe + 4H_2O \rightarrow Fe_3O_4 + 4H_2, \quad \Delta_r H = -151.12 kJ/kg \text{ (exothermic reaction)} \qquad \text{(R1)}$$

In order to accelerate the conversion process during the steam treatment, furnace temperatures between 450°C and 570°C are applied.

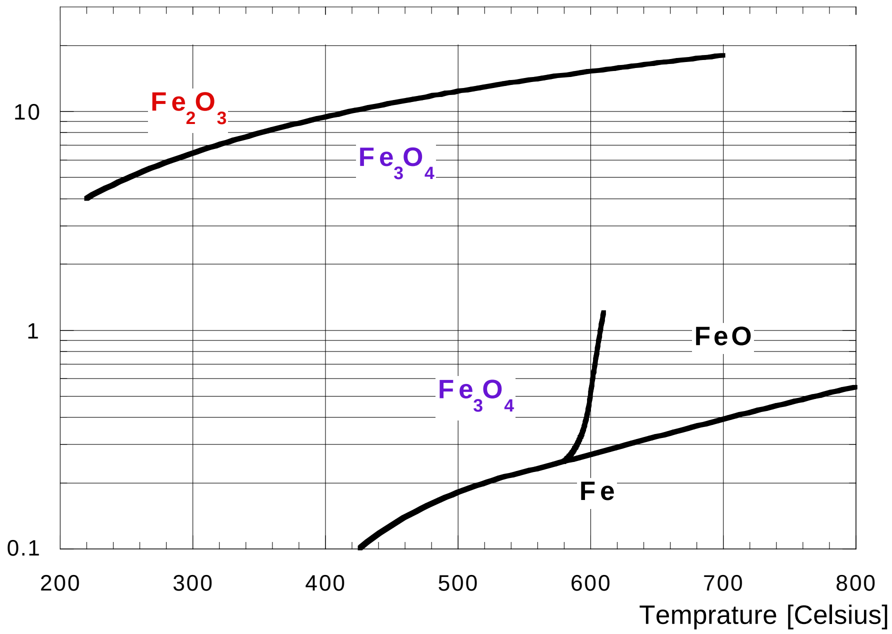

fig 1: Fe_3O_4 formation as a function of the critical variables H_2O/H_2 ratio and temperature.

The actual characteristic of the steam treatment process consists of the fact that the reaction not only takes place on the surface of the sintered parts but also within the pore spaces of the part in as far as these are connected with the external surface of the sintered parts with porous passages.

The Fe_3O_4 depicted is very dense and hard and adheres securely to the iron framework of the PM parts. It is characterised by good resistance to corrosion and achieves a layer thickness of up to 0.006 mm. A layer thickness beyond this is no longer possible because the blue iron oxide then allows no more water vapour to penetrate.

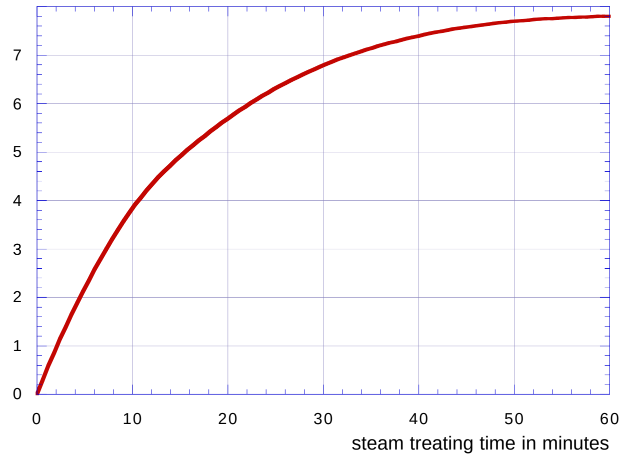

fig 2: Fe_3O_4 formation [in % weight gain] as a function of reaction time.

The H_2O/H_2 ratio and the temperature are the critical variables for the desired reaction. In the case of solid parts (e.g. transformer sheets) the maximum oxide layer thickness is formed as quickly as thirty minutes under the reaction conditions.

In the case of the treatment of porous sintered iron parts, a much longer treatment time must be reckoned with. On the one hand, this depends on the diffusion direction of the oxidising gas in the pore framework, on the other, on the direction of the opposed diffusion of the hydrogen formed during the reaction.

Diagrams which describe the increase in weight as a consequence of the oxide formation in dependence on the reaction time (diagr. Regel) give us information on the reaction time on porous PM parts. The reaction time correlates directly with the conveyor speed in the case of the continuous furnace.

After a reaction time of 10 minutes already 50% of the oxide formation possible in the PM part has been achieved. However, at least 60 minutes are necessary in order to achieve the maximum possible weight increase of approximately 8 %. Within this period the lowest layers of the PM part have also been involved in the reaction.

Delays in reaction due to transport should be taken into consideration during steam treatment of PM parts just to be on the safe side. Typical treatment times in continual steam furnaces are around two hours for this reason.

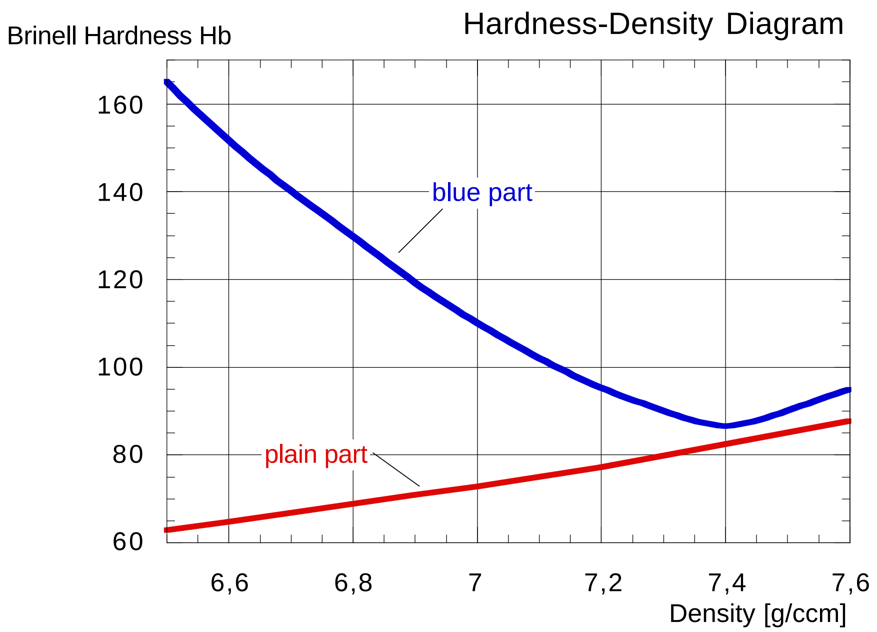

fig 3: Hardness of non treated PM part and steam-treated PM part is a function of its density.

2.2 Alteration of the material characteristics

In order to make clear the influence of the oxide amount taken up in the sintered structure on the material characteristics, the following diagrams showing the dependence of hardness, tensile strength and elongation on the density were compiled.

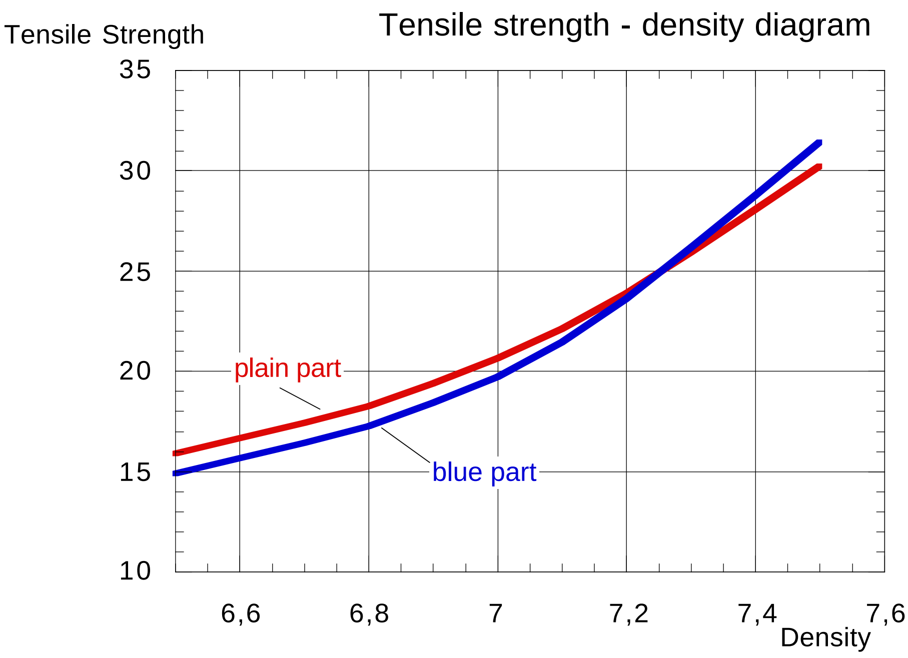

fig 4: Tensile strength of non treated and steam treated PM part as a function of density.

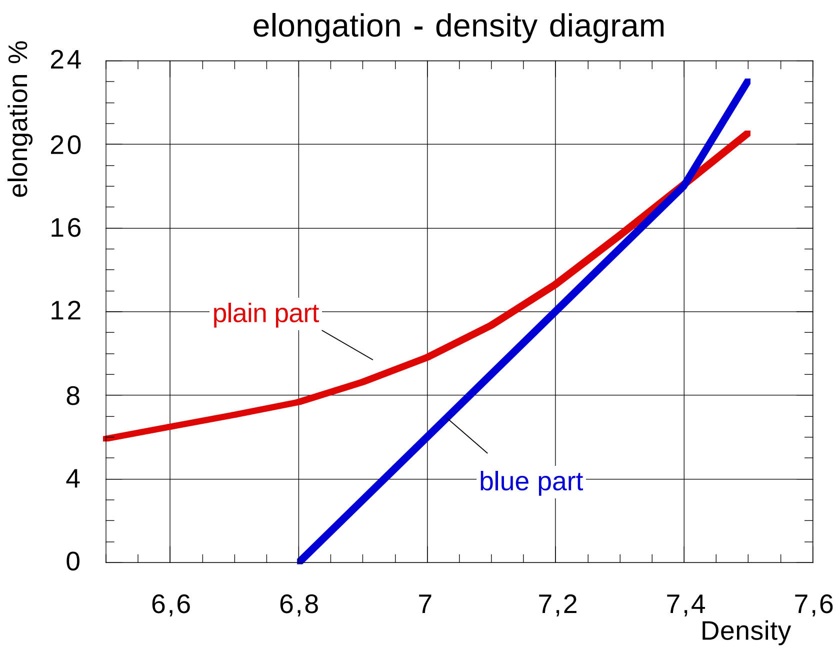

fig 5: Elongation of non treated and steam treated PM part as a function of density.

The decrease in density is a measure of the greater porosity within the sintered part. On the curves returned, the fact is remarkable that in the case of increasing porosity, i.e. decreasing density, the hardness of the parts increases in a surprising way after steam treatment, while the tensile strength is not altered in any significant way by the steam treatment.

The rule of thumb of F.W. Regel is valid: ”for one part with a density of 6.7 g/ccm the hardness is doubled by steam treatment.”

2.3 Practical execution of steam treatment in the Contiblu steam furnace.

The Contiblu furnace consists of a horizontal, gas-tight reaction space with a multi-functional gas heating and a modular-design air cooling area.

The PM parts are placed on the belt of the conveyor furnace and they run through a temperature and atmospheric profile in a gas-tight muffle.

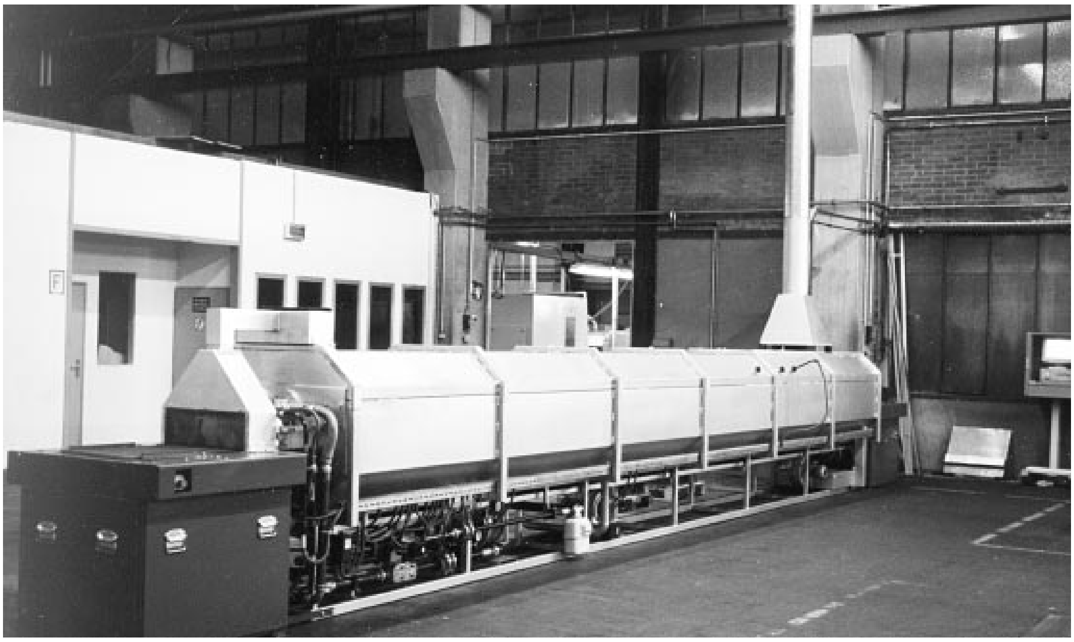

fig 6: Picture of Contiblu steam-treating furnace.

In the first step the parts are heated up to a temperature at which any remaining oil or emulsion is evaporated.Thus parts soaked or retreated in oil or emulsions can be blued just as easily as bare, dry sintered parts.

The sintered parts, now bare, are heated up to the reaction temperature of approximately 570°C and are surrounded by the oxidising reactive-gas-atmosphere.

During this process the oxygen bound in the water vapour reacts at the iron to Fe_3O_4 forming hydrogen. The oxidising effect of CO_2 is to a great extent still negligible at these temperatures. The oil vapours occurring as well as the hydrogen formed are extracted together with part of the protective gas from the muffle and are burnt in the furnace. The heat released is used for helping to heat the furnace.

The process described above hardly differs from conventional steam treatment processes. Only the oil and emulsion remnants and, most of all, the hydrogen formed are exploited thermally.

The generation of the protective gas or the provision of the steam is, however, different in the Contiblu process. During the complete combustion of hydrocarbons, water vapour and carbon dioxide are formed:

e.g. complete oxidation of methane with air.

$$CH_4 + 2O_2 + 2(0.79/0.21)N_2 \longrightarrow CO_2 + 2H_2O + 2(0.79/0.21)N_2 \qquad (R2)$$

It is precisely this reaction that takes place in the protective gas burner of the Contiblu furnace. The water vapour formed is led together with the CO_2 and N_2 into the muffle and then flows around the PM parts. In this way the Contiblu furnace can do without boilers, water pipes and afterburner chambers. Calcium deposits in the boiler and pipelines are thus no longer a problem. The great advantage of the protective gas / water vapour generation in the furnace by burning natural gas or propane is the great energy efficiency of the process.

Thus the burners in the Contiblu furnace serve the function of protective gas generation (water vapour generation) and burning of residual oil and hydrogen alongside heating the furnace.

3 Economic point of view

As we are furnace designers, we are naturally interested to improve the efficiency of furnace processes. To know how much water vapour and energy is required for steam-treating iron PM-parts let´s look at the balance of substances and the balance of energy around the Conti-blu-furnace:

3.1 How much water vapour is required?

Basis: 100kg/h Fe with a chemical turnover of 5% = **89.52 mol Fe**

Reaction: $3Fe + 4H_2O \longrightarrow Fe_3O_4 + 4H_2$ (R1)

=**119.36mol H_2O**

To generate this amount of 119.36mol H_2O we burn natural gas. (here we calculate with methane, as the main component of natural gas).

Reaction: $CH_4 + 2O_2 + 2(0.79/0.21)N_2 \longrightarrow CO_2 + 2H_2O + 2(0.79/0.21)N_2$ (R2)

= 59.68mol CH_4

In other words 1.33 m^3/h methane are needed for generating the reqiured amount of water vapour.

3.2 How much energy is required?

Heating up the parts needs about **8.8kW**, with an estimated heat loss at the furance walls and belt of appr. **5kW**.

3.2.1 How much energy is generated by the exothermic reaction (R1), by burning hydrogen and the reaction gas (R2)?

We can see that the reaction R1 is exothermic with a reaction enthalpy of :

$\Delta_r H_{R1}$ = -1118.4 kJ/mol - 4(-241.82)kJ/mol = -151.12 kJ/mol

Calculating with the basis of 100kg/h Fe input and the mentioned turnover of 5%, this means that **1.24kW** are generated by the exothermic reaction.

The produced hydrogen can be burnt also. The chemically bound energy of the generated hydrogen again will contribute with **8.01kW**

Burning methane not only generates the desired water vapour but also energy, which can be used for heating: 1.3m3/h —> **13kW**.

This means this process has an energy surplus of about **10kW**!

The exhaust gases to be extracted are completely combusted, basically therefore CO_2, H_2O

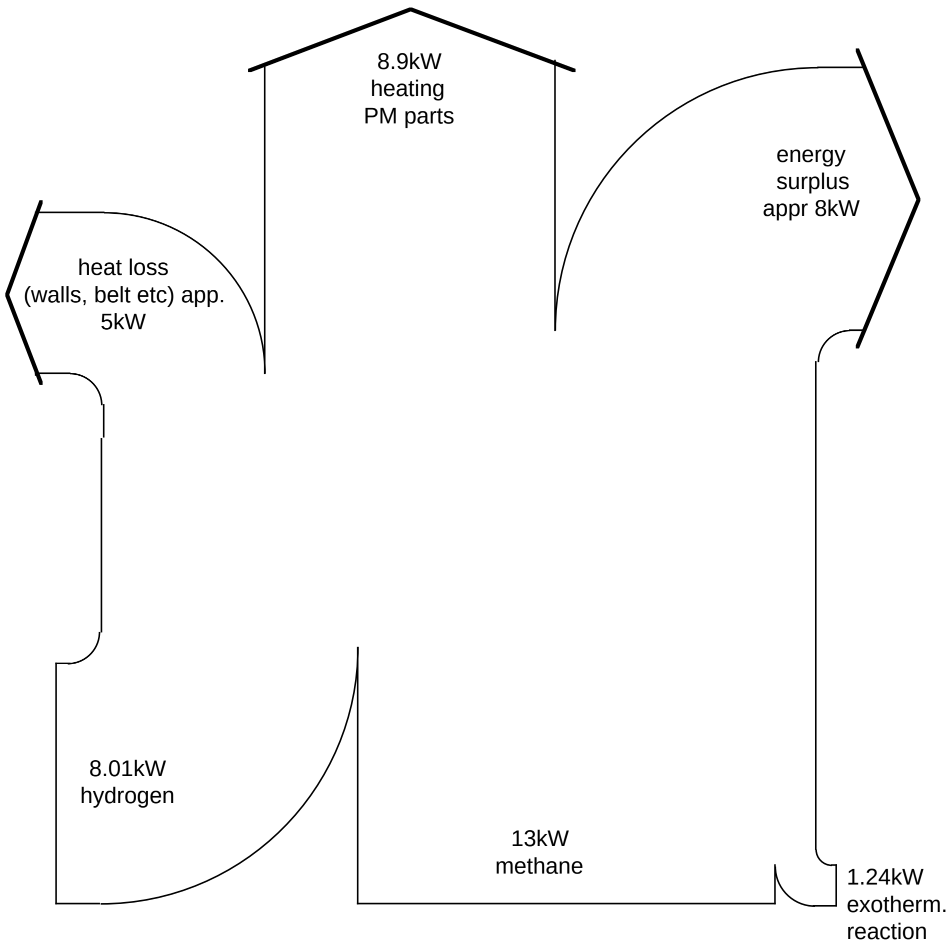

fig 4: Schematic overview where "energy comes and goes to" inside the Contiblu-furnace.

and N_2.We calculate in the following with typical natural gas prices of $1.80 - $7.0 per 1000 cubic feet (this corresponds to 6.5 cents to 25 cents per m^3 natural gas). In comparison to a conventional, continual steam furnace which is electrically heated (35 kW) and requires an external water boiler (30kW) - and specific electr. costs of 2.5 - 9 cents/kWh the Contiblu process makes savings of up to **$35000** per annum possible (at 6000 operating hours).

4 Summary

The combination of integrated protective gas generation, exhaust gas postburning and furnace heating make it possible to continually blue iron sintered parts very economically and with a consistent high quality. Increase in hardness, thickness of layer of the PM parts steamed by the Contblu are in no way of lesser quality than the best results of conventional steam furnaces with much longer treatment times.

All settings of the Contiblu furnace are PC controlled and extensively automated. A data base connection is matter of course just as data acquisition to ISO 9000ff standard. The plant can thus be operated easily even by inexperienced furnace staff.

Thanks to its simple design, its economy with regard to purchase price and maintenance, low environmental impact and, last but not least, its simple operation with best results, the continual steam furnace is an interesting alternative which will, perhaps, make the steam treatment of PM parts more common in the future.

5 Literature:

1. Regel F.W.: Grundlagen der Dampfbehandlung von Metallen, Härtereitechn. Mitteilungen 18

2. v, Lenel, F.: Porous Iron Article and Method of Making sames, US Patentschrift 2187589

3.Freier, R. und H. Kickenberg: Betrachtungen zum Fe_3O_4 - H_2O - H_2 System des Dampfkes-sels, Mitt. des VDB H.50, 1974

4. Regel F.W.: Die Anwendung des Dampfbehandlungsverfahrens bei gesinterten Eisenteilen, Mannesmann-Pulvermetalurgie, Mönchengladbach., 1965

5. Bocchini G.F., Gallo A., Montevecchi I.: Il trattamento in atmosfera di vapore di particolari in acciaio sinterizzato, La Metallurgia Italiana, 1983

6. Sarnes R.: Verfahren zum Oxidieren von Sintereisenteilen, Deutsche Patentschrift DE 3614444 C2, !986