Technical press

Oxidation Protection for Metals and Alloys

The best protective and reaction gas for every application

Under the brand name Neutrotherm®, the Messer Group is a distributor of inert gases low in hydrogen, with which e.g. iron, copper and aluminium alloys can be protected against oxidation during heat treatment. Hydrogen-rich gas mixtures, which have proven themselves as a protective and reaction gas in the case of chrome alloys for instance, are distributed under the Messer brand name Hydrotherm®.

Hydrogen brings brightness and cleanliness.

It is the nature of things: if metal is heated until it glows, it reacts with oxygen and oxidises. Initially, only the unwelcome oxide layer is apparent; the drop in quality of the material usually only becomes clear at a later point in time. In order to prevent oxygen from the air being carried into the furnace and reaching the batch material, the metallurgic heat treatment, i.e. the phase in which the required properties are practically burnt into the metal, takes place under an atmosphere of protective gas. In some cases, it is sufficient to use nitrogen (N_2) as the inert gas to prevent oxidation of the metal surface. However, depending on the alloy and the properties required, a reactive gas is additionally needed which is then dosed into the furnace - gas which is diluted with nitrogen or, depending on the application, also with argon.

Perfect protection against oxidation thanks to hydrogen (H_2)

In the field of metallurgy, hydrogen has proven itself to be an ideal reducing agent. It is used,

- to anneal stainless steel without oxidation,
- for the re-crystallisation of heat-resistant special steels,
- for cleaning surfaces of metal by removing carbon residues,
- for annealing non-ferrous alloys such as copper, bronze, nickel silver or brass,
- for increasing the cooling performance of continuous annealing furnaces (in conjunction with liquid nitrogen),
- in high convection bell-type furnaces,
- for sintering moulded components of iron and (non-ferrous) powders,
- for the reduction of metal oxides, such as tungsten oxide, as well as
- for the blank annealing of hardened steels after hardening.

The Messer Group provides its customers with N_2/H_2 mixtures in two fundamentally different concentrations for every application requirement:

- Collected together under the trade name Neutrotherm® are "low hydrogen“ mixtures with up to four percent by volume of hydrogen, which are suitable primarily as protective gases in the heat treatment of iron, copper or aluminium alloys. The mixtures can be used safely at temperatures below 750 °C; they are not explosive at room temperature either.
- The trade name Hydrotherm® stands for gas mixtures which can contain up to 100 percent hydrogen and are suitable as protective and reaction gases for chrome-rich alloys (heat treatment up to 1150 °C), and for avoiding an unwelcome oxide layer on the surface of the material, also at extremely high temperatures.

Although the methods of heat treatment are similar in many respects, they cannot be reduced to a common denominator. On a case by case basis, specifics have to be taken into account which, for instance, make it necessary to modify the composition of the protective and reaction gas mixture. Of general importance is the principle that, in metallurgy, a multitude of applications exist which depend on the use of hydrogen - with or without reduction of oxides.

Examples of Application from Industrial Use

Annealing chromium-rich and scale-resistant steels

After cold rolling, rust-resistant steel strip 1.4301 (X5CrNi18 10) is continuously treated in a bright annealing furnace until re-crystallization; after cooling to room temperature, it should be completely bright when leaving the plant. The smallest change in the prevailing atmosphere in the furnace could however lead to the initiation of the chromium-oxidation process. A dew point of around minus 25 °C, corresponding to 0.063 percent by volume of water (H_2O), and a furnace temperature of 1050 °C, causes an alloy of 18 percent by weight chromium to oxidise. The equation of this reaction is:

$$2\,Cr + 3\,H_2O \leftrightarrow Cr_2O_3 + 3\,H_2 \qquad (1)$$

The resulting oxide layer can vary in colour, depending on the temperature and time spent in the furnace (see Fig. 1). With a shift from yellow-red to blue-green, the thickness of the layer increases; the higher the temperature and the longer the time spent in the furnace, the thicker the oxide layer.

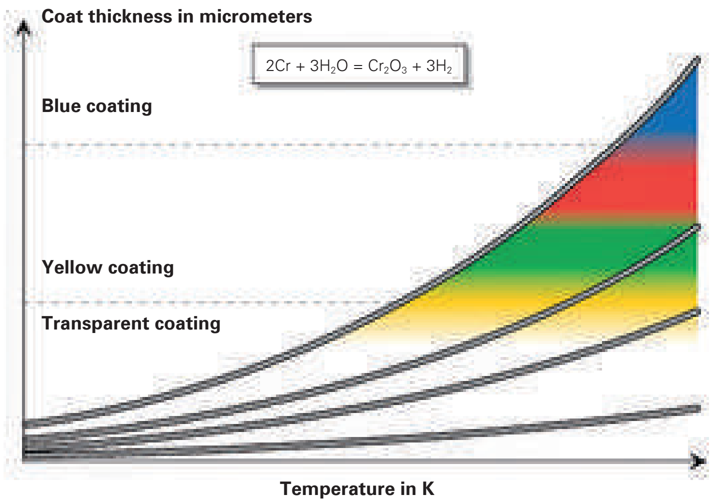

Figure 1: Kinetics of the formation of chromium oxide of an alloy with 20% chromium content.

The diagram shows the thickness of the oxide layer to be expected at different temperatures and oxidation times. Depending on the thickness of the oxide layer, various annealing colours form. Under 0.03 µm, which corresponds to 300 Ångström (1Å = $1*10^{-10}$ m), the very lightly-oxidised surfaces still appear to have a metallic brightness.

Discolouration - the oxidation of the surface of the metal - can be prevented by using pure hydrogen and a dew point of -50 °C and below, which equates to 0.004 percent by volume of water in the atmosphere of the hot furnace. Consequently, not only is the steady state of the water content in the furnace atmosphere responsible for the absolute "brightness" of the surface, but also the conditions under which the steel cools down. In order to prevent the formation of chromium oxide during the entire duration of heat treatment, the humidity in the furnace should at all times be well below the stability line. This will prevent an oxide layer from forming in the cooling phase, i.e. when temperatures decrease. If steels containing manganese, niobium and chromium as alloy elements are to be protected from oxidation, then the steady state dew point must be at -70 °C or below. In this extremely dry atmosphere, the formation of a grey or matt oxide layer on the surface of the metal will be prevented. In order to achieve this, the use of very dry technical gases is necessary.

Figure 2 helps to illustrate to what extent the moisture content must be reduced in order to prevent oxide forming in the balance phase and during the cooling of the alloy. The stability increases in the sequence manganese, niobium, chromium, titanium, silicon and aluminium, the prevention of the formation of oxide becomes more difficult. The oxidation of titanium, silicon and aluminium can generally not be prevented.

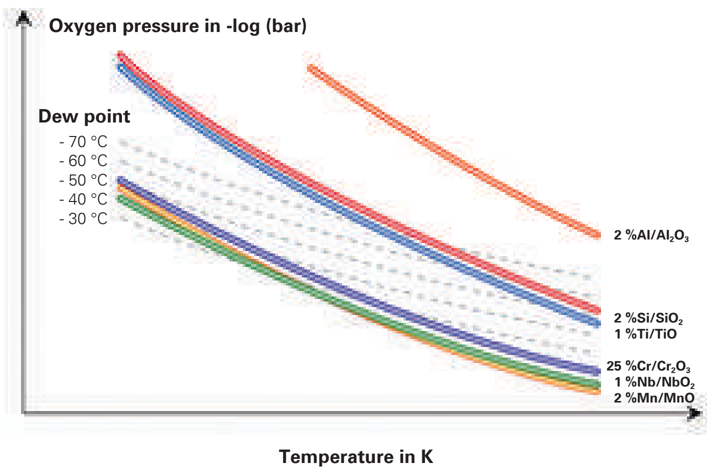

Figure 2: Oxidation limits of various steel alloys, depending on partial pressure of oxygen, dew point and temperature.

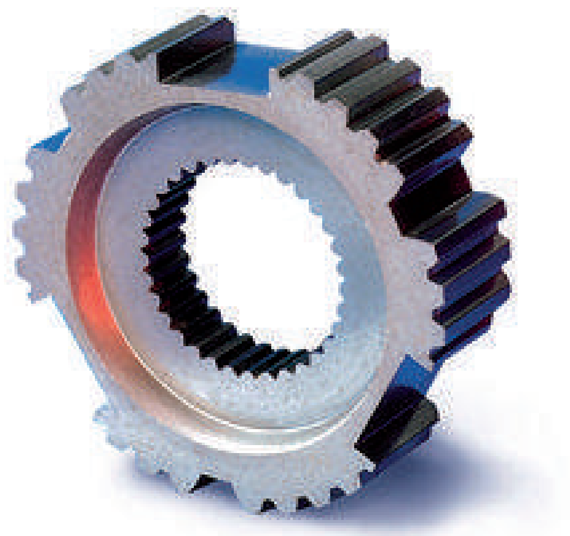

Figure 3: Sintered pressed parts

Sintering of metal powders

Pressed parts of metal powders are sintered in continuously operating furnaces. The pressed green sinter become stable and compact, provided that the atmospheric oxygen in the pores combines with hydrogen during the heating and sintering phase and the water resulting from this is removed. If the water

Figure 4: Sinthering in conveyor furnace

is removed quickly, a selective oxidation of the alloy elements such as carbon, chromium and manganese can be prevented.

Production of bi-metallic strips: Special bronze powder is applied to the steel strip, then the piece is sintered in the conveyor furnace, both layers being tightly bonded to each other.


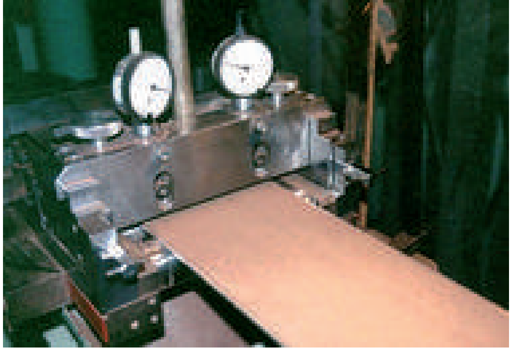


Figure 5: Sintering of bronze powder on steel strip under controlled nitrogen/hydrogen protective gas

Thanks to the use of very dry hydrogen and pure nitrogen as diluting gas, the distribution of the alloy phases produced in the course of the production of powder does not change during sintering. The phases remain intact and well mixed. The prevailing moisture content in the various areas of the sintering furnace is continuously measured in order to calculate the minimum concentration of hydrogen necessary.

Annealing of copper and copper alloys

Pure copper is a very noble metal which forms oxide only with oxygen. At temperatures of up to around 350 °C, a reddish copper oxide develops (Cu_2O), at higher temperatures black CuO.

$$4\,Cu + O_2 \leftrightarrow 2\,Cu_2O + O_2 \leftrightarrow 4\,CuO \quad (2)$$

Pure copper

The soft annealing of copper can easily be carried out using nitrogen with a small amount of hydrogen added. Usually 2 to 4 percent by volume of H_2 is sufficient to convert the atmospheric oxygen which enters the furnace into water, i.e. before copper oxide forms. It is important to ensure that when cooling the charge to below 350 °C, the metal is not oxidised by atmospheric oxygen.

Nickel silver

The soft annealing of nickel silver (copper with 20 - 30 percent by weight nickel) requires a higher hydrogen concentration in order to prevent the selective oxidation of the nickel, which is not as noble as copper. A practical instance demonstrated that atmospheric oxygen entering the continuously operating pusher furnace forms nickel oxide on the material being annealed. After the holding temperature had been reached, the oxide was reduced again by the hydrogen which was present, leading to a kind of "mirror" being formed on the alloy. The demixing of the alloy would substantially reduce the corrosion resistance of heat exchanger pipes in subsequent use.

Brass and bronze

Brass is often annealed in air, even though a kind of passive zinc oxide layer forms on the surface of the metal, which means that further oxide can only form very slowly. However, in some cases it may be necessary to prevent the formation of this hard oxide layer. The optimal concentration of hydrogen for the piece to be annealed is calculated empirically, with the recrystallisation temperature and the required properties of the alloy being taken into account.

Bronzes must always be annealed in a controlled atmosphere. They do not passivate and in contact with air would oxidise to a high degree, also leading to the formation of tin oxide and copper oxide.

In the processing of brass and bronze, gas mixtures with a hydrogen content of 20% are used. Clearly visible: with increasing hydrogen content, the surfaces of the metal become lighter and more brilliant.

Figure 6: Copper tubes annealed in a hood furnace

Hydrogen for cleaning surfaces

Hydrogen is suitable not only as a means of reduction or in order to improve thermal characteristics, but also for cleaning surfaces. In the course of metal processing, extrusion or rolling lubricants often remain on the material. This is a very unfavourable situation in the sense that the residues can burn into the surface during heat treatment. These unwanted residues can be removed in the course of rinsing cycles using nitrogen and hydrogen, carried out while the material is in the furnace. In this instance, a degree of purity is achieved which meets the requirements of e.g. the automobile industry or medical engineering.

Figure 7: Coils on the floor of a bell-type furnace with high-convection technology

Reduce costs thanks to tailor-made gas mixtures

Every application requires its own adequate protection and reactive gas. The choice of protective and reaction gas used (nitrogen, hydrogen, argon or mixtures) depends on the specific requirements. The gases and gas mixtures required are put together individually and the quantities necessary determined on site by trials. Only in this way can production quality be increased and operating costs reduced.

The re-crystallisation annealing of scale-resistant steels is still achieved today in individual cases by using ammonia cracked gas. For this purpose, ammonia is cracked thermally in heated generators. One cubic metre of ammonia produces two cubic metres of cracked gas, which consists of three parts hydrogen and one part nitrogen (see reaction 3).

$$2\ NH_3 \leftrightarrow 3\ H_2 + N_2 \qquad (3)$$

The quality of the protective gas produced is determined primarily by two criteria: 1. the purity of the ammonia used and 2. as far as possible, a fully completed cracking process. Even small traces of residual ammonia give a matt and greyish appearance to the surface of the treated steel. However, this is avoided by the use of high-purity hydrogen and nitrogen. The "new process gas" used in heat treatment consists of technical gases and features dew points of -70 °C and lower.

As has been shown in practice, the new optimised gas mixture needs less hydrogen to achieve annealing results comparable to those achieved using ammonia cracked gas. In continuously operating furnaces such as pusher or conveyor furnaces, the specific gas costs can be reduced noticeably as a result.

A further advantage of the high purity of hydrogen and nitrogen: The reforming time of a furnace is shortened after shutdown and annealing operations can be started again without delay.

Use the properties of hydrogen for the process

In comparison to all other gases, hydrogen has noticeably higher thermal conductivity and specific heat capacity. Nitrogen/hydrogen mixtures possess equally favourable thermal properties. Among other uses, these mixtures are deployed in the annealing of strip coils or wire coils in bell-type furnaces with high-convection technology.

Gas	Density [kg/m³]	Thermal conductivity	Specific heat capacity [kJ/kgK]
Nitrogen	1.1307	0.02566	1.0410
Hydrogen	0.0813	0.18610	14.3000
Argon	1.6130	0.01782	0.5216
Helium	0.1614	0.15000	5.1931

Table 1: Physical properties of gases at 25 °C and 1 bar absolute

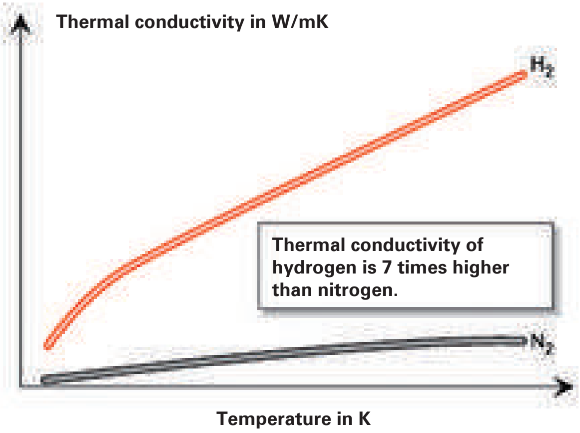

Figure 8: thermal conductivity of hydrogen and nitrogen

Hydrogen has 7 times more thermal conductivity than nitrogen and 13 times more specific heat capacity.

Consequently, hydrogen accelerates the transfer of thermal energy to or from the charge being annealed. At the same time, H_2 ensures that the entire charge is heated through more evenly. Due to the better temperature distribution within the charge being annealed, the heating up and cooling down times for a load can be shortened by up to 20 percent, so the output of a furnace can be considerably increased.

Figure 10: Nitrogen/hydrogen-mixer for gas mixtures

Purification systems for very high purity gases

Messer offers its customers with a range of gas-purifying systems which allow gases of the highest purity to be produced. In this way, residues of water and oxygen can be easily and safely removed.

Figure 9: Storage vessel for liquid nitrogen (standing) and gaseous hydrogen (horizontal)

Figure 11: Oxisorb® purifying station

Arguments for hydrogen and nitrogen

- Correct gas mixtures for first class results
- Save costs by optimal hydrogen content
- Reduced gas requirements for each application
- Constant availability of hydrogen and nitrogen
- Tried-and-tested secure storage
- Low investment costs

Advantages of hydrogen/nitrogen at a glance:

- Higher purity of the technical gases
- Measuring and concentration as needed
- Consistent quality due to reproducible mixtures
- Nitrogen as a safe purging gas
- Less protective gas used
- Better quality of finish
- Increase in productivity possible
- Flexibility when changing the annealing task
- Increase in the range of products

Hydrogen in the field of metallurgy

A question of the right relationship

Hydrogen (H_2) in its purest form is the most common element in the universe. Down here on Earth, however, one seldom comes across it on its own but mostly in heterogeneous compounds, primarily with oxygen with which it forms the very stable compound water. This fact has led to it becoming the most important reducing agent in metallurgy. During the annealing of alloys, hydrogen is always in demand when a perfect surface is called for.

A little insight into the chemistry of hydrogen in the heat treatment of alloys: H_2 has a high affinity to oxygen; both react very easily leading to the formation of water. No solids are deposited on the metal alloy. Whether or not an oxide forms on the metal surface during annealing depends essentially on the chemical composition of the alloy and on the effective atmosphere.
Show me your oxide and I'll tell you what kind of metal you are: The stability of the oxide is characteristic for each metal. Whether it oxidises in the furnace or its oxide is reduced by equation (4),

$$MeO + H_2 \leftrightarrow Me + H_2O \quad (4)$$

depends primarily on which direction the reaction runs or on the prevailing concentration of water and hydrogen as well as the respective temperature. The purity of the hydrogen used and the condition of the furnace also affect the reaction procedure.
Whether an existing furnace can be converted from the previously used gas mixtures (such as Exogas, monogas or ammonia cracked gas) to hydrogen and nitrogen depends mainly on the technical condition of the plant and also on the materials to be annealed as well as the quality required. Which concentration of hydrogen is necessary for reliable and reproducible operation of the plant must be tested by trials on site in each case. It is important that no oxygen, whether in compound or unbonded form, gets into the furnace or the cooling area. In addition, the proportion of water to hydrogen created should be kept as low as possible in order to prevent an oxidation of the charge.
The Messer Group not only has the necessary know-how when it comes to gases, the company also has experience in technical applications which has been gained over many years in the implementation of furnace concepts for the oxide-free annealing of metal alloys.

Every part needs the optimal hydrogen concentration.

Perfect tubes

You work in industry as an applications expert
and have specific questions on this article?

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