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(54) Titre : PROCÉDES PERMETTANT D'ÉVITER LES ADHÉRENCES AU COURS DU PROCESSUS DE RECUIT DE
BANDE D'ACIER EN ATMOSPHERE CONTENANT DE L'HYDROGÈNE

(54) Title: PROCESS FOR AVOIDING STICKERS IN THE ANNEALING OF COLD STRIP UNDER HYDROGEN-
CONTAINING ATMOSPHERES

(57) **Abrégé/Abstract:**

When cold strip steel is annealed, diffusion welds, so-called stickers, frequently form on the strip's surface. In order to avoid these, the cold strip, above 600°C (holding time) is coated by oxidation with a thin surface film which prevents sticking. Below 600°C, during the cooling phase, this surface film is removed by reduction. In the case where a protective gas comprising hydrogen is used in an amount of greater than 5%, with the remainder being nitrogen, carbon dioxide is preferably added as an oxidizing agent. The process is controlled via a defined oxygen partial pressure. The reduction is performed via the hydrogen.

ABSTRACT

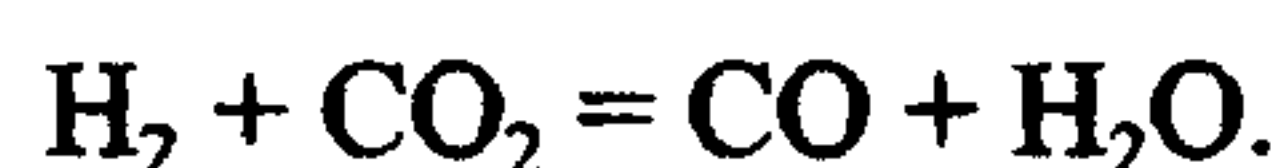
When cold strip steel is annealed, diffusion welds, so-called stickers, frequently form on the strip's surface. In order to avoid these, the cold strip, above 600°C (holding time) is coated by oxidation with a thin surface film which prevents sticking. Below 600°C, during the cooling phase, this surface film is removed by reduction. In the case where a protective gas comprising hydrogen is used in an amount of greater than 5%, with the remainder being nitrogen, carbon dioxide is preferably added as an oxidizing agent. The process is controlled via a defined oxygen partial pressure. The reduction is performed via the hydrogen.

PROCESS FOR AVOIDING STICKERS IN THE ANNEALING OF COLD STRIP UNDER HYDROGEN-CONTAINING ATMOSPHERES

This invention relates to a process in a bell-type, preferably high convection furnace under a protective gas comprising 75% up to 100% of hydrogen with the remainder being nitrogen and utilizing heating, holding and cooling phases.

Cold strip steel is annealed in the form of tight coils in pot furnaces, bell-type furnaces or roller conveyor furnaces. In recrystallization annealing in closed furnaces, such as bell-type furnaces, and in particular high-convection furnaces, diffusion welds, so-called strip stickers, are frequently formed between the turns of the cold strip. Subsequently in the temper rolling mill, these strip stickers increase the resistance to coil unwinding, as a result of which buckles or material cracks form on the strip's surface.

DE 42 07 394 C1 describes a process for avoiding these strip stickers. According to this process, the surface of the cold strip wound up to form tight coils is coated above 600°C by means of defined oxidation processes with a thin surface film which prevents the sticking of the turns. During the cooling phase, below 600°C, this surface film is removed again by reducing the oxides. This is performed by changing the water gas equilibrium. The entire annealing process takes place in an annealing furnace, in particular a bell-type furnace, under an N₂-H₂ protective gas mixture containing at most 5% of H₂ and with the addition of defined amounts of CO₂. The entire reaction process is assigned to the water gas reaction



The reaction between hydrogen and carbon dioxide causes intensive steam formation which is a function of the thermodynamic state of the system. This is favored by a high H₂ or CO₂ concentration and high temperatures. Table 2 below and Figure 2 show, for example, the temperature-dependent change in concentration in a starting mixture of 5% H₂ and 1% CO₂. The H₂O and CO curves coincide. The temperature is plotted on the x

axis and the concentration of the gas components is plotted on the y axis. Steam formation increases with increasing temperature. At 700°C, these values are still below 1% by volume. Increasing the CO₂ concentration in the starting mixture increases the steam formation up to approximately 2% by volume. The amount of CO₂ is fixed and depends on the surface area of annealing material treated. An appropriate oxidizing ratio of the CO₂ and CO partial pressures is achieved by changing the steady-state equilibrium of the water gas reaction. This is achieved by a higher throughput of the protective gas.

TABLE 2

Changes in the gas composition after heating for the homogeneous water gas reaction

T°C	CO %	CO ₂ %	H ₂ %	H ₂ O %	K _p
100	0.06	0.94	4.94	0.06	0.00094
200	0.18	0.82	4.82	0.18	0.00881
300	0.34	0.66	4.66	0.34	0.03789
400	0.49	0.51	4.51	0.49	0.10562
500	0.62	0.38	4.38	0.62	0.22583
600	0.71	0.29	4.29	0.71	0.40571
700	0.78	0.22	4.22	0.78	0.64618

TABLE 3

Changes in the gas composition after heating for the homogeneous water gas reaction

T°C	CO %	CO ₂ %	H ₂ %	H ₂ O %	K _p
100	0.76	6.64	91.84	0.76	0.00094
200	2.06	5.34	90.54	2.06	0.0088
300	3.59	3.81	89.01	3.59	0.038
400	4.79	2.61	87.81	4.79	0.1
500	5.6	1.8	87	5.6	0.2
600	6.26	1.14	86.34	6.27	0.4
700	6.62	0.78	85.98	6.62	0.65

A protective gas having a hydrogen content of 92.6% is described in Table 3, above, and Figure 3. As a comparison between Table 3 and Table 2 shows, at H₂ contents >5%, unreasonable steam concentrations of up to approximately 6.6% by volume (at 700°C) are formed. The appropriately oxidizing CO₂-CO ratio is not achieved in any temperature range. At high CO₂ concentrations, the oxidation proceeds in an uncontrolled

manner in the H_2 - H_2O system at low, therefore undesired, temperatures, in which case the possibility of a subsequent reduction of the strip's surface is not provided. These results listed in Table 3 have been clearly confirmed in studies carried out in the laboratory. An admixture of 5 to 10% by volume of CO_2 to the hydrogen at treatment temperatures of $680^\circ C$ caused formation of water to such a great extent that these studies had to be terminated in order to prevent destruction of the analytical instruments. The content of hydrogen in the protective gas in sticker-free annealing of cold strip is therefore restricted to a maximum of 5% by volume in DE 42 07 374 C1.

Strip stickers further occur when cold strip is treated in high-convection furnaces under protective gases containing $>5\%$ hydrogen. A process for annealing cold strip would therefore be desirable by means of which strip stickers could be avoided even when protective gases containing up to 100% H_2 are used.

In the drawings:

Fig. 1 is a graph showing changes in oxygen partial pressure;

Figs. 2 and 3 are graphs showing temperature dependent changes in gas concentrations for defined structure mixtures.

This invention therefore provides a process for avoiding strip stickers during the annealing of cold strip under protective gases having a hydrogen content $>5\%$.

Specifically, this invention provides a process for avoiding stickers in the annealing of cold strip steel in a bell-type furnace using a protective gas comprising $>5\%$ to 100% of hydrogen, with any remainder being nitrogen, and which includes the phases of heating, holding and cooling, the improvement which comprises coating the cold strip during the holding time with a thin surface film by oxidation at a temperature above $600^\circ C$, by establishing an oxidizing partial pressure ratio

$$P(CO_2)/P(CO) > 1$$

by adding 0.3 g to 0.6 g of carbon dioxide per m^2 of annealing material surface to the protective gas and highly disrupting the thermodynamic equilibrium of the homogeneous water gas reactions ($K \ll 0.01$). In one embodiment, the protective gas comprises between 75% and 100% by volume of hydrogen.

Only by means of the surface film formed by the process of this invention is protection achieved from the sticking together of individual turns of the cold strip under a protective gas having a hydrogen content greater than 5%, preferably having a hydrogen content greater than 70%, in particular 100%. The prerequisite therefor is extremely high disruption of the thermodynamic equilibrium of the homogeneous water gas reaction. This means virtually suppressing the course of the reaction as described by $\text{H}_2 + \text{CO}_2 = \text{CO} + \text{H}_2\text{O}$. Test operations with approximately 60t annealing batches have surprisingly shown that cold strip can be coated with a surface layer, and thus can be treated so as to be sticker-free, in closed furnaces, for example in bell-type furnaces, with high convection even under protective gas containing 100% H_2 with the addition of CO_2 .

By reason of the high output of the gas circulation fans used in high-convection furnaces, the flow velocities of the circulated H_2 protective gas at temperatures of 600 to 750°C are so high that the homogeneous water gas reaction can scarcely still take place and the steady-state equilibrium departs very substantially from the thermodynamic equilibrium. According to the invention, steady-state equilibria of $K \ll 0.01$ are employed here. Steady-state equilibrium is taken to mean here an actual state which is calculated mathematically by the following formula on the basis of analysis of the gas composition:

$$K = \frac{P_{\text{CO}} \cdot P_{\text{H}_2\text{O}}}{P_{\text{H}_2} \cdot P_{\text{CO}_2}}$$

The quotient K becomes $\ll 0.01$ only when the divisor is very large and the dividend is very small, which denotes a virtual cessation of the reaction. By this means, it surprisingly becomes possible to achieve an oxidizing partial pressure ratio (P) of carbon dioxide (CO_2)/carbon monoxide (CO). Steam formation in this case is greatly restricted.

The homogeneous water gas reaction is in this case unusable for controlling the process of the invention. It is controlled rather via the dissociation of the admixed defined amount of CO_2 as described by:



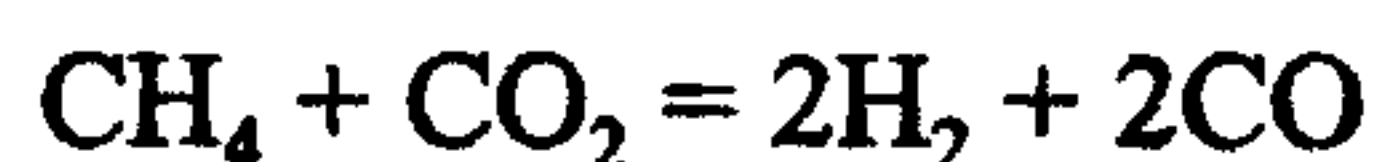
An oxygen partial pressure resulting from this reaction is set as required in the protective gas atmosphere. The process of coating the strip surface with a surface film which

prevents the sticking of the turns is carried out under a defined O_2 partial pressure. This can be defined as the quotient of the partial pressures (P) of CO_2 and CO and must not be less than 1 in the oxidation process above $600^\circ C$.

Figure 1 shows graphically the changes in the oxygen partial pressure (PO_2). In this figure, PO_2 is shown as a logarithmic function of temperature and time. The CO_2 admixture phase can clearly be seen. This is terminated at the start of the cooling phase. Surface films built up in this way with an amount of CO_2 of 0.3 to 0.6 g per m^2 of annealing material surface prevent the sticking of individual turns in the coil. A high reducing power of the hydrogen in the cooling phase ensures the breakdown of this surface film below $600^\circ C$.

During the holding time in a pure hydrogen atmosphere, intense methane formation takes place because H_2 reacts with the carbon originating as a product of cracking from the volatilization phase (heating) in accordance with the equation $H_2 + C = CH_4$.

Methane contents higher than about 2% by volume have an adverse effect on the establishment of the required oxygen partial pressure which is critical for the coating with a protective surface film. The admixed CO_2 then reacts with the methane in accordance with the following reaction:



The carbon dioxide is thus broken down and new CO forms to such an extent that the ratio of the partial pressures (P)

$$P(CO_2)/P(CO) < 1$$

is established and as a result of this a defined coating of the strip surface with a protective surface film is not possible, or not possible economically.

In order to carry out the proposed coating process free from interference, the methane content in the last phase of the holding time, prior to the CO_2 admixture, must not exceed a concentration of approximately 2% by volume of the protective gas atmosphere. If low-carbon and carburization-sensitive steels are treated by the process of the invention, e.g. titan microalloy IF steel (special deep-draw steel), it is necessary to decrease the C level of the protective gas atmosphere to 0.003%.

CLAIMS:

1. In a process for avoiding stickers in the annealing of cold strip steel in a bell-type furnace using a protective gas comprising nitrogen and greater than 5% to 100% by volume of hydrogen and which includes the phases of heating, holding and cooling, the improvement which comprises coating the cold strip steel during the holding time with a thin surface film by oxidation at a temperature above 600°C, by establishing an oxidizing partial pressure ratio

$$P(\text{CO}_2)/P(\text{CO}) > 1$$

by adding 0.3 g to 0.6 g of carbon dioxide per m² of annealing material surface to the protective gas and highly disrupting the thermodynamic equilibrium of homogeneous water gas reactions.

2. The process as claimed in claim 1 wherein the bell-type furnace uses high convection.

3. The process as claimed in claim 1 or claim 2, wherein, during the cooling phase at temperatures below 600°C, a partial pressure ratio of

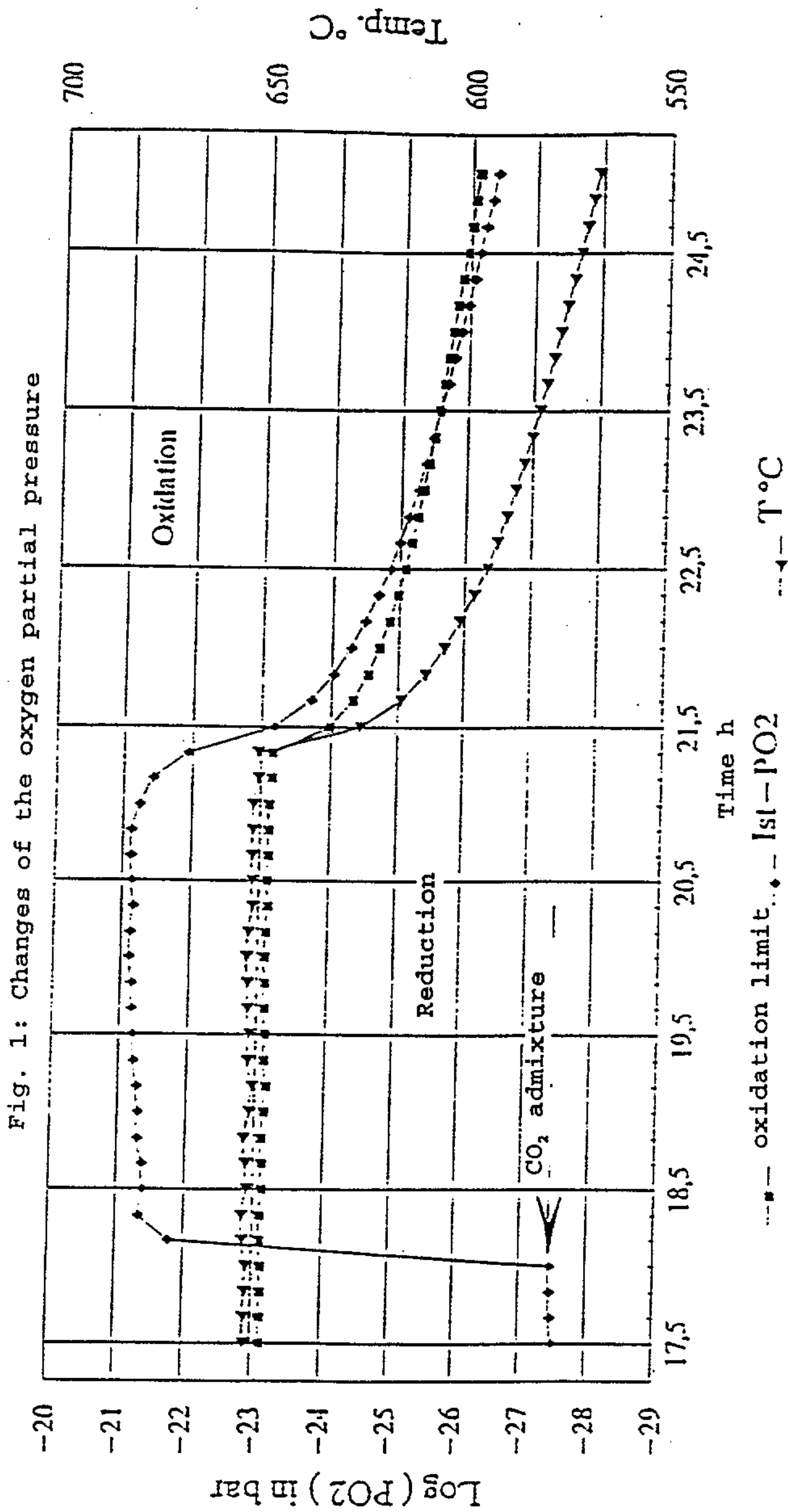
$$P(\text{CO}_2)/P(\text{CO}) > 1$$

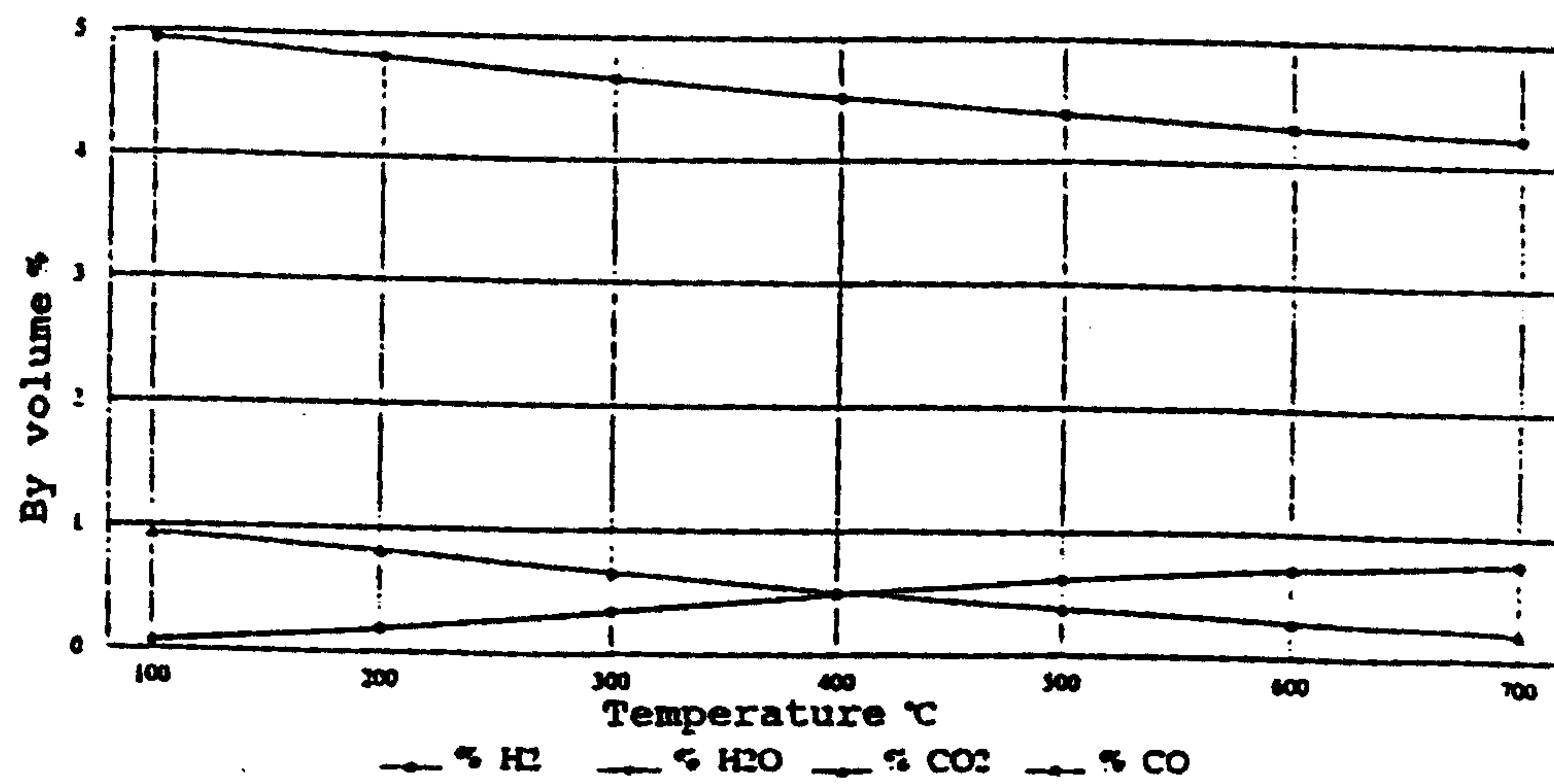
is established for reduction of the surface film.

4. The process as claimed in claim 3, wherein steam content in the protective gas is set below 1.5% by volume during the CO₂ admixture and the surface film is reduced by hydrogen during the cooling phase.

5. The process as claimed in claim 3, wherein the protective gas has a methane content below 2% by volume prior to the CO₂ admixture.

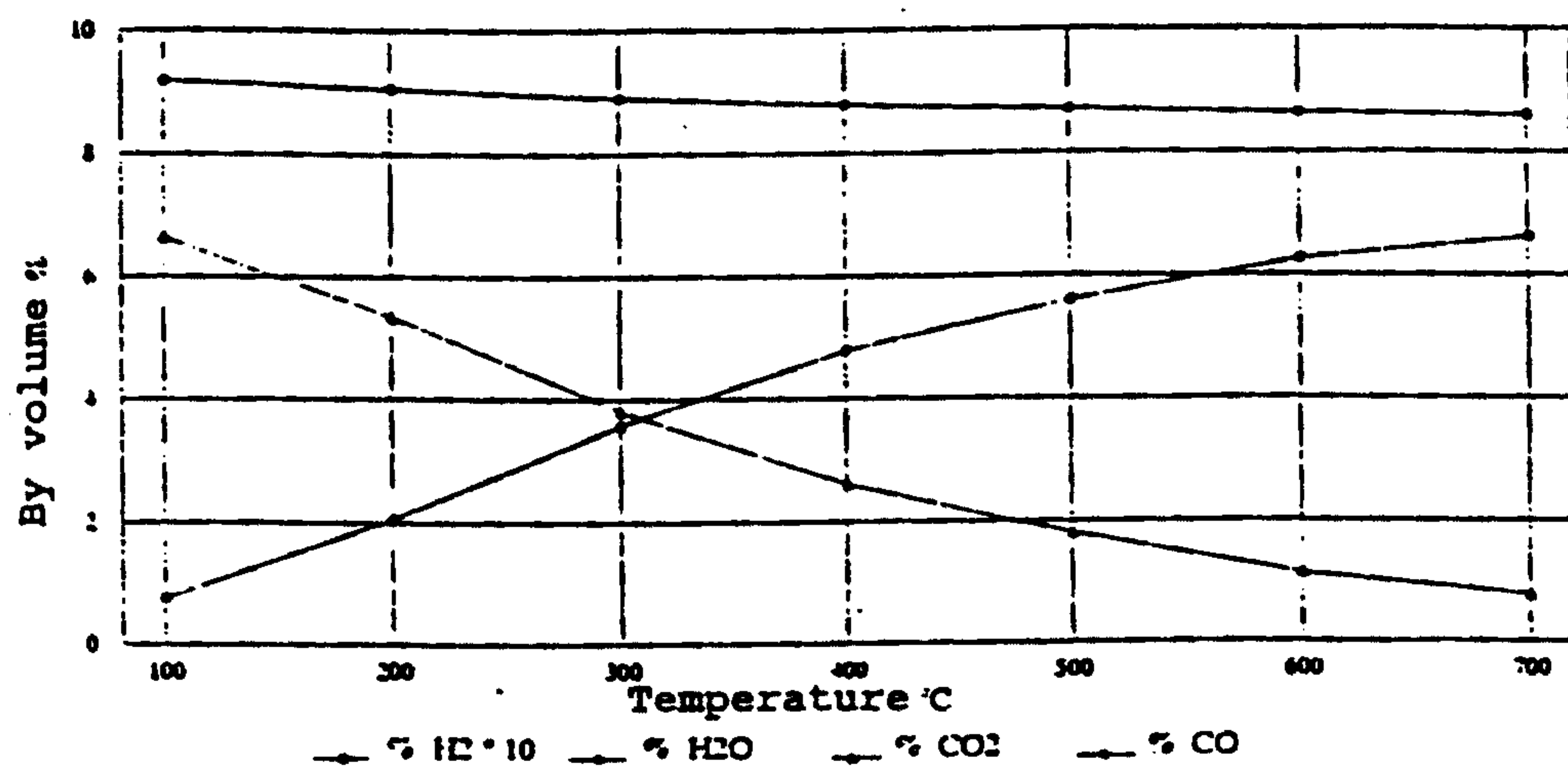
6. The process as claimed in any one of claims 1 to 5, wherein the protective gas comprises between 75% and 100% by volume of hydrogen.





Starting mixture: 5%H₂; 1%CO₂; 0.004%H₂O

FIG. 2 (PRIOR ART)



Starting mixture: 92.6% H_2 ; 7.4% CO_2 ; 0.004% H_2O

FIG. 3 (PRIOR ART)