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(54) **METHOD FOR HEAT TREATING METALLIC WORK PIECES**

(57) According to the method for heat treating at least one metallic work piece according to the present invention said at least one metallic work piece is subjected to a predetermined temperature time profile (1) in a furnace, wherein at least intermittent a process gas is introduced into the furnace atmosphere to define the composition of said furnace atmosphere, wherein the introduction of the process gas is controlled regarding at least one of the following parameters: the volume of the process gas introduced into the furnace and the composition of the process gas in such a way that during at least one of the following operations: heating up and cooling down the at least one work piece while the temperature of the furnace is within a predetermined critical temperature range in which internal oxidation occurs within the metal of the work piece being defined by a lower critical temperature (T_L) and an upper critical temperature (T_U) the furnace atmosphere is low in oxygen whereas above said upper critical temperature (T_U) the furnace atmosphere is defined independently of the oxygen content in the furnace atmosphere.

The method according to the present invention allows heat treatment processes with a significantly re-

duced internal oxidation while allowing a broad choice of process gases for temperatures above the upper critical temperature (T_U).

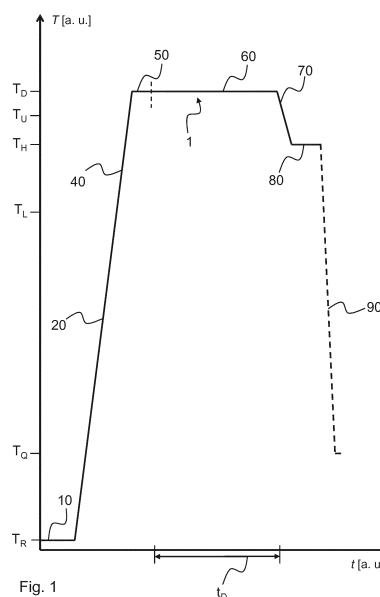


Fig. 1

Description

[0001] The method for heat treating metallic work pieces allows to perform a heat treatment of metallic work pieces while avoiding internal oxidation having a rather broad choice of process gases, in particular for use in atmospheric furnaces.

[0002] Metallic work pieces are frequently subjected to heat treatment processes, e. g. for annealing, carburizing and the like. In these processes internal oxidation is unwanted. Methods for avoiding or reducing internal oxidations are known e. g. from EP 0 662 525 A1 in which a mixture of nitrogen and hydrogen is used as a process gas while heating the work piece to the carburizing temperature. Further, it is disclosed that even during carburizing the furnace atmosphere has to fulfill specific requirements regarding its oxygen activity. This method reduces the internal oxidation significantly, nevertheless, it has the drawback that the possible choice of the process gas for defining the furnace atmosphere is limited. From prior art processes it is known to control the furnace atmosphere regarding its carbon activity by using oxygen sensors or lambda sensors to control the partial oxygen pressure. In particular, for low partial oxygen pressures these control mechanisms are limited.

[0003] Therefore, it is an object of the present invention to propose a heat treatment process for metallic work pieces overcoming at least in part the problems known from prior art and in particular allowing the reduction of internal oxidation while allowing a larger choice of process gases compared to prior art.

[0004] This problem is solved by the features of the independent claim. Dependent claims are directed to advantageous improvements.

[0005] According to the method for heat treating at least one metallic work piece is subjected to a predetermined temperature time profile in a furnace, wherein at least intermittent a process gas is introduced into the furnace atmosphere to define the composition of said furnace atmosphere, wherein the introduction of the process gas is controlled regarding at least one of the following parameters: the volume of the process gas introduced into the furnace and the composition of the process gas in such a way that during at least one of the following operations: heating up and cooling down the at least one work piece while the temperature of the furnace is within a predetermined critical temperature range in which internal oxidation occurs within the metal of the work piece being defined by a lower critical temperature and an upper critical temperature the furnace atmosphere is low in oxygen whereas above said upper critical temperature the furnace atmosphere is defined independently of the oxygen content in the furnace atmosphere.

[0006] The term subjection of at least one work piece to a pre-determined temperature time profile is to be understood in such a way that the temperature of at least one work piece is controlled over time. This can e. g. be performed in batch furnaces by varying the temperature

of the furnace over time following a predetermined cycle, or in continuous furnaces having e. g. a plurality of zones of different temperatures through which the at least one metallic work piece is moved. Preferably, the furnace is a batch furnace.

[0007] The term low in oxygen in the context of this document is to be understood in such a way that the furnace atmosphere has

- a dew point of less than -10°C , in particular less than -15°C , preferably -20°C or less and/or
- an oxygen activity of less than 10^{-25} bar and/or
- a carbon monoxide (CO) content of less than 3 Vol.-%.

[0008] For avoiding or reducing internal oxidation it is important to have a furnace atmosphere without an oxygen source understood as a source for atomic or ionic oxygen during a critical temperature range in which internal oxidation occurs. Extensive experiments performed by the applicants have revealed that there is a specific temperature range which is critical for the generation of internal oxidation. The critical temperature range is defined by a lower critical temperature and an upper critical temperature. The values of these critical temperatures depend on the alloying elements of the metal of the work pieces. E. g. for manganese as alloying element the lower critical temperature is about 700°C whereas the upper critical temperature is about 900°C . Outside the critical temperature range internal oxidation is negligible. Nevertheless, even below the lower critical temperature range the oxygen content of the furnace atmosphere has to be low as then surface oxidation can occur which is usually undesired as well.

[0009] An oxygen source is of course gaseous oxygen or humidity coming from air ingress but also water, whereas another one can be carbon oxides like CO or CO_2 . An oxygen source can be oxides on the surface of the at least one work piece which are reduced during chemical reactions with e. g. hydrogen.

[0010] Depending on the desired level of internal oxidation to be reached it is sufficient to have a furnace atmosphere low in oxygen either during heating the at least one metallic work piece within the critical temperature range and/or during cooling down the at least one metallic work piece within the critical temperature range. Nevertheless, if a significantly low level of internal oxidation is desired it is advantageously possible to have a furnace atmosphere low in oxygen both during heating and cooling.

[0011] Preferably, the method according to the present invention is used for carburizing and/or hardening. The work pieces are preferably made of steel, preferably case-hardened steels and heat-treatable steels (quenched and tempered steels), preferably high-alloy case hardened steels. In particular, the method according to the present invention is advantageously usable for steels alloyed with titanium, manganese, silicon and/or

chromium,.

[0012] The critical temperature range is the temperature range in which internal oxidation takes place. Surprisingly, the depth of the internal oxidation in the final work piece is mostly depending on the availability of oxygen for promoting internal oxidation in a specific temperature range only. Therefore, the present invention is based on the application of a process gas allowing a low oxygen furnace atmosphere as defined above in the critical temperature range while heating, whereas above this critical temperature range a furnace atmosphere with a higher oxygen partial pressure can be applied. This allows above the critical temperature range to use e. g. an endogas (comprising hydrogen, nitrogen and carbon monoxide, optionally carbon dioxide and/or water) or a gas mixture comprising carbon monoxide and hydrogen as a process gas for controlling the furnace atmosphere above the critical temperature range. It is essential to reach an atmosphere low of oxygen as defined above already at lower critical temperature range. Therefore, frequently, the process gas below the lower critical temperature and even directly after equipping the furnace with the work piece is oxygen free. This influences the furnace atmosphere in such a manner that when reaching the lower critical temperature the furnace atmosphere is low in oxygen as defined above. Above the upper critical temperature oxidation is negligible if the furnace atmosphere comprises e. g. endogas or a mixture of carbon monoxide and hydrogen and, preferably, nitrogen and/or argon. Influence on the formation of oxides have beside the partial pressure of oxygen in the furnace atmosphere the temperature and the enthalpy of formation of the respective oxide which can be estimated according to the Ellingham diagram.

[0013] Possible oxygen sources for atomic oxygen can be impurities in the atmosphere, air ingress when work pieces are placed in the furnace or are taken out of the furnace. Further oxygen sources are leaks in the furnace through which ambient air can enter the furnace and carbon monoxide, carbon dioxide, oxygen and water in the furnace atmosphere.

[0014] The critical temperature range is defined as the temperature range in which internal oxidation takes place. The critical temperature range is preferably defined depending on the alloying elements of the metal. Experiments of the applicant have revealed that outside this critical temperature range the tendency of usual alloying elements to form oxides is tolerable resulting in an acceptable layer thickness of the respective layer having internal oxides.

[0015] Due to the oxidation of an alloying element the content of dissolved atoms of the alloying element close to the surface of the work piece is reduced which results in diffusion of the respective atoms from deeper regions of the work piece to the surface region. Therefore, the formation of internal oxides is strongly depending on the chemical affinity of the respective alloying element to oxygen and on the mean diffusion velocity or the respective

diffusion coefficient of the alloying element. This condition is fulfilled e. g. for chromium, silicon, manganese and titanium.

[0016] Internal oxidation is characterized due to this effect in particular by an accumulation of manganese in the precipitation of oxides and an accumulation of chromium close to the surface. Due to the reduction of the amount of unbound chromium and manganese the transformation characteristics of the material is changed. The critical quenching velocity is raised, the formation of perlite cannot be suppressed, therefore, as a result the surface layer is not fulfilling the requirements regarding hardness.

[0017] In particular, applicant has found in tests that if manganese is one of the alloying elements the temperature range in which internal oxidation occurs is about 700°C to 900°C. This is in particular advantageous for the steel 16MnCr5.

[0018] According to an improvement below the lower critical temperature the process gas is oxygen free, in particular consisting of at least one inert gas, preferably nitrogen and/or argon, in particular nitrogen.

[0019] It is necessary to provide a furnace atmosphere with low available oxygen levels already at rather low temperatures, because it is necessary to reduce both the oxygen being in the furnace atmosphere itself, e. g. due to leakage of the furnace and the oxygen generated by chemical reactions, e. g. by reducing oxides on the surface of the metallic work piece. Therefore, it is frequently necessary to change the furnace atmosphere already at low temperatures to ensure that the atmosphere within the critical temperature range is low of oxygen according to the definition provided above following the present invention. This can be done by introducing as a process gas an oxygen free gas like e. g. nitrogen and/or argon, in particular nitrogen.

[0020] According to an improvement for controlling said furnace atmosphere low of oxygen at least for a temperature within the critical temperature range the process gas comprises at least one of the following gases:

- hydrogen (H₂);
- nitrogen (N₂);
- at least one hydrocarbon; and
- methane (CH₄).

[0021] Preferably, a mixture of hydrogen and nitrogen is used to control the furnace atmosphere in the critical temperature range. In particular, binary mixtures of hydrogen and nitrogen are used, preferably 30 Vol.-% [volume percent] to 50 Vol.-% hydrogen and 70 Vol.-% to 50 Vol.-% nitrogen, in particular 35 Vol.-% to 45 Vol.-% hydrogen and 65 Vol.-% to 55 Vol.-% nitrogen, in particular 40 Vol.-% hydrogen and 60 Vol.-% nitrogen.

[0022] The preferred range of 35 Vol.-% to 45 Vol.-% hydrogen in nitrogen has been found to be advantageous. The hydrogen in the process gas is used to reduce the oxygen chemically bound in the oxides on the metallic

work piece. The preferred hydrogen content ensures a homogeneous carbon-profile of the work piece after the treatment. A lower hydrogen content was found to create inhomogeneous carbon profiles. A higher hydrogen content is possible but is usually undesirable from an economical point of view.

[0023] If it is necessary to generate a carbon activity in the furnace atmosphere at least one hydrocarbon can be added to the process gas. This is advantageous in particular when it is desired to carburize the work piece. In this case it is possible to use a process gas including at least one hydrocarbon to generate a carburizing atmosphere in the furnace at temperatures above the critical range.

[0024] For example, it is possible to add propane (C_3H_8) and/or methane (CH_4) to have a carbon source and create a carbon activity. The carbon activity can be adjusted by the amount of hydrocarbon in the process gas. Particular preferred is the adjustment of the carbon activity by adding methane, particular preferred to a mixture of hydrogen and nitrogen, as it has been found that soot formation is reduced compared to situations in which e. g. propane and/or acetylene have been added to a respective mixture. Therefore, the use of methane as a carbon source to present a carbon activity is advantageous for the quality of the final product.

[0025] The term at least for a temperature within the critical temperature range is to be understood in such a manner that even at temperatures below the lower critical temperature such a gas mixture can be used as a process gas.

[0026] According to an improvement for controlling said furnace atmosphere for a temperature above the upper critical temperature the process gas comprises at least one of the following gases or gas mixtures:

- endogas;
- a gas mixture of carbon monoxide and hydrogen;
- dissociated alcohol, in particular methanol;
- an inert gas like nitrogen (N_2) and/or argon (Ar); and
- carbon monoxide (CO).

[0027] An endogas is a gas mixture of hydrogen, nitrogen and carbon monoxide (CO). Optionally, carbon dioxide (CO_2) and/or water (H_2O) can be part of the endogas as well. A second option is a gas mixture of carbon monoxide and hydrogen. Both process gases contain oxygen atoms in the form of CO which is available for reaction with alloying elements in the metal which is particularly preferred steel. Above the critical temperature range the risk for internal oxidation is significantly reduced allowing the use of oxygen-containing process gases above the critical temperature range. The use of these gases allows e. g. the use of the carbon in the gases e. g. from the dissociated alcohol like in particular methanol for carburizing of the metal.

[0028] The above-identified process gases used above the upper critical temperature allow in particular

to control the processes in the furnace and in particular its furnace atmosphere using oxygen sensors and/or lambda sensors.

[0029] As a process gas within the critical temperature range it is possible to use at least in part a dry inert gas like argon or nitrogen, preferably nitrogen, before changing to the afore-mentioned process gas, preferably a mixture of nitrogen and/or argon and hydrogen. The change of the process gas to said mixture of nitrogen and/or argon and hydrogen is preferably performed at a temperature of 750 °C and above.

[0030] According to a preferred embodiment the upper critical temperature is 900°C, whereas the lower critical temperature is 700°C. This is particularly advantageous if the relevant alloying element is manganese.

[0031] According to an improvement the process gas is at least one inert gas which is introduced into the furnace atmosphere after equipping the furnace with the at least one work piece for a predetermined time or until a predetermined purge temperature is reached.

[0032] This allows the purging with an inert gas like nitrogen and/or argon to reduce the oxygen levels in the furnace atmosphere which usually increases significantly after equipping the furnace with the at least one work piece as there is air ingress including humidity if the furnace is open and/or air is adhered to the work piece. The purging action with at least one inert gas allows a quick reduction of the oxygen level in the furnace atmosphere.

[0033] According to a further improvement the work piece is carburized at a carburizing temperature above the upper critical temperature while a carburizing atmosphere is maintained in the furnace for a carburizing time.

[0034] During this carburizing step it is possible to control the furnace atmosphere based on the signal of at least one oxygen sensor and/or lambda sensor. The temperature at which the carburizing atmosphere is created in the furnace is depending on the metal quality, alloying elements and the desired time of carburizing. Usually, said temperature is at 900 °C or above limited by undesired changes in the material structure of the metal of the work piece.

[0035] The furnace atmosphere during carburizing (carburizing atmosphere) comprises particularly one of the following gas mixtures:

- endogas; and
- a mixture of nitrogen and dissociated methanol,

with an optional addendum of a hydrocarbon.

[0036] The carburizing atmosphere during carburizing provides carbon for the carburizing process i. e. includes carbon sources and has a significant carbon activity. Usually, the carbon activity is between 0,8 to 1,1 % carbon. The duration of the carburizing time, the carburizing temperature and the contents of the furnace atmosphere during carburizing are preferably determined based upon the metal of the work piece, in particular depending on the alloying elements in the metal, the surface of the at

least one work piece and/or the desired carbon (profile) to be reached by the carburizing process.

[0037] According to an improvement the at least one metallic work piece is quenched after carburizing after the furnace temperature has been lowered to a hardening temperature.

[0038] According to an improvement the at least one work piece is made of one of the following materials:

- steel;
- a case-hardened steel;
- a heat-treatable steel;
- a quenched steel; and
- a tempered steel.

[0039] In a particular preferred embodiment the at least one work piece is made of high-alloy case hardened steel. The method according to the invention is preferably usable with steels having titanium, chromium, silicon and/or manganese as alloying elements.

[0040] In the following, an exemplary schematic temperature time profile for a heat treatment including a carburizing step according to the present invention is discussed with reference to the sole Fig. 1 although the invention is not limited to the embodiment shown.

[0041] In Fig. 1 a schematic temperature time profile 1 for a method for heat treating at least one metallic work piece according to an embodiment of the present invention in a batch furnace is depicted. In the temperature time profile 1 the temperature T is drafted against the time t both in arbitrary units. Both axes are not to scale but merely schematic.

[0042] Prior to equipping the furnace with the work pieces the furnace is purged with nitrogen until a dew point of -15°C is reached. Depending on the type of furnace the temperature of the furnace is either room temperature or a temperature significantly above room temperature, i. e. above 800°C or the like. Even in the latter case the furnace temperature will significantly drop due to the introduction of the comparatively cold work pieces having a large thermal capacity. Therefore, in the following a low temperature (room temperature) is depicted when starting the process but it is understood that this could be a higher temperature as well.

[0043] Starting at a furnace temperature equal to room temperature T_R or laboratory conditions (e. g. 20°C) a furnace is provided with one or more metallic work pieces in a first step of equipping 10. During this step 10 of equipping the furnace is open and in fluid communication with the ambient atmosphere. To limit the ingress of ambient air the furnace can be further purged with an oxygen free gas, e. g. with nitrogen and/or argon during the step 10 of equipping. This can improve the safety of the process as the furnace is further inertized and a reaction with burnable gases can be avoided. The surfaces of the work pieces that are to be hardened have to be accessible for the atmosphere inside the furnace to allow a reaction of atoms or molecules in furnace atmosphere with atoms

or molecules within the work pieces.

[0044] Depending on the kind of furnace it is possible that the temperature of the furnace is not the ambient temperature as assumed above but is at a certain temperature level, e. g. in the range of 860°C . Usually by opening the furnace and introducing the work pieces having ambient temperature the temperature within the furnace drops significantly below 700°C . Further, the ingress of atomic oxygen sources cannot be avoided even by purging with at least one inert gas as e. g. the surface of the work piece comprises oxides acting as oxygen sources as well as gaseous oxygen bound to the surface by adhesion or the like.

[0045] After equipping 10 the furnace is heated up to a furnace temperature equal to a upper critical temperature T_U of a critical temperature range being critical for internal oxidation in a step of heating 20. The lower critical temperature T_L for internal oxidation is in this example with manganese as the predominant alloying element 700°C and is in general determined depending on the metallic material of the work pieces to be heat treated. Different concentrations c_M of alloying elements that are dissolved in the lattice or between grains of the raw material contribute to an increased or decreased lower limit temperature T_L . The current furnace temperature is monitored via one or more temperature sensors allowing an exact process control. Already during said primary heating 20 a process gas low of oxygen has to be fed to the furnace, as even if there is no internal oxidation surface oxidation could occur which is undesired as well.

[0046] In a temperature range from room temperature T_R up to the lower critical temperature T_L inner oxidation of the surface areas of the work pieces is limited, even if there is Oxygen (O_2) or Carbon Dioxide (CO_2) or any other possible oxygen source available inside the furnace whereas surface oxidation can occur nonetheless.

[0047] By introducing process gas low of oxygen the furnace atmosphere inside the furnace is replaced by the process gas and all possible oxygen donors in the atmosphere are removed. By adding hydrogen of at most 5 Vol.-% to the furnace atmosphere while reaching a temperature of 400°C in the furnace the oxides on the surface of the furnace and/or the at least one work piece are reduced. At temperatures of 750°C and above it is possible to increase the hydrogen content in the process gas.

[0048] When increasing the furnace temperature starting from 700°C no inner oxidation can occur, as there are no sources for oxygen atoms that could adhere and dissolve in the surface areas of the work pieces.

[0049] In a step of protective gas feeding 40 a process gas is fed into the furnace while the furnace temperature is further increased to a diffusion treatment temperature T_D . The process gas comprises hydrogen and nitrogen, preferably between 35 to 45 Vol.-% hydrogen in nitrogen. By the hydrogen being part of the furnace atmosphere the oxides on the surface of the furnace and/or the at least one work piece are reduced generating water in the atmosphere. This water vapor is then purged by the proc-

ess gas entering the furnace, thereby reducing the dew point of the furnace atmosphere. Optionally, methane (CH_4) may be additionally fed to the furnace in order to act as a further carbon (C) donator. In contrast to higher carbohydrates like propane (C_3H_8), methane (CH_4) is not creating carbon black (soot) at high furnace temperatures. Therefore, no additional cleaning step has to be performed afterwards. Depending on the raw material used for the work pieces the diffusion treatment temperature T_D is in the range from 900 °C to 950 °C. Similar as the lower limit temperature T_L the diffusion treatment temperature T_D is increased or decreased depending on different concentrations c_M of alloying elements in the raw material.

[0050] Once the diffusion treatment temperature T_D is reached the furnace atmosphere is changed by changing the composition of the process gas to a carburizing atmosphere. The process gas is fed to the furnace in a step of feeding process gas 50. This process gas is an endogas consisting of a mixture of 20% carbon monoxide (CO), 40% hydrogen (H_2) and 40% nitrogen (N_2). The carbon monoxide (CO) acts as a carbon donator or carbon source. The respective carbon atoms adhere at the surfaces of the work pieces and diffuse into the work pieces.

[0051] In a step of diffusion treatment 60 the furnace temperature is kept constant at the diffusion treatment temperature T_D (or carburizing temperature) in order to yield reproducible results. During a diffusion treatment time t_D of the diffusion treatment 60 the surface areas of the work pieces are carburized. Thereby carbon (C) atoms originating from the carbon monoxide (CO) adhered to the surface of the work pieces, and, subsequently, diffuse into the at least one work piece. In the surface areas the carbon (C) atoms dissolve in the lattice of the raw material and are deposited at interstitials of the lattice (hexagonal spaces in the face-centered cubic austenite lattice).

[0052] The longer the diffusion treatment time t_D is chosen, the deeper the carbon (C) atoms can diffuse into the work pieces during carburization. The diffusion treatment time t_D is commonly in the range of 3 h to more than 8 h. The furnace atmosphere can be changed again by changing the process gas entering the furnace at a later stage of the diffusion treatment 60. Depending on the total diffusion treatment time t_D a process gas consisting of a mixture of nitrogen (N_2), and methanol (CH_3OH) can be introduced into the furnace about 1 h to 2 h before the end of the total diffusion treatment time t_D .

[0053] After the carburization in diffusion treatment step 60 the furnace is provided with a process gas comprising only nitrogen and/or argon and hydrogen in a cooling step 70, while the furnace temperature is reduced to a lower hardening temperature T_H . The temperature T_H is about 840 to 880 °C for a hardening step 80. It is possible to add an amount of a source of carbon e. g. by adding a hydrocarbon or the like to the furnace atmos-

phere during the diffusion treatment step 60.

[0054] Finally, a step of quenching 90 is applied. In order to produce a martensitic lattice that yields high hardness, the work pieces are rapidly quenched in oil from the lower temperature T_H of 840 to 880 °C to a quenched temperature T_Q , which is between 20 °C and 200 °C depending on the raw material and the desired grain structure. Due to the rapid cooling the carbon (C) atoms have no time to diffuse out of their interstitials and to build carbon grains at grain boundaries of the iron matrix. Instead the carbon (C) atoms are squeezed in the smaller interstitials of the ferrite lattice (body-centered cubic) that is thereby deformed into the martensitic lattice (body-centered tetragonal lattice).

[0055] The mechanical properties may be further adapted to the intended purpose of the work pieces by additional processes like tempering, etc. Thereby, the high stiffness may for example be reduced and the toughness further increased.

[0056] The method according to the present invention allows heat treatment processes with a significantly reduced internal oxidation while allowing a broad choice of process gases for temperatures above the upper critical temperature T_U .

Reference Numerals

[0057]

1	temperature time profile
10	equipping
20	heating
40	protective gas feeding
50	process gas feeding
60	diffusion treatment
70	cooling
80	hardening
90	quenching
t	time
t_D	diffusion treatment time
T	temperature
T_D	diffusion treatment temperature
T_H	hardening temperature
T_L	lower critical temperature
T_R	room temperature
T_Q	quenched temperature
T_U	upper critical temperature

Claims

- Method for heat treating at least one metallic work piece by subjecting the at least one work piece to a predetermined temperature time profile (1) in a furnace, wherein at least intermittent a process gas is introduced into the furnace atmosphere to define the composition of said furnace atmosphere, wherein

the introduction of the process gas is controlled regarding at least one of the following parameters: the volume of the process gas introduced into the furnace and the composition of the process gas in such a way that during at least one of the following operations: heating up and cooling down the at least one work piece while the temperature of the furnace is within a predetermined critical temperature range in which internal oxidation occurs within the metal of the work piece being defined by a lower critical temperature (T_L) and an upper critical temperature (T_U) the furnace atmosphere is low in oxygen whereas above said upper critical temperature (T_U) the furnace atmosphere is defined independently of the oxygen content in the furnace atmosphere.

2. Method according to claim 1, wherein below the lower critical temperature (T_L) the process gas is oxygen free.

3. Method according to one of the preceding claims, wherein for controlling said furnace atmosphere low of oxygen at least for a temperature within the critical temperature range the process gas comprises at least one of the following gases:

- hydrogen (H_2);
- nitrogen (N_2);
- at least one hydrocarbon; and
- methane (CH_4).

4. Method according to one of the preceding claims, wherein for controlling said furnace atmosphere for a temperature above the upper critical temperature (T_U) the process gas comprises at least one of the following gases or gas mixtures:

- endogas;
- a gas mixture of carbon monoxide (CO) and hydrogen (H_2);
- dissociated alcohol, in particular methanol (CH_3OH);
- an inert gas; and
- carbon monoxide (CO).

5. Method according to one of the preceding claims, wherein the upper critical temperature (T_U) is $900^\circ C$.

6. Method according to one of the preceding claims, wherein the lower critical temperature (T_L) is $700^\circ C$.

7. Method according to one of the preceding claims wherein the process gas is at least one inert gas which is introduced into the furnace atmosphere after equipping the furnace with the at least one work piece for a predetermined time or until a predetermined purge temperature is reached.

8. Method according to one of the preceding claims, wherein the work piece is carburized at a carburizing temperature above the upper critical temperature (T_U) while a carburizing atmosphere is maintained in the furnace for a carburizing time.

9. Method according to claim 8, wherein the carburizing atmosphere comprises at least one of the following

- a) an endogas or
- b) a mixture of nitrogen (N_2) and methanol (CH_3OH) and at least one hydrocarbon.

10. Method according to one of the preceding claims 8 or 9, wherein the at least one metallic work piece is quenched after the carburizing after the furnace temperature has been lowered to a hardening temperature (TH).

11. Method according to one of the preceding claims, whereas the at least one work piece is made of one of the following materials:

- steel;
- a case-hardened steel;
- a heat-treatable steel;
- a quenched steel; and
- a tempered steel.

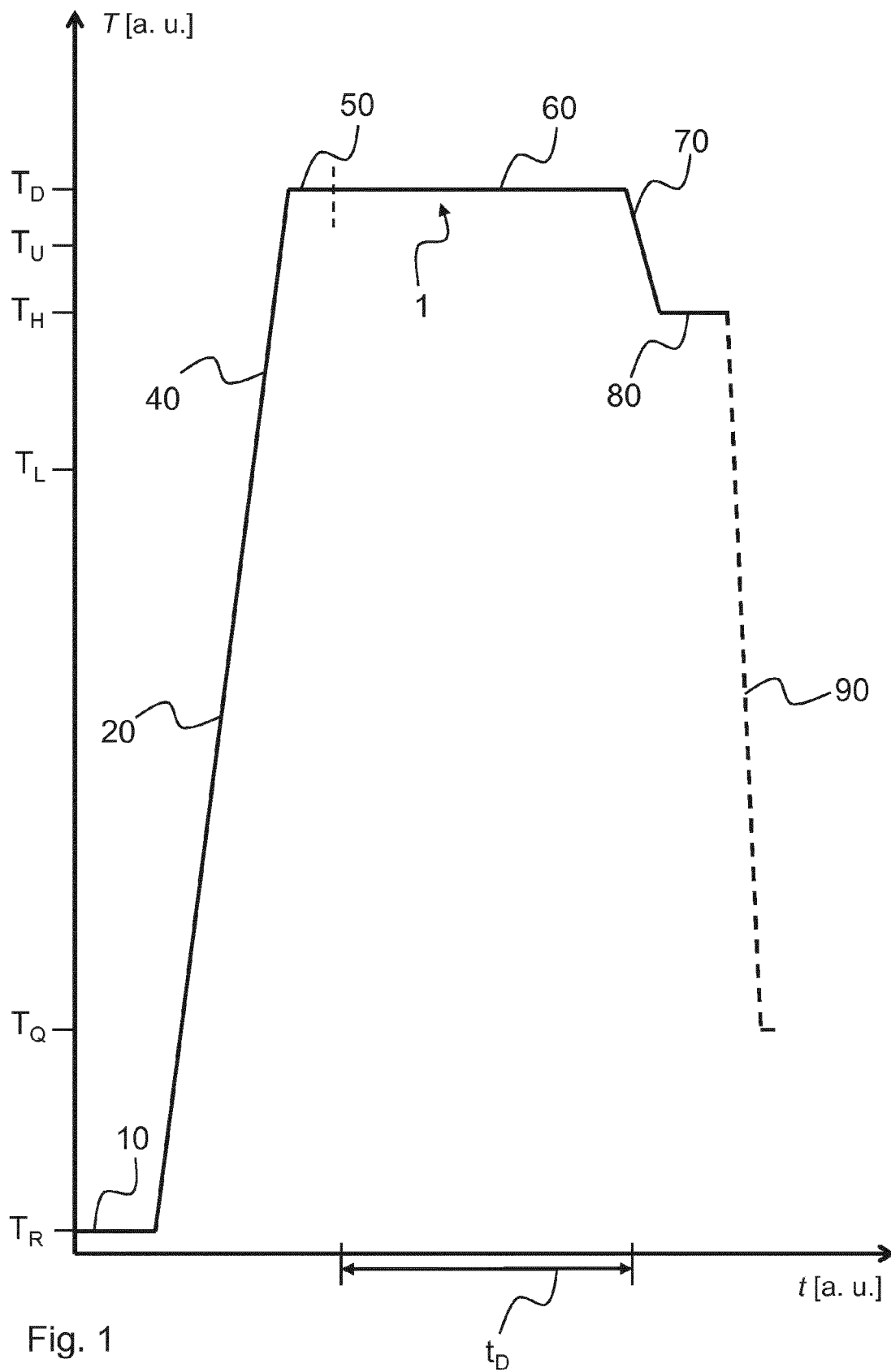


Fig. 1



EUROPEAN SEARCH REPORT

Application Number
EP 15 19 4562

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DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	WO 2012/048669 A1 (IPSEN INT GMBH [DE]; GROBLER HENDRIK [DE]; EDENHOFER BERND [DE]) 19 April 2012 (2012-04-19) * claims 1-15; figures 1,2 *	1-11	INV. C21D1/76 C21D11/00 C23C8/22 C23C8/26
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The present search report has been drawn up for all claims			
Place of search Munich		Date of completion of the search 9 May 2016	Examiner Catana, Cosmin
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