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A METHOD OF CARBONITRIDING METAL ALLOY COMPONENTS AT
LOW PRESSURE

DESCRIPTION

Technological field

The subject of this invention is a method of carbonitriding metal alloy components

It is particularly applicable to the carbonitriding of steel components, particularly high chromium steels
5 that can be used in high technology industries and the automobile industry.

State of the prior technology

Carbonitriding is a thermo-chemical process
10 involving the simultaneous diffusion of carbon and nitrogen from the surface of a ferrous alloy in the solid state. Generally it is carried out in a sealed furnace, in which a controlled atmosphere is maintained. The atmosphere is made up of a support gas
15 to which is added, if required in order to achieve the desired carbon potential, a carbon enrichment gas, and in addition, a nitrogen containing gas. Generally, the support gas is an endothermic generator gas comprising an alkane, which is oxidized to carbon monoxide CO
20 since the oxidation is carried out with less air than would be required for the stoichiometric reaction which would convert all the carbon into CO₂. The gases which are used can be nitrogen-methanol mixtures or endothermic mixtures based on hydrocarbon and ammonia,
25 as described in "Les Techniques de l'Ingénieur", M1226-8 on 14th July 1994, [1].

Hence, the traditional method uses atmospheres which all contain oxygen due to the presence of or to the formation of CO. The oxygen released by the decomposition of the CO leads to surface oxidation of the steel which, on the one hand slows up the absorption of carbon and, on the other hand leads to structures which are damaging to the mechanical properties of the treated component, for example, contact fatigue. It should be noted that components that are carbonitrided in this way are most often utilized as they are, without any mechanical retouching of the surface.

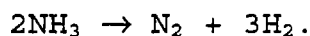
Document FR-A-2 663 953 [2] describes a method and an installation for the case hardening of metal alloy components at low pressure which avoids the presence of oxygen. This low pressure technique however has never been considered for carrying out carbonitriding treatments.

20 Description of the invention

The subject of this invention is a carbonitriding method which allows one to avoid the presence of harmful oxygen during the thermo-chemical treatment for diffusion of carbon and nitrogen into the metal alloy component.

According to the invention, the method of carbonitriding metal alloy components consists of subjecting said components to the action of a fuel mixture made up of ethylene and hydrogen and to the action of a nitriding gas consisting of ammonia at a pressure less than 100 hPa and at a temperature of from about 750 to 1050°C.

In this method, carbon is supplied by the direct dissociation of a hydrocarbon, in this case ethylene, within the confines of a furnace under vacuum, and the nitrogen supply stems from the dissociation of ammonia gas, in accordance with the heat activated reaction :



According to the invention, for this carbonitriding treatment, the temperatures used are higher than those usually used for this type of reaction, which are generally in the range of from 400 to 600°C.

At the higher temperatures used in the invention, the dissociation reaction of the ammonia is thermodynamically total, but its kinetics are slow. Because of this, there still remains ammonia to be dissociated at the component, which generates active nascent nitrogen. It is for this reason that ammonia can be used to supply the nitrogen.

On the other hand, the fact that one is working under reduced pressure allows one to benefit from the gas passing within the charge at a speed greater than that of the dissociation kinetics.

The pressure used can particularly be within the range of 10 to 100 hPa.

One of the other advantages of the method of the invention is to be able to enrich the surface of the component in carbon and in nitrogen within a temperature range that is much broader, from about 750 to about 1050°C depending on the enrichment sequence being considered. In effect, making use of the ethylene dissociation reaction at low pressure allows one to supply carbon from 750°C upwards and therefore by reducing the temperature one can benefit from the much

greater nitriding power of ammonia since the availability of atomic nitrogen, which is useful for diffusion, is much greater. This allows one to increase the possibilities for surface enrichment in carbon and
5 in nitrogen.

Hence, according to the invention, desired degrees and depths of enrichment in carbon and in nitrogen can be obtained by choosing, in an appropriate way, the flow rates of ethylene and of ammonia, the temperature
10 and the duration of the treatment by the fuel mixture and the nitriding gas as a function of the alloy that constitutes said components.

According to the invention, the carbonitriding can be carried out by subjecting said components to the
15 simultaneous action of the fuel mixture and the nitriding gas, or by subjecting said components to the successive action of the fuel mixture and the nitriding gas.

The treatment can also be carried out by subjecting
20 said components to the simultaneous action of the fuel mixture and the nitriding gas and then subjecting them to the action of the nitriding gas alone.

These steps can be repeated and combined with one another using different flow rates, temperatures and
25 durations, within the ranges given above.

Finally, the method of the invention can comprise an additional step of a diffusion treatment of the components under vacuum, after they have been subjected to the action of the fuel mixture and the nitriding
30 gas. Such a treatment can be carried out at a temperature from about 750 to about 1050°C under pressures that do not exceed 100 hPa.

The metal alloys capable of being treated by the method of the invention can be of various types. In particular, one can use steels and super-alloys based on cobalt. Among the steels, the method is
5 advantageously applicable to the treatment of steels that can be passivated and which contain, for example 2 to 9 % chromium and to the treatment of stainless steels containing for example 9 to 18 % of chromium thanks to the low pressure technique. Furthermore, the
10 treatment of such steels allows them to be enriched in nitrogen to a high degree that can reach 4 %.

At the present time, for certain applications associated with wear, these stainless steels are used in the case hardened state. After case hardening and
15 usage treatment, the hardened surface layer is very rich in chromium carbides, which seriously harms the corrosion resistance of these alloys which are naturally not oxidisable before case hardening.

Because, at the surface one is able to substitute
20 part of the carbon with nitrogen, precipitates of a different kind are allowed to form and they consume less chromium from the matrix. The nitrogen can also in part, go into solid solution in the matrix, its beneficial action on corrosion behavior in this form
25 being already recognized.

Therefore, through its flexibility, the method of the invention allows these steels, in their surface layer to be provided with the C/N ratio that offers the best compromise in properties sought for example,
30 between resistance to wear and resistance to corrosion.

In fact, by widening the temperature range, by the possibility of stringing together in a simple way various sequences of carbon and/or nitrogen enrichment

either simultaneously or alternately, the invention allows one to create very varied carbon and nitrogen gradients and this on a very diverse range of steels, even passive ones.

5 Another subject of the invention is steel components obtained by this method. These components can be, for example components made of steel that can be passivated comprising 2 to 9 % of chromium, which are enriched in nitrogen on their surface up to a level
10 of 2 % by mass, or stainless steel components comprising 9 to 18 % chromium, which are enriched in nitrogen on their surface up to a level of 4 % by mass.

In order to implement the method of the invention, one can use a so-called double vacuum furnace with hot
15 walls or a furnace with cold walls, such as the devices described in FR-A-2 663 953.

By way of example, the method can comprise the following steps :

1) preliminary evacuation of the furnace chamber
20 down to a pressure of 10^{-1} hPa in a way that eliminates the air,

2) filling the chamber with nitrogen at atmospheric pressure,

3) charging the chamber containing the metal
25 components and drawing a vacuum in the chamber to about 10^{-2} hPa,

4) heating to about the austenitization temperature with staging if necessary and holding this temperature for 30 minutes for homogenization of the components,

30 5) introduction of hydrogen preferably to about 500 hPa, or less depending on the type of furnace,

6) a carbonitriding treatment which can be carried out in different ways :

- a) a period of carbon enrichment by introducing the fuel gas ethylene followed by a period of nitrogen enrichment by introducing ammonia, or the reverse, or
- 5 a') a period of carbon and nitrogen enrichment by introducing ethylene and ammonia simultaneously,

7) possibly an enrichment treatment, analogous to that in step 6), or a diffusion treatment under vacuum

10 at a temperature of 750 to 1050°C, under a pressure of 10^{-1} hPa, for example, and

8) introduction of nitrogen into the furnace for the purposes of unloading it.

It should be noted that steps 6) and 7) can be

15 repeated several times if necessary.

During the passage of the ethylene and ammonia gases, the pressure in the chamber is preferably maintained at about 25 hPa.

20 Detailed description of embodiments

Other characteristics and advantages of the invention will emerge from the examples of embodiments which follow and which it is understood are given for illustrative purposes only and are non-limitative.

25 In the examples which follow, the alloys listed in Table 1 have been used. Their compositions (% by mass) are also given in Table 1.

In these examples, the general operational method described above has been followed for steps 1 to 5 and

30 8 and steps 6 and 7 have been carried out using different flow rates of ethylene and ammonia and different sequences of enrichment and/or diffusion.

In all the examples, a preliminary austenitization step is carried out under vacuum at 10^{-2} hPa, at a temperature of 850°C for 30 minutes. Then steps 6) and 7) are carried out under the conditions given in Table 2. In this Table, the reference numbers of the alloys used have been specified, their compositions being given in Table 1.

In examples 1 and 2, step 6) corresponds to a carbonitriding with simultaneous introduction of ethylene and ammonia and step 7) is a diffusion treatment under vacuum.

In examples 3 and 4, step 6) corresponds to a carbonitriding with simultaneous introduction of ethylene and ammonia (at a lower flow rate) and step 7) is a nitriding treatment by ammonia alone.

In examples 5 and 6, step 6) corresponds to a carburising and step 7) to a nitriding.

In examples 7 to 9, step 6) corresponds to a carbonitriding with simultaneous introduction of ethylene and ammonia, but the flow rate of ammonia is very high and step 7) is a diffusion treatment under vacuum.

In examples 10 to 16, only step 6) is carried out which corresponds to a carbonitriding with simultaneous introduction of ethylene and ammonia for a period of time greater than that used for the previous examples.

The results obtained in each example, that is to say, the profiles of surface enrichment in carbon and in nitrogen (in % by mass) for each of the alloys treated are given in Tables 3 to 8.

The results obtained in examples 1 to 6 on the traditional carbonitriding variations are close to

In examples 7 to 9, good results are obtained on treating alloys that are richer in chromium and hence
5 more passive.

In examples 10 to 16, it may be observed that one can superficially achieve very high nitrogen values with stainless steels rich in chromium where the percentages of nitrogen respectively reach 2.86 and 4 % nitrogen in examples 14 and 15. Hence nitrogen is, in part replacing the surface carbon, which allows layers to be obtained with particular properties.

The method of the invention is therefore advantageous since it leads to degrees of nitrogen enrichment that are much higher than those that can be
15 obtained by the traditional methods of carbonitriding where the nitrogen contents in the surface are at the most about 0.3 %.

20 References quoted

- [1] : Techniques de l'ingénieur M 1226-8 on the 14th
July 1994

- 25 [2] : FR-A-2 663 953

Table 1

Steel	C	Ni	Cr	Mo	V	Al
20 NC 6	0.17	1.60	0.85			
27 CD 4	0.27		1.0	0.2		
20 CD 12	0.25		3.0	0.4		
32 CDV 13	0.30		3.0	1.0	0.20	
40 CAD 6.12	0.40		1.8	0.25		1.0
20 DN 34.13	0.20	3.0		3.5		
Z 15 CN 17.03	0.16	2.0	17.0			
Z 12 CNDV 12	0.12	2.5	11.5	1.6	0.30	

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Table 2

Ex	Steel	Step 6)					Step 7)			
		t (°C)	time (min)	C ₂ H ₄ (l/h)	NH ₃ (l/h)	P (hPa)	t (°C)	time (min)	NH ₃ (l/h)	P (hPa)
1	20NC6	850	45	50	300	25	850	45	-	0.1
2	27CD4									
3	20NC6	850	45	50	300	25	850	45	100	25
4	27CD4									
5	20NC6	850	45	50	300	-	850	45	100	25
6	27CD4									
7	27CD4									
8	32CVD13	850	45	50	600	25	850	45	-	0.1
9	Z15CN1703									
10	20CN6									
11	27D4									
12	20CD12									
13	40CAD6.12	850	360	50	300	25				
14	Z12CNDV12									
15	Z15CN1703									
16	20DN34.13									

Table 3

Ex	1		2	
Alloy	20 NC 6		27 CD 4	
Depth (mm)	C %	N %	C %	N %
0.05	0.50	0.304	0.61	0.324
0.15	0.45	0.215	0.58	0.223
0.25	0.45	0.113	0.51	0.122
0.35	0.33	0.039	0.47	0.043
core	0.19	0.0059	0.27	0.0080

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Table 4

Ex	3		4	
Alloy	20 NC 6		27 CD 4	
Depth (mm)	C %	N %	C %	N %
0.05	0.72	0.297	0.75	0.279
0.15	0.66	0.203	0.69	0.189
0.25	0.57	0.114	0.61	0.102
0.35	0.46	0.049	0.51	0.037
core	0.19	0.0059	0.27	0.0081

Table 5

Ex	5		6	
Alloy	20 NC 6		27 CD 4	
Depth (mm)	C %	N %	C %	N %
0.05	0.79	0.148	0.82	0.165
0.15	0.71	0.094	0.72	0.078
0.25	0.56	0.029	0.57	0.028
0.35	0.37	0.0092	0.44	0.012
core	0.19	0.0059	0.27	0.0081

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Table 6

Ex	7		8		9	
Alloy	27 CD4		32CDV13		Z15CN17.03	
Depth (mm)	C %	N %	C %	N %	C %	N %
0.05	0.63	0.22	0.34	0.73	0.89	2.00
0.15	0.58	0.19	0.60	0.29	0.77	0.08
0.25	0.54	0.12	0.55	0.03	0.33	0.05
0.35	0.46	0.05	0.44	0.01	0.20	0.05

Table 7

Ex	10		11		12		13	
Alloy	20NC6		27CD4		20CD12		40CAD6.12	
Depth (mm)	C %	N %	C %	N %	C %	N %	C %	N %
0.05	0.98	0.52	0.93	0.44	0.60	0.89	0.81	0.98
0.15	0.86	0.51	0.86	0.44	0.54	0.80	0.77	0.84
0.25	0.81	0.45	0.79	0.41	0.54	0.55	0.89	0.48
0.35	0.73	0.31	0.77	0.31	0.73	0.12	0.80	0.04
0.45	0.65	0.20	0.66	0.24	0.57	0.04	0.66	0.01
0.55	0.56	0.09	0.51	0.15	0.46	0.02	0.57	0.01

Table 8

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Ex	14		15		16	
Alloy	Z12CNDV12		Z15CN17.03		20DN34.13	
Depth (mm)	C %	N %	C %	N %	C %	N %
0.05	0.41	2.86	0.61	4.00	0.57	0.53
0.15	2.07	0.26	2.45	0.36	0.53	0.41
0.25	1.32	0.07	1.21	0.08	0.50	0.31
0.35	1.62	0.04	0.51	0.05	0.46	0.19
0.45	0.22	0.03	0.26	0.04	0.40	0.11
0.55	0.14	0.03	0.20	0.04	0.35	0.08

CLAIMS

1. A method of carbonitriding metal alloy components, in which said components are subjected to the action of a fuel mixture made up of ethylene and hydrogen and to the action of a nitriding gas
5 consisting of ammonia, at a pressure of less than 100 hPa and at a temperature of from about 750 to 1050°C.

2. A method according to Claim 1, in which the pressure is from 10 to 100 hPa.

3. A method according to any one of Claims 1 and 2,
10 in which the metal alloy is a steel.

4. A method according to Claim 3, in which the flow rates of ethylene and ammonia, the temperature and the duration of the treatment by the fuel mixture and the nitriding gas are chosen in such a way that nitrogen
15 enrichment ranging up to 4% by mass, of the surface of the component is obtained.

5. A method according to any one of Claims 1 to 4, in which the metal alloy is a steel that can be passivated and which comprises 2 to 9% by mass
20 chromium.

6. A method according to any one of Claims 1 to 4, in which the metal alloy is a stainless steel that comprises 9 to 18% by mass chromium.

7. A method according to any one of Claims 1 to 6,
25 in which said components are subjected to the simultaneous action of the fuel mixture and the nitriding gas.

8. A method according to any one of Claims 1 to 6, in which said components are subjected successively to
30 the action of the fuel mixture and the nitriding gas.

9. A method according to any one of Claims 1 to 6, in which the components are subjected 1) to the

simultaneous action of the fuel mixture and the nitriding gas and then 2) to the action of the nitriding gas alone.

10. A method according to any one of Claims 1 to 9,
5 in which, after having subjected the components to the action of the fuel mixture and the nitriding gas, the components are subjected to a diffusion treatment under vacuum at a temperature of from about 750 to 1050°C.

11. A method according to Claim 5, in which the
10 surface of said component is enriched in nitrogen up to a content of 2 % by mass.

12. A method according to Claim 6, in which the surface of said component is enriched in nitrogen up to a content of 4 % by mass.