ENERGY SAVING BY AN ACCELERATED CARBURIZING PROCESS[1]

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Abstract
One of the most important heat treating processes is carburizing of steel. However, the relatively long process times makes carburizing (and related thermochemical processes) a particularly energy consumptive and costly process. If significant reductions in process times or temperatures could be achieved, this would result in reduced energy consumption and substantial process cost savings. There have been a limited number of references describing different methods of carburizing process acceleration. In this paper, an overview of one process that is relatively widely used in China will be provided.

Key-words: Thermochemical process; Carburizing process acceleration

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INTRODUCTION

Although various methods of accelerating the carburizing (and carbonitriding) process including the use of rare earth metals have been published [1,2,3]. Although numerous subsequent references were published which offered great hope to the industry, none of these methodologies reached commercialization. More recently, the so-called BH Catalyzing Technology was developed at Northwest University in China which was successfully commercialized at: the China First Automobile Corporation (Underpan company), Dongfeng Automobile Corporation(Gear box company), three of the four largest bearing manufacturers, and many manufactures of gear, chain, piston pins. In some cases, these companies achieved lower process temperature and decreased distortion along with finer grain size. Other companies achieved faster process times thus increasing production efficiency and reducing production costs. The objective of this paper is to provide an overview of the industrial application of the Chinese BH Catalyzing Technology.

DISCUSSION

Part 1 – Process Mechanism

Currently, three processes have been identified which may result in an acceleration of the carburizing process: a) oxidation erosion technology, b) rare earth catalysis and c) the Chinese BH Catalysis Technology. A brief overview of each will be provided here.

a. Oxidation Erosion Technology

It is well-known that surface oxidation and also contamination with cutting and scouring fluids can potentially produce a passivation layer on the steel surface. This layer will inhibit carbon diffusion into the surface of the steel during the carburizing or process. If this passivation layer can be effectively removed, diffusion of carbon will be accelerated. Conceptually, this can be accomplished in two ways:

One method can be designated as the "Surface Pre-oxidation Method" which is performed by heating the workpiece to 400-500°C without atmosphere protection. This will produce an oxidation film:

$$3\ Fe + 2\ O_2 \rightarrow Fe_3O_4$$

During the carburizing process, the CO in the atmosphere will reduce Fe_3O_4 to ferrite:

$$Fe_3O_4 + 4\ CO \rightarrow Fe + 4\ CO_2$$

Ferrite formed in this way is "activated" since there is no oxide layer to inhibit carbon diffusion into the steel surface which results in accelerates diffusion kinetics. Although the "Surface Pre-oxidation Method" is used in practice, experience has shown that it only facilitates uniformity and has no substantial affect on carburizing speed.

The second method is designated as the "Chemical Erosion Method " which is conducted by the addition of a strongly erosive agent such as CCl_4, HF and iodine salt during carburizing. These chemicals erode and activate the surface of workpiece by removing the diffusion inhibiting layer resulting in an acceleration of the carbon diffusion process. However, for obvious reasons including corrosiveness toward the component being carburized and the equipment and fixtures and toxicity of the eroding chemicals, this method is rarely used commercially.

b. Rare Earth Catalysis

Rare earth metals include those of the Lanthanide and Actinide series, Group 3 and Periods 6 and 7 in the periodic table. Examples include: lanthanum (La), actinium (Ac) and cerium (Ce). Although rare earth metal penetration into the an lattice to form a solid solution does not conform to the Hume-Rothery rules of formation of solid solutions (difference in atomic diameter between the solvent and solute should be less than 15%) [4] nor do they conform to Vegard's Law (crystalline solid-solution alloys have unit cell dimensions that are frequently linear with concentration) [5] however, it has been shown that rare earth metals such as cerium do not only diffuse into steel along the grain boundaries but also into the internal grain structure [6]. It has been further shown that when rare earth metals are mixed with carburizing reagents such as kerosene and methanol and introduced into a furnace atmosphere at 850-910°C, carburizing and carbonitriding reactions are significantly enhanced [7-12]. It was reported by Yuan that the catalytic mechanism involves rare earth metal reaction with surface oxides during the carburizing process [8] and the rare earth metal subsequently diffuses into the metal to a significant depth [7,8]. An approximately 20% increase in case depth (0.35% C) was achieve with rare earth catalysts versus conventional, uncatalyzed processes. Also the ise of rare earth metals permits reduced carburizing times or the use of lower temperatures which can result in substantial energy savings. However, research on the use of rare earth metals in heat treatment thermal processing is still underway and at the present time these processes are not widely practiced in industry.

c. BH Catalysis Technology

Of the three methods proposed to accelerate the carburizing process, only the proprietary BH Catalysis Technolog is widely used in the Chinese heat treament industry. It is assummed that the overall BH process, which can be used for either carburizing or carbonitriding, embodies four steps:

1. The so-called BH-Catalyzer facilitates decomposition of the source of materials used to generate carbon or nitrogen for surface adsorption.
2. Upon formation, the active carbon and nitrogen species are dispersed in the gas phase;
3. Activated carbon and nitrogen subsequently form a layer (gaseous boundary layer membrane) by adsorption which surrounds the workpiece (adsorption) as illustrated in Figure 1;
4. The activated carbon and nitrogen species in the boundary gaseous membrane are then absorbed into the surface and then diffuse into the steel to form the carbon and/or carbon-nitrogen enriched case.

The first and second step reactions are very fast. The third step reaction is somewhat slower and the fourth step is proposed to be rate determining. (Although proposed, the actual reaction kinetics have not been determined.) Steps three and four are vital to the BH Catalysis process.

During carburizing the active elements of atmosphere contact with workpiece create following chemical reaction which leads to the formation of the gaseous boundary layer membrane at the steel interface as shown in Figure 1:

$$CO+H_2 \rightarrow [C]+H_2O\uparrow \quad CH_4 \rightarrow [C]+2H_2\uparrow \quad 2CO \rightarrow [C]+CO_2\uparrow$$

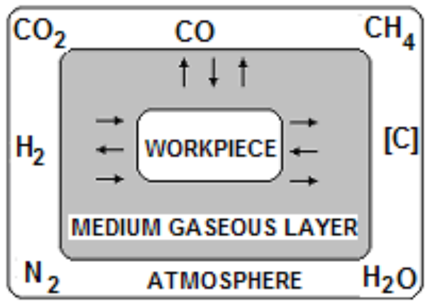

Figure 1. Medium gaseous membrane formation.

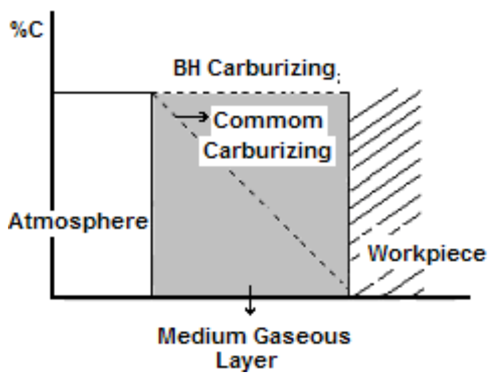

Figure 2. Carbon concentration gradient formed within the gaseous membrane.

During the carburizing process, a carbon concentration gradient carbon is formed within the gaseous boundary layer membrane where the carbon concentration at the steel interface is less than at the outside of the membrane layer as shown in Figure 2($\Delta C=C1-C2$). One of the functions of the BH Catalysis process is to "shock" the gaseous boundary layer film that is formed thus reducing the carbon gradient. This will produce a more uniform carburized case.

At this time, the structure of the diffusing carbon species has not been identified although it would seem that it may involve a sterically smaller cationic carbon intermediate as opposed to atomic C-1 carbon. This may be consistent with observed faster carbon diffusion during ion carburizing processes. Figure 3 illustrates the expected carbon profile for a slower C-1 diffusion process versus a faster carbocation diffusion process. The carbocation diffusion produces a smoother carbon gradient from the surface through the case. (However, the actual reaction and diffusion mechanism is currently being determined).

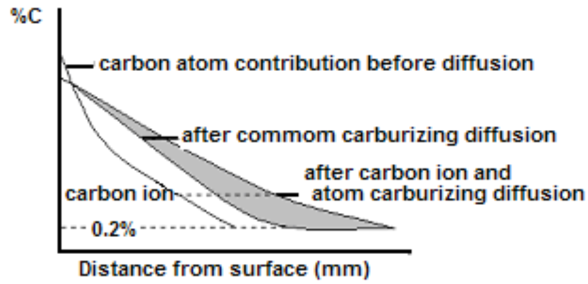

Figure 3. Comparison of the expected carbon profiles in the case after carburizing for C-1 carbon vs carbocation diffusion.

During conventional carburizing, if atmosphere is decomposition incomplete or if the decomposition too fast, the absorbing carbon species will not be absorbed by workpiece surface and the presence of carbonaceous carbon (carbon black or “soot”) will increase. The BH catalyst solution contains a micro-dosage of a decomposition agent to control carburizing reagent decomposition speed, thereby limiting carbon black formation. The BH catalysis process therefore provides for improved control of the carbon potential, optimizes the concentration of the diffusing carbon species and reduces consumption of the carburizing reagents.

An advantage of the reduced heating time and temperature is that a finer grain size will be produced along with correspondingly less distortion. This is consistent with production experience to be discussed below.

Part 2. Industrial applications of BH Catalysis Technology

Of the different carburizing process technology enhancements described above, the BH Catalysis Technology is currently in greatest use industrially. Some examples include: FAW (oilpan factory), DFAC(gear box factory), three of the four largest bearing manufactures in China, and various gear manufacturers in Harbin ,Datong, Zhuzhou, Wuhan(Shuangjun),Jiangsu(Feichuan),Hubei(□□)□and Shanghai Fifth Branch Automobile Gear Corparation. All of these companies have adopted BH catalyzing technology. The diffusion processes using BH Catalysis Technology include: all the types of continuous furnaces, sealed quench furnaces, pit-type furnaces, belt furnaces, and others. In addition to conventional endo gas, atmospheres include: methanol, ethanol, acetone, nitrogen methanol, and kerosene.

One example of the successful use of BH Catalysis is the production of half-axle gears (20CrMo) in a 105 kW pit-type carburizing furnace at the Jinggong Gear Factory of DFAC. In this case, the BH catalyst was added to kerosene or methanol. A summary of the carburizing process without and with the BH catalyst is provided in Figure 4A and 4B respectively.

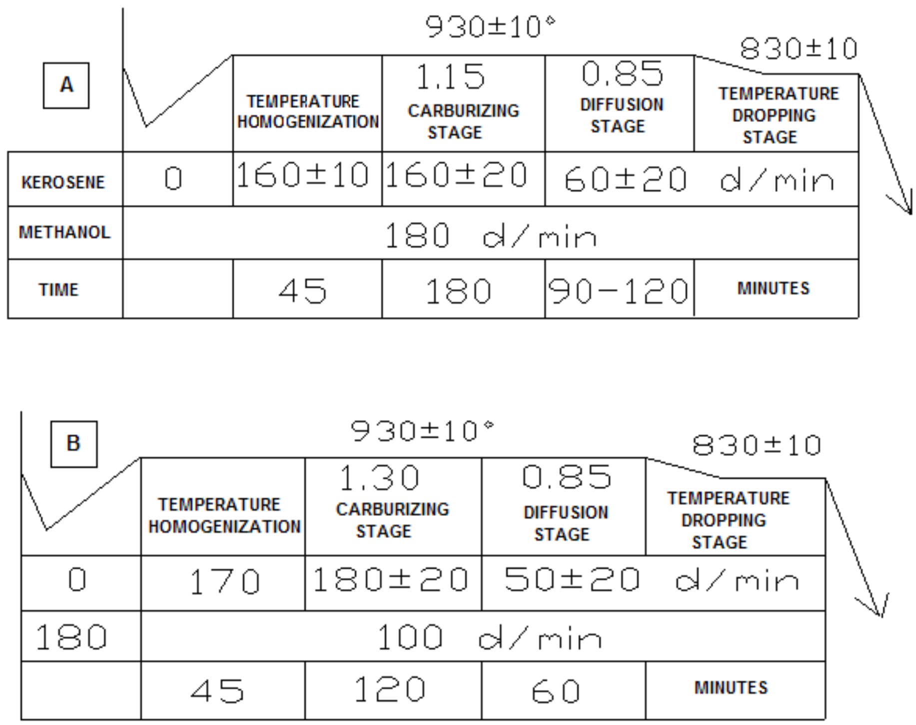

Figure 4. Summary of carburizing process: A. without BH catalyst and B. with BH catalyst.

Table 1 provides a summary of experience gained to date with BH catalyzed carburizing processes in more than 50 sealed quench furnaces throughout China. Although most of the furnaces are are manufactured by Chinese furnace companies (RICLIN, FAW and Fengdong) , some of the furnaces evaluated are Ipsen furnaces. The results obtained shows that approximately 20% reduction in carburizing time and approximately 25% reduction in total energy consumption while providing equivalent case depth and hardness.

Table 1. The average performance of more than 50 furnaces before and after the use of BH Catalyst Technology.

	Carbide Grade(*)	**M/A**	**Surface hardness (HRC)**	**Hardened layer depth (mm)**	**Average cycle (hour)**	**Average electricity consumption per furnace(**)**
Without BH Catalyst	Grade 1-2	Grade 1-5	58-62	1.0-1.2	10.2	360°
With BH Catalyst	Grade 1-2	Grade 1-4	58-62	1.05-1.15	8.1	270°

(*) National carbide dimension and distribution standard in China
(**) 1° in the electricity consumption means 1KW.h

In another application, the Hubei Vehicle Company evaluated the BH Catalyst Technology in a Richlin Box-Type Multi-functional Furnace for the heat treatment of helical corner gears. The results of this study showed:

- Improvement in fatigue life.
- A 25% improvement in carburizing efficiency when comparing performance before and after the use of the BH catalyst at the same furnace temperature.
- The productivity improvement offsets the added cost of the use of the BH catalyst.
- Significant improvement in deformation is obtained which results in a considerable improvement in noise reduction (75-78 db decrease)

Harbin Zhuzhou Automobile Gear Factory evaluated the use of BH Catalyst Technology using a continuous furnace. The results, summarized in Table 3, show that the time to achieve the same case depth was reduced from 60—65min to 45 min, and the furnace output was increased by 20%.

Table 2. Quality test results for Hubei Vehicle Company Helical Corner Gears Before and After the Use of BH Catalyst

		Before BH Catalyst Use					After BH Catalyst Use				
Hardened layer depth(mm)		1	2	3	4	5	1	2	3	4	5
Carbide		1.2	1.1	1.3	1.25	1.2	1.2	1.15	1.15	1.1	1.15
M,A		4	5	3	5.5	4.5	3	1.5	2	2.5	2
Surface hardness (HRC)		4.5	3	5	3.5	4	3	2.5	3	3.5	3
Inside hardness (HRC)		59	60	59	62	60	60	62.5	61	60	61
Defor-mation	Inside hole	0.06	0.07	0.09	0.10	0.08	0.06	0.05	0.06	0.06	0.06
	Inner section	0.12	0.15	0.12	0.13	0.13	0.10	0.11	0.09	0.08	0.09
	Outer section	0.09	0.10	0.11	0.09	0.10	0.08	0.07	0.08	0.06	0.07

Table 3. Harbin Zhuzhou Automobile Gear Factory Continuous Furnace Results

	BH Catalyst	Degrease furnace	Zone 1	Zone 2	Zone 3	Zone 4	Zone 5
Temp. (°C)	Original	480	840	900	930	910	830
	BH	480	870	900	930	910	830±10
CP□	Original	------	------	------	1.10□	1.0□	0.80□
	BH	------	------	------	1.20□	1.0□	0.80□
acetone	Original	------	------	3—4	16	20	0
	BH	------	------	5—6	16—18	0	0
methanol	Original	------	------	50	50	50	30
	BH	------	------	40	30	30	50

The FAW Heat Treatment Factory uses BH Catalyst technology for the gear production (both drivers and driven gears) in a pusher furnace. The Table 4 summarizes the heat treatment conditions of both processes and shows that they obtained a 25% increase in production rate with the use of the BH catalyst.

Table 4. Summary of FAW Pusher Furnace Results Before and After the Use of the BH Catalyst

Zone		1	2	3	4	5
Temp (°C)	No Catalyst	900	930	940	900	840
	With BH Catalyst	900	930	940	900	840
Carbon potential	No Catalyst	/	/	1.15	0.100	0.80
	With BH Catalyst	/	/	1.30	0.100	0.80
RX M^3/h	No Catalyst	6	5	4	5	5
	With BH Catalyst	4	3	3	4	5
BH Catalyst ml/h	No Catalyst	0	0	0	0	0
	With BH Catalyst	/	3	3	3	/
pushing cycle	**No BH Catalyst**	**Carburizing layer control to 1.2-1.6 mm, 48min./unit.**				
	With BH Catalyst	**Carburizing layer control to 1.2-1.6 mm, 36min./unit.**				

Measurement of the carbon distribution showed that more uniform diffusion had occurred with the gears produced by the BH Catalyzed process. An abrasion test using an abrading wheel of GGr15 (0.95%-1.05% C; 0.15%-0.35% Si; 0.25%-0.45% Mn; 1.40%-1.65%Cr) was conducted for 10 hours to determine the maximum abrasion width. The results illustrated in Figure 4 show that the abrasion performance is significantly improved with the use of the BH catalyst.

CONCLUSION

A very brief introduction to three methods of accelerating carburizing and carbonitriding diffusion processes which include: a. Oxidation erosion technology, rare earth metal catalysis and the so-called BH-Catalyst Technology. The BH Catalyst Technology is a proprietary process that is widely used throughout China. Typically 20-25% productivity improvements can be used because of faster carbon diffusion rates. Alternatively, it is possible to conduct carburizing processes at a lower temperature and achieve an approximately 20% reduction in energy consumption. These benefits provide an enormous potential benefit to the heat treater.

Work is currently in progress to provide a better mechanistic understanding of the chemistry and surface and diffusion mechanisms involved in the BH catalyst process.

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ECONOMIZANDO ENERGIA ATRAVÉS DE UM PROCESSO ACELERADO DE CEMENTAÇÃO

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Resumo

A cementação é um dos mais importantes processos termoquímicos mais importantes para o aço. Entretanto, devido aos longos tempos envolvidos, há o consumo de grande quantidade de energia, o que resulta na elevação dos custos nesse processo. Reduções em tempo ou temperatura, resultariam em uma acentuada redução do consumo dessa energia, acarretando uma diminuição nos custos. A literatura mostra um número limitado de trabalhos nesta área. O objetivo desse trabalho é descrever um processo, já bastante difundido na China, que permite a reduzir o tempo da cementação.

Palavras-chave: Processo termoquímico, Aceleração do processo de cementação

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