

Vacuum Carburizing Steel Alloys Containing Strong Carbide Formers

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Abstract

Carburizing grades of high strength steels, such as Ferrium C-64 alloy, contain strong carbide forming elements such as chromium and molybdenum. Alloys with high amounts of strong carbide formers can form stable carbides during carburization that effectively block carbon diffusion and retard the carburization process. This is especially true for low pressure carburization. To achieve the desired case depth, the low pressure carburization process consists of a series of rapid boost and longer time diffusion cycles. One problem is how to determine an acceptable carburization schedule. This paper will discuss a methodology used to develop the data for Ferrium C-64 so that a proper low pressure carburizing schedule could be determined. Integral parts of this methodology are experiments to determine carbon diffusion rates, carbide formation kinetics, and carbide dissolution kinetics, and use of these data in computer software to simulate the process and to determine the proper schedule.

Introduction

A great deal of steel alloy development over the last few decades has focused on achieving ultra-high strengths in carburizing steels for application in gears and shafts. The basis for this emphasis has been increasing the power density of power trains without increasing weight or decreasing performance life. Indeed, improved steels have been produced, including alloys such as Pyrowear 53, Pyrowear 675, Ferrium C64, and CSS-422L. Major alloying elements include strong carbide formers such as chromium, molybdenum, and vanadium. Other elements, such as nickel and cobalt, are added for other property enhancement reasons. The high amounts of the strong carbide forming elements affect the carburization process, as explained in this paper.

Figure 1 shows graphically what happens during gas carburization.[1] A carbon potential, C_p , exists within the furnace chamber due to the gas composition. The base carbon of the steel part, C_0 , is lower than the gas carbon potential, so carbon is deposited on the part surface and is diffusing into the part. As the surface reaction continues, a boundary layer, β , exists as the neighboring gas carbon potential is reduced. D_c

is the diffusion coefficient of carbon in the steel. With time, the surface carbon level, C_s , increases, and the carbon level within the steel increases. This figure depicts Fick's Law of Diffusion.

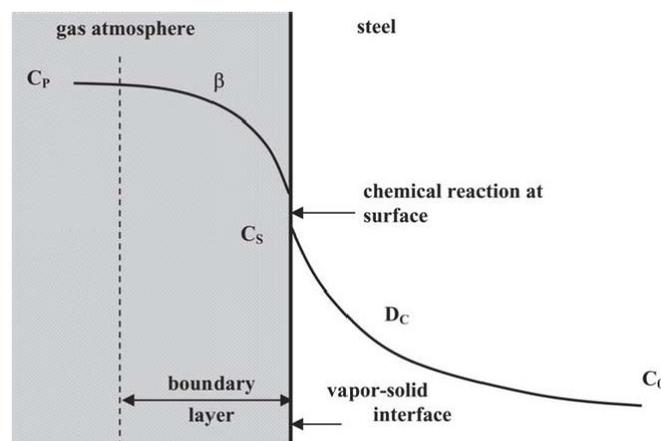


Figure 1: Graphic representation for gas carburization.[1]

Table I lists major alloying elements for commonly carburized steel grades and for several of the newer high strength grades. The more traditional grades, indicated by the light shading, have levels of strong carbide formers that total less than 1 weight percent, and conventional gas carburization is the main process applied to develop the high carbon case. Grades such as 9310 and P53 have intermediate levels of strong carbide forming elements and can be either gas or low pressure carburized. The higher alloy grades, indicated by the dark shading, are typically low pressure carburized because of their carbide forming tendency. Their ease of forming alloy oxides on the surface during gas carburization also is a factor in favoring the use of LPC for these grades.

Very simple equations are used to calculate the development of the carburized case in terms of time, temperature, and atmosphere carbon potential. Because the gas carburizing times are long, i.e. several hours, the change in surface carbon level is usually overlooked and carbon potential is immediately applied to the surface of the part. An example calculation of

Table 1: Carburizing Steels Showing Base Carbon Level and Amount of Strong Carbide Forming Elements.

Alloy	%C	%Cr	%Mo	%V	Other
1020	0.2	-	-	-	
4120	0.2	0.5	0.17	-	
4320	0.2	0.5	0.25	-	
5120	0.2	0.8	-	-	
8620	0.2	0.5	0.2	-	
9310	0.1	1.2	0.12	-	
P53	0.1	1.0	3.0	2.0	Mn, Si, Cu
P675	0.07	13.0	1.8	0.6	Co
C64	0.11	3.5	1.75	-	Co, W
CSS-422L	0.12	14.0	4.75	0.6	Co
M50	0.12	4.5	4.0	1.2	Ni
NiL					

total case depth for gas carburization is found in equation (1) below:

$$\text{Case depth} = f * \sqrt{t} \quad (1)$$

where t is time in hours and f is a temperature dependent factor that is essentially a diffusion related term. Notice that there is no relation to different modes of diffusion (boundary or bulk), and there is no provision for alloy effects. Yet, this equation works fairly well for the commonly carburized grades of carbon and low alloy steel.

Many equations to characterize carbon diffusion in iron and low alloy steels have been developed over the many years that carburization has been practiced. Three commonly used equations for diffusion coefficient D expressed as cm²/s are:

$$D(T,C)=0.47*\exp[-1.6*C]*\exp[-(37000-6600*C)/R/T] \quad (2)$$

$$D(T,C)=(0.04+0.08*C)*\exp[-31350/R/T] \quad (3)$$

$$D(T,M,C)=(0.146-0.036*C*(1-1.075*Cr)+\sum k_1*M)*\exp[-(144.3-15.0*C+0.37*C^2+\sum k_2*M)/R_k/T] \quad (4)$$

where T is temperature, °K,
C is weight percentage of carbon,
k₁ and k₂ are multiplying factors for specific elements,
M is weight percentage of Mn, Si, Ni, Cr, Mo, or Al,
R is the universal gas constant, 1.986 cal/mol/°K, and
R_k is the gas constant expressed as kJ/mol/°K.

These equations are valid within particular chemistry ranges, as discussed in references [2] for eq.(2), [3] for eq.(3), and [4] for eq.(4). A graphical comparison of these equations is shown in Figure 2, where it is obvious that diffusion coefficient increases markedly with temperature, and also with carbon content. What is not as clear is the effect that alloying elements, especially chromium, have on carbon diffusion.

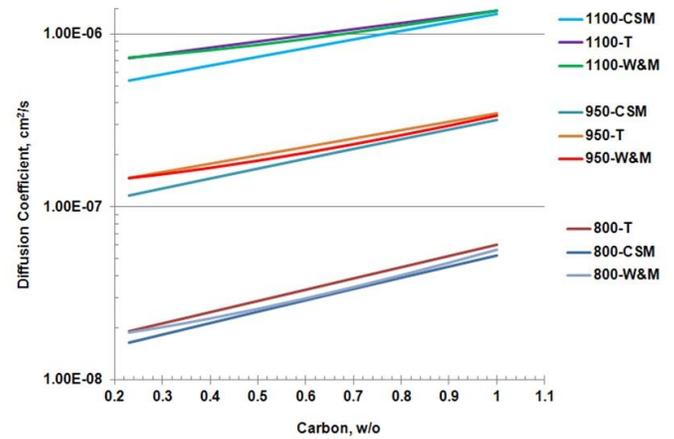


Figure 2: Calculated diffusion coefficient as a function of carbon percentage at three temperatures, 800 C, 950 C and 1100 C. 'T' is for eq.(2), 'W&M' is for eq.(3), and 'CSM' is for eq. (4).

As the chromium content is increased, the phase diagram changes, with the austenite field shrinking.[5] Figure 3 shows a section of the Fe-C phase diagram and Figure 4 shows an isopleth for the Fe-C-Cr ternary phase diagram for 5% Cr. In Figure 3, austenite saturation with carbon does not occur at carburizing temperatures until the carbon level exceeds about 1.5%C. At higher temperatures, even more carbon is dissolved in austenite. Figure 4 for 5%Cr shows that the austenite phase field is smaller at this Cr level, and the eutectoid composition also is decreased somewhat. The reduced size and shift of the austenite zone means that austenite will saturate at lower carbon levels in steels with higher chromium content than steels with lower chromium content, and alloy carbides can more readily form. For steels with yet high chromium content, such as P675, the austenite field is indeed small and alloy carbide formation is pronounced. The possibility of forming many types of carbides becomes widely spread over the elevated temperature range. While these diagrams are for equilibrium and carburizing is a transient condition, the diagrams show the increased difficulty of avoiding carbide formation during carburization as carbon is added to higher chromium content steels. Reference [6] reports that chromium effectively decreases the diffusion of carbon in steel, and this is largely a result of the strong affinity of chromium for carbon. Keep in mind that Table I shows that austenite stabilizers such as Ni and/or Co are often used in high Cr and Mo steels to counteract the shrinkage of the austenite field.

Iron-Carbon Phase Diagram

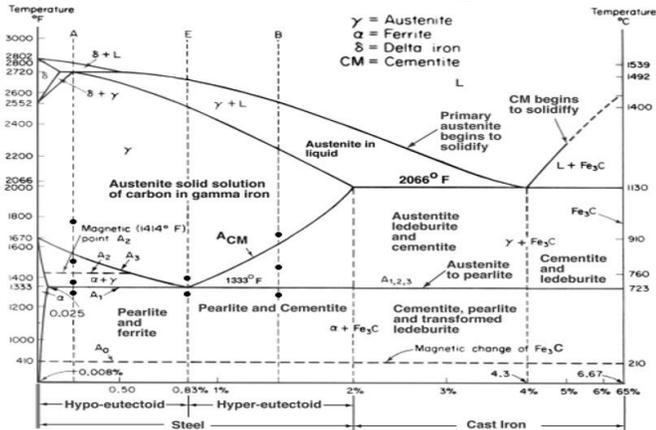


Figure 3: Portion of Fe-C equilibrium phase diagram.[5]

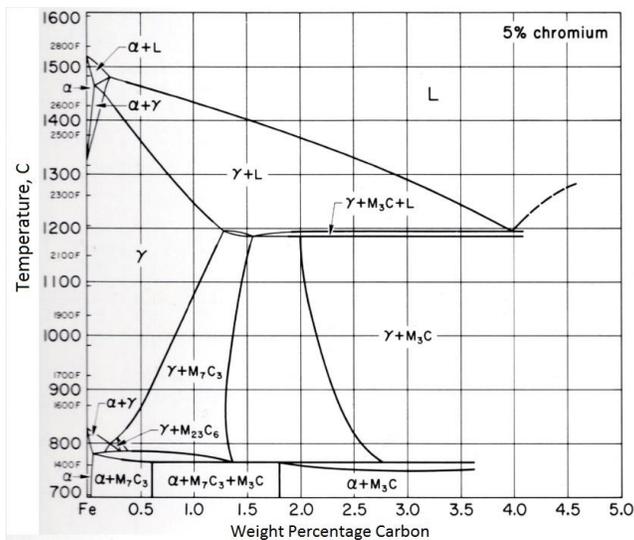


Figure 4: Isoleth from Fe-Cr-C ternary phase diagram for 5% Cr.[5]

Because the austenite phase field exists under tighter bounds of temperature and carbon level in high strength steels, carburization becomes more difficult. The simple equation mentioned no longer holds as the possible formation of carbides greatly affects diffusion; effectively carbide formation blocks carbon diffusion.[7] The carburizing process must be designed with carbide formation in mind.

The carbon source in low pressure carburizing is a gas or mix of gases that dissociate at the hot part surface to deposit carbon. The scenario that is effective for low pressure carburizing of steels alloyed with strong carbide formers such as Cr and Mo is to use a series of boost and diffuse steps. Once the load of parts has been heated to the carburizing temperature and a low pressure established, a carbon source gas such as acetylene (C_2H_2) is introduced at a low partial pressure. Often hydrogen gas is used to clean or activate the part surfaces before the carburizing gas is introduced. Also, an inert gas such as nitrogen may be added with the carbon source

gas as a circulation aid and to dilute the carbon source gas. The carbon source gas dissociates directly on the hot part surfaces, instantly providing carbon that is available to diffuse into the steel. Investigators have reported that the gas dissociation first decays the gas molecules to intermediate radical forms that then breakdown to crystalline graphite.[8,9] Hydrogen gas is typically the other product of the dissociation. This pure carbon then diffuses into the steel, with diffusion down grain boundaries superseding diffusion into austenite grains. The concentration of carbon in grain boundaries promotes carbide formation if the gas dissociation reaction is allowed to continue for too long of time or if the partial pressure of carrier gas is too high (too much dissociation). If this boost time is too long for the amount of carbon gas present, surface carbides will form that block carbon diffusion, eventually causing soot and even tar to form. Hence, a short, controlled boost time is typical, meaning the partial pressure of the carbon source gas is reduced to allow time for any minute carbides that formed to dissolve and carbon diffusion to occur to reduce the surface carbon level. Once sufficient diffusion has occurred, the carbon source gas is reintroduced and the boost step scenario repeats. As the process continues, the boost times remain short and the diffuse step times increase since the surface austenite saturates and more time is needed to lower the surface and near-surface carbon levels by diffusion.

Experiments were run using acetylene as the carbon source gas and Ferrum C64 alloy steel to characterize the low pressure carburization process.

Experimental Results and Discussion

Low pressure carburization trials were run using cylinders with a diameter of ~100 mm. LPC tests were conducted following different boost & diffuse schedules and temperatures to generate different carbon and hardness profiles in these cylinders. Using the combinations of profiles and LPC schedules, carbon diffusion was characterized for Ferrum C64. An example trial schedule is shown in Figure 5. As shown, it is a series of four short boost and diffuse steps, followed by a long diffuse step.

The procedure for determining the carbon profile was to carefully machine a 0.05 mm layer from the cylinder using a sharp single point lathe cutter while collecting the chips. By sequentially doing this, individual bags of chips with different carbon content were collected. Then, each segregated collection of chips was subjected to LECO testing to determine the carbon content. This is not a fool-proof method, but with care, the results are accurate. A major problem to avoid is overheating of the chips and/or bar during single point turning, which would result in reduced carbon measurement for that sample set. Microhardness measurements were taken on metallographically prepared mounted sections, and can be compared against the carbon values.

Hardness and carbon profiles determined for four different trial runs are plotted in Figure 6. The relationship between

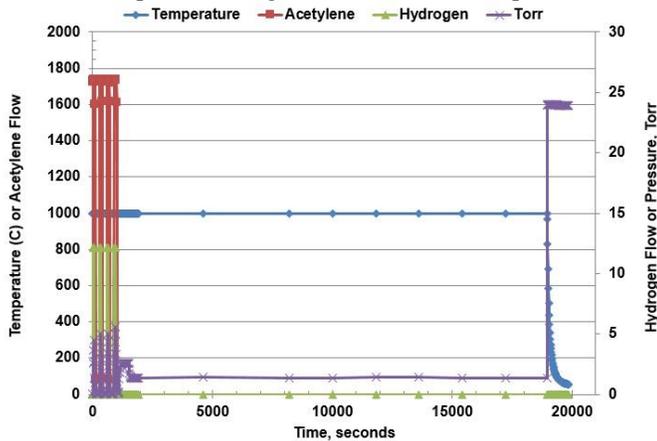


Figure 5: Example LPC schedule followed in one trial run.

hardness and carbon level for a martensite microstructure for C64 is not documented. However, the published data sheet for C64 reports that the Jominy hardness is HRC 43 and that typical core hardness values in carburized parts should be HRC 47 to 50.[10] From Figure 6, the measured microhardness of HRC 45 at a depth of 2 mm his should be at the base carbon level of 0.11%. Runs 1-3 were at a carburizing temperature of 1000° C, and run 4 used a temperature of 940° C. The boost total time was the same for all runs, but the total diffuse time increased from run 1 to run 3, with the diffuse time for run 4 being the same as that of run 2. Observations from Figure 6 are that longer diffuse total time gave deeper penetration of carbon, and that the higher carburization temperature of 1000° C gave a deeper case than the lower 940° C carburizing temperature. These observations were as expected, and they are more easily observed from the hardness data. The carbon data has a lot of variation and is more difficult to interpret. Complicating the issue is the possibility of carbide formation and interference with pure diffusion of carbon through the austenite lattice during carburization.

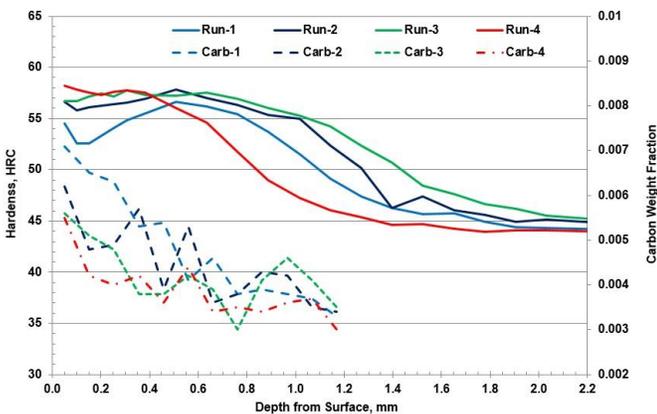


Figure 6: Hardness and carbon profiles measured for a LPC trial.

Predicting the development of the final carbon profile must include decisions about carbon saturation of austenite, possible

carbide formation and growth, carbide dissolution, and carbon diffusion. Figure 7 shows a framework for such decision making in determining a proper boost – diffuse schedule for an LPC process. Material property data needed to simulate carburization includes is shown in the block labeled ‘Steel Grade.’ A part will have a specification for carburization that as a minimum includes case depth (usually hardness at a specified depth) and surface hardness. These may be specified at particular location(s), and hardness is specified rather than carbon level because it is much easier to measure. For simulation, the part geometry must be known, and for LPC the total surface area to be carburized should be known since the carbon source gas will dissociate on the surfaces of parts and provide the amount of carbon needed to fulfill the case requirement. Once the carrier gas type is specified, the calculations can be made to determine time to saturate austenite at the carburization temperature, i.e. boost step, and the time needed to diffuse carbon away from the surface, i.e. diffuse step. Then the number of boost and diffuse steps can be determined to meet the specified case requirements.

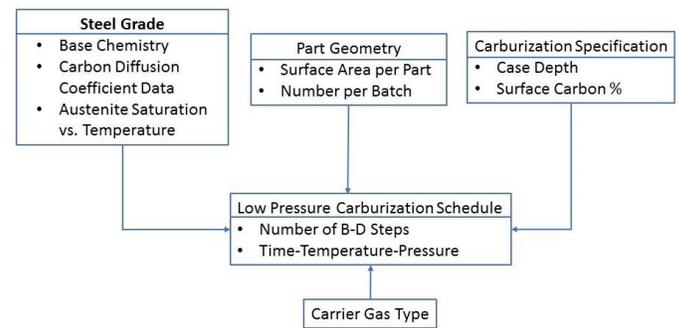


Figure 7: Framework for LPC simulation software.

Figure 8 shows results for a simulation that used nine boost and diffuse steps in an LPC run. There are two curves each for two locations, position 501 on the surface and position 492 at a depth of 0.25 mm below the surface. The solid lines are carbon weight fraction predictions, and the dashed lines are normalized carbide size predictions. This boost diffuse schedule is predicted to produce carbides at the surface that form during the first boost and persist through the entire LPC process. The subsurface location is predicted to form carbides during the last long diffuse step, but these dissolve after forming. From the plot, carbide formation is predicted to occur when the carbon weight fraction hits 0.010. To prevent any carbide formation, the carbon weight fraction should remain below this level **for the steel properties used in this model**. The emphasis on this last phrase is important as the plot in Figure 7 is not for C64, but it is for a similar alloy.

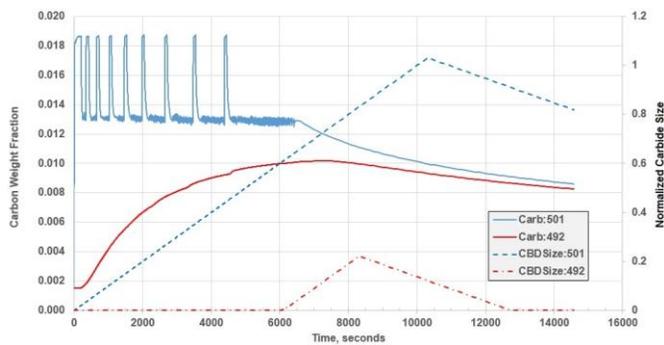


Figure 8: LPC simulation results for a hypothetical high alloy steel that shows carbide formation and dissolution during a nine step boost – diffuse schedule.

Summary

Modeling carburization of higher alloy content steels, especially alloys containing chromium contents above 1.0%, requires more than a simplified mass diffusion model. Carbide formation, carbide growth and dissolution all can impact the development of the carburized case. Low pressure carburization has the added complication of rapid carbon build up on the part surface due to direct dissociation of the carbon source gas right on the hot part surface. However, this rapid carbon build up brings with it the ability to more rapidly develop a desired case and also the ability to tailor the shape of the carbon profile. An accurate and comprehensive simulation software gives the heat treater or part designer the ability to take advantage of LPC capabilities while avoiding the possible detriments of excessive surface and grain boundary carbides or surface contamination by soot or tar.

References

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