

# New-Formula Acetylene Cool for Heat Treatment

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Acetylene with DMF solvent enables benefits of low-pressure vacuum carburizing

The vacuum carburizing process continues to evolve, constantly offering new and improved process innovations (Refs. 1 and 2). Chemical acetylene with DMF solvent is one of these technological breakthroughs, and an especially important one for gear heat treatment.

Low-pressure carburizing (LPC) has proven itself the technology of choice for precision-carburizing of high-performance gearing (Refs. 3 and 4). In recent years acetylene and acetylene-based mixtures have become the preferred choice in the industry (Ref. 5). What users are discovering is that the type of acetylene being used has an enormous impact on productivity and quality.

## Technical Advantages

Acetylene helps shorten carburizing cycle times and improves uniformity of case depth. This is due in part to its higher carbon flux value (Table 1) and an ability to penetrate blind holes, with 12:1 (Ref. 6) through 20:1 (Ref. 7) length-over-depth ratios now possible. An example: when using acetylene for low-pressure vacuum carburizing, the case depth in the root of gear teeth approaches 90 percent of that in the active flank, making it an extremely attractive hydrocarbon choice.

Carbon flux—that is, the transfer of carbon to the steel surface from the source supplying the carbon—depends on the actual load surface area and carbon yield (Table 2), or carbon availability from the carburizing gas that is used. The carbon yield is the amount of carbon transferred into the parts, relative to the amount of carbon supplied to the treatment chamber by injecting the carburizing gas. For acetylene, the carbon yield has been found to be in the range of 65 percent or greater (Refs. 2 and 7). This has been independently verified in a number of field installations (Refs. 1 and 8); no other hydrocarbon gas approaches this value. The amount of transferred hydrocarbon is a function of several factors, including:

- Length of the pulse
- Temperature
- Gas volume (i.e., flow) into the vessel
- Pulse parameters (constant vs. variable flow)
- Surface area of the load

Gas purity has also been found to increase carbon yield (Ref. 8), with more carbon being available at the part surface per cubic-meter (cubic foot) of gas injected.

## The LPC Story

The history of vacuum carburizing (Table 3/OR SIDEBAR) is a fascinating one. The process was invented in late 1968 and subsequently patented (U. S. Patent No. 3,796,615, U. S. Patent RE 29,881) by Herbert W. Western, director of research and development for C. I. Hayes, Inc., Cranston, RI. The process

**Table 1 (Ref. 9)—Carbon flux values in LPC**

Hydrocarbon Species	Dissociation Products	Average Carbon Flux (g/m <sup>2</sup> -h)
Acetylene C <sub>2</sub> H <sub>2</sub>	2C + H <sub>2</sub>	150
Cyclohexane C <sub>6</sub> H <sub>12</sub>	C <sub>x</sub> H <sub>y</sub> + C + H <sub>2</sub>	[a]
Ethylene C <sub>2</sub> H <sub>4</sub>	CH <sub>4</sub> + C	120
Methane CH <sub>4</sub>	CH <sub>4</sub> + C	<5
Propane C <sub>3</sub> H <sub>8</sub>	C <sub>x</sub> H <sub>y</sub> + C + H <sub>2</sub>	130

Notes: a) Not reported.

**Table 2 (Ref. 8)—Decomposition characteristics of hydrocarbon gases used in LPC**

Gas Species	Decomposition Characteristic <sup>a</sup>	Effectiveness <sup>b</sup> (%)
Acetylene	Catalytic	65 – 85
Methane	Thermal	5 – 20
Propane	Thermal	5 - 20

Notes

a) Thermal decomposition limits the carbon available to workload and creates a higher percentage of unwanted by-products.

b) Effectiveness in this context is another term for carbon yield.

**Table 3 (Ref. 10)—Significant developments in the history of vacuum carburizing**

Year	Activity
1968/1969	Vacuum carburizing technology invented and introduced to industry (oil quench vacuum furnaces); methane was the original hydrocarbon choice at 13 mbar (10 torr); equipment limitations slowed commercial development.
1972	The first true production vacuum carburizing furnaces were introduced; process limitations using methane were fully understood; propane was introduced as the hydrocarbon gas of choice at 200–400 mbar (150–300 torr); soot and tar formation required increased maintenance.
1977	Experiments and patenting of acetylene-based carburizing (former Soviet Union); technology remained virtually unknown outside the Soviet Union.
1979/1980	Commercial development slows dramatically as problems with propane are difficult to overcome.
1980–1995	Various attempts at making the vacuum carburizing process more tolerant, including operation at lower operating pressures; development of high-pressure gas quenching technology; chemical acetylene with DMF solvent introduced to the non-heat treat industry by Praxair.
1994–1996	Introduction and patenting of acetylene-based, low-pressure carburizing (Japan) under 10 mbar (7.5 torr).
1999–2000	Commercialization resumes in earnest using acetylene; propane-based systems are slowly being phased out; introduction of modular vacuum carburizing technology by ALD Vacuum Technologies GmbH.
2006	Chemical acetylene with DMF solvent first introduced to heat treat industry and first used commercially at ALD.
2007–Present	Rapid growth and acceptance of vacuum carburizing technology; equipment and process synergy; growth of modular technology.

was commercialized in early 1969. However, full acceptance of the process involved nearly three decades of work and countless contributions from all over the world. The development effort involved such areas as:

- Improvements in the design and construction of vacuum furnaces
- Development of low-pressure carburizing methods
- Process optimization—especially the selection of hydrocarbon gas
- Development of optimized gas-injection methods and flow/pressure controls
- Creation of empirical databases and design of process simulators
- Development of high-pressure gas quenching technology and optimization of oil quenching techniques
- Availability of low-cost carburizing alloys specifically designed to take advantage of vacuum carburizing and gas quenching, including high-temperature capability
- Innovations in fixture materials, including the use of carbon/carbon fiber composite materials

## The Process Explained

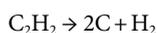
LPC is a recipe-controlled, boost/diffuse process. By contrast, atmospheric gas carburizing is controlled via carbon potential. In vacuum carburizing, the process-related parameters such as temperature, carburizing gas-flow, time and pressure are adjusted and controlled to achieve the desired case profile in the parts.

Recipe development by means of simulation programs (Fig. 1) allows the user to determine a sequence of carburizing and diffusion steps in which carbon profile as a function of depth can be predicted. Typical input parameters of the software include:

- Material
- Carburizing temperature
- Targeted carburizing depth
- Targeted surface carbon content
- Surface carbon content limit
- Load surface area

Input back into the simulation allows cycle refinements to take place.

**Why acetylene?** Acetylene is a catalytically decomposable hydrocarbon, which essentially means that it will break down into its elemental constituents (Eq. 1, Fig. 2) in the presence of a hot metal surface in a vacuum furnace operating at low pressure—typically at or below 10 mbar (7.5 Torr). Other hydrocarbons (e.g., methane, propane) are thermally decomposable, which means that they will break down immediately upon entry into the hot zone of the vacuum furnace, negating the ability of the carbon to react with the surface of the steel and creating unwanted hydrocarbon byproducts (Table 4).



The complete chemical reaction (Fig. 3) is actually more complex than that shown in Equation 1, and consists of nine separate reactions. A detailed explanation of acetylene pyrolysis can be found in the literature (Refs. 13–16).

**Types of acetylene.** Acetylene can be supplied as welding- or industrial-grade (transported in

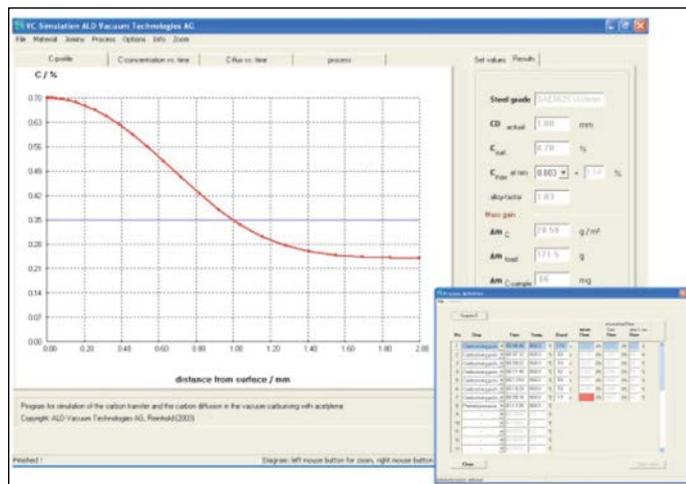


Figure 1 LPC simulation program (all photographs courtesy of ALD Vacuum Technologies GmbH).

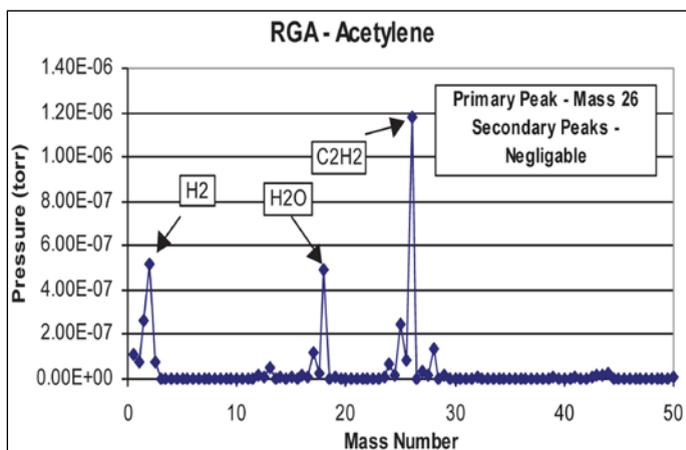


Figure 2 (Ref. 11)—Acetylene decomposition: RGA analysis.

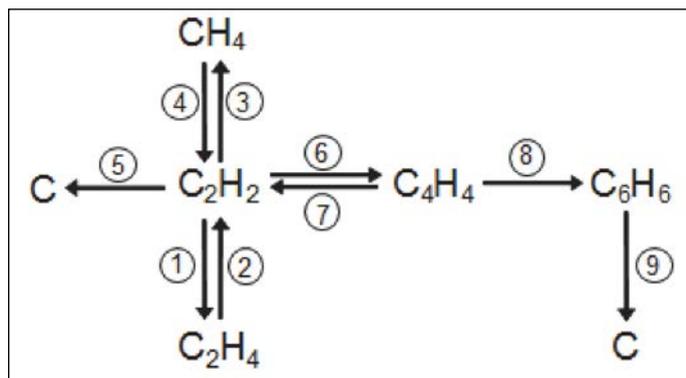


Figure 3 (Ref. 13)—Dissociation reactions during acetylene pyrolysis.

Gas Species	Undesirable Byproducts (%)	Undesirable Byproducts (species)
Industrial Acetylene (with acetone solvent)	5	Sulfides (500 ppm), phosphine/arsine (500 ppm) and ammonia (50 ppm).
Chemical Acetylene (with DMF solvent)	0.5+	Ethylene
Methane	5	
Natural Gas <sup>[a]</sup>	15	
Propane	10	Heavy hydrocarbons <sup>[b]</sup>

Notes:

a) Unsuitable for lpc (due to oxygen content and contaminants in the gas).

b) Includes propylene, iso-butane, butane, methane, pentane, n-pentene, and others.

**Table 5 (Ref. 1)—Hydrocarbon choices for LPC**

Family	Combinations
<b>Acetylene &amp; Acetylene Mixtures</b>	100% Acetylene (C <sub>2</sub> H <sub>2</sub> ) <sup>[a]</sup>
	Acetylene + Nitrogen <sup>[b]</sup>
	Acetylene + Hydrogen <sup>[c]</sup>
	Acetylene + Ethylene (C <sub>2</sub> H <sub>4</sub> ) + Hydrogen <sup>[d]</sup>
	Acetylene + Cyclohexane
<b>Cyclohexane &amp; Cyclohexane Mixtures</b>	100% Cyclohexane (C <sub>6</sub> H <sub>12</sub> ) <sup>[e]</sup>
	Cyclohexane + Acetylene
<b>Methane &amp; Methane Mixtures</b>	100% Methane (CH <sub>4</sub> ) <sup>[f]</sup>
	Methane + Propane <sup>[g]</sup>
<b>Propane &amp; Propane Mixtures</b>	100% Propane (C <sub>3</sub> H <sub>8</sub> )
	Propane + Methane <sup>[f]</sup>
	Propane + Hydrogen
	Propane + Butane (C <sub>4</sub> H <sub>10</sub> )

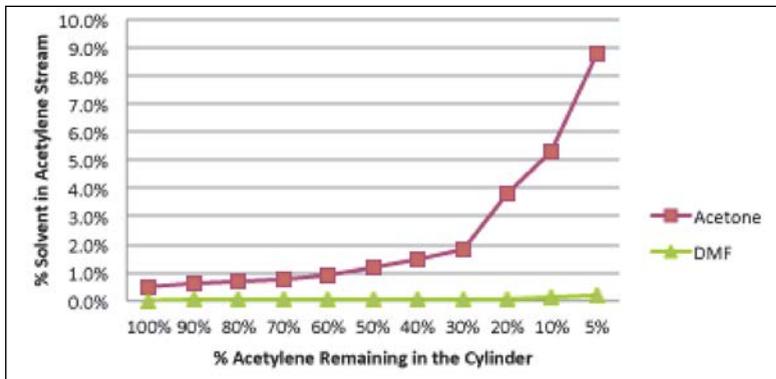
Notes:

- a) Chemical acetylene with DMF solvent preferred
- b) Typical dilutions up to 50 percent
- c) Typical dilution 7:1 (U.S. Patent 7,514,035, Solar Atmospheres Inc.)
- d) Typical ratios of acetylene to ethylene to hydrogen are 3:2:1 or 2:2:1 (U.S. Patent 7,550,049, Seco/Warwick Corp.)
- e) Cyclohexane (U.S. Patent 7,267,793, Surface Combustion, Inc.)
- f) Temperatures above 955°C (1,750°F) recommended unless plasma-assisted  
Typical dilution: 40/60 to 60/40 (methane/propane)

**Table 6 (Ref. 5)—Solubility comparison**

Property	Acetone	DMF
Boiling Point (°C)	56.5	152
Acetylene Solubility <sup>[a]</sup>	425	400

Notes: a) g/L of solution at 21°C and 17 atmospheres



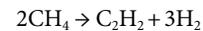
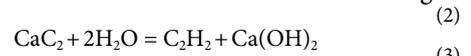
**Figure 4 (Ref. 17)—Solvent carry-through in the acetylene stream.**

**Table 7 (Ref. 17)—Percentage of solvent carry-through**

Cylinder Capacity (%)	Acetone	DMF
100	0.5%	0.010%
90	0.6%	0.012%
80	0.7%	0.015%
70	0.8%	0.018%
60	0.9%	0.020%
50	1.2%	0.027%
40	1.5%	0.035%
30	1.8%	0.049%
20	3.8%	0.072%
10	5.3%	0.132%
5	8.8%	0.207%

acetone), and chemical-grade (transported in dimethylformamide or DMF). Industrial-grade is produced by the reaction of calcium carbide and water (Eq. 2). Byproducts include sulfides, phosphine, arsine and ammonia—all of which are unwanted contaminants in vacuum carburizing.

By contrast, chemical acetylene is the result of hydrocarbon (typically, natural gas) cracking (Eq. 3), the major byproduct of which is ethylene, which is also used as a hydrocarbon source in vacuum carburizing.



**Why chemical acetylene with DMF solvent?** As early as 1999, industrial-grade acetylene in acetone and various acetylene gas mixtures (Table 5) was replacing older types of hydrocarbon gases throughout the heat treat industry. Acetylene dramatically reduced the amount of carbon build-up in the furnaces, simplifying maintenance and improving uptime productivity.

While good news for the industry, it came at somewhat of a cost premium; i.e., only 70–75 percent of industrial-grade acetylene gas could be used from each bottle to avoid introducing acetone into the process. But with the introduction of chemical acetylene with DMF solvent, as much as 95 percent of the gas could be used from each bottle. As a result, the heat treater no longer has to purchase more acetylene bottles to perform the very same process. The more bottles on-site, the more storage space needed, as well as increased handling and safety concerns (e.g., more piping and hookups). In addition, there is an ambient temperature limitation for industrial-grade acetylene bottles—they must be stored above 4°C (39°F). In summary, chemical acetylene offers higher gas purity, which, in turn, offers even more control of the carburizing process while using less gas and requiring less equipment maintenance.

**The role of stabilizing solvents.** Due to acetylene's triple bond between carbon atoms, it is fundamentally unstable and will decompose if compressed. Under pressure, an explosive exothermic gas reaction will occur if the gas pressure exceeds 100 kPa (15 psi). This makes transport of the gas under pressure dangerous, unless a stabilizing transport solvent is used. Acetone (C<sub>3</sub>H<sub>6</sub>O) and dimethylformamide (C<sub>3</sub>H<sub>7</sub>NO)—or DMF—are the transport solvents of choice.

But acetone, while a proven transport solvent, has the disadvantage of high volatility, as it tends to vaporize and leave with the acetylene gas when acetylene is withdrawn from the cylinder. This is problematic for vacuum carburizing. By contrast, DMF has a boiling point about 100°C (212°F) higher than acetone, with similar solubility. Thus DMF is less likely to volatilize (Table 6) and be carried by the gas stream into the vacuum furnace.

DMF also provides higher gas yield (Fig. 4, Table 7), as it is 40 times more stable than acetone. While acetone introduces oxygen into the process—and with it the potential for intergranular oxidation/intergranular attack (IGO/IGA)—DMF is more stable over a wider range of temperatures (-18°C to 0°C), making it far less likely to be introduced into the gas stream.

### Case Study: ALD Thermal Treatment

ALD Thermal Treatment, in Port Huron, MI has been using chemical acetylene with DMF solvent since 2006. Increased yield from individual cylinders (over 20 percent more gas) was an important consideration, as was the storage and usage of acetylene in northern climates. Flow restrictions occur with industrial-grade acetylene below 4°C (40°F). By contrast, chemical acetylene has no flow-related issues—even at -18°C (-30°F). Another requirement was purchasing in bulk as opposed to simply buying individual cylinders. Chemical acetylene can be purchased in trailer quantities (Fig. 5), with up to 200 bottles linked together as a single unit. This became an increasingly important consideration as the organization grew from an initial installation of four carburizing chambers to the present-day 40-plus chambers. Another consideration is the purchase of a trailer for dedicated use, which can be refilled by the gas supplier. In this way, cross-contamination from other users is avoided.



**Figure 5** A typical trailer set-up: chemical acetylene with DMF solvent.

A small set of bottles is still required off the trailer to continue operation while the trailer is being changed out. These bottles are re-charged with the acetylene from the trailer, unlike industrial-grade acetylene, which cannot be recharged in this manner. Finally, from a process and process control standpoint, it was soon discovered that less gas was required and a volume reduction of approximately 40 percent was realized.

Here's what ALD Thermal Treatment found regarding *industrial-grade acetylene* in individual cylinders:

- The percent of acetylene in each cylinder (solvent, volume) varies
- The number of times a bottle has been recharged affects gas purity and acetylene yield
- The number of contaminants in each cylinder varies over time

- Flow rate limitation exists, as each cylinder must flow separately into the acetylene system
- Temperature of each bottle affects both flow rate and volume of solvent drawn into the gas stream
- Purity (as delivered) varies between 95 and 98 percent
- Only 70–75 percent of a bottle can be used; if bottles are not changed promptly, you will pull contaminants from the bottom of the bottle into the vacuum furnace
- The customer pays for a fully charged bottle, even if they don't use the volume in each bottle
- The pressure in each acetylene cylinder is roughly 16.9 bar (245 PSI); the maximum withdrawal pressure is 1.03 bar (15 PSI), with a flow rate equivalent to one-seventh of cylinder capacity; each bottle must be independent in the piping system and cannot run in series
- Depending on volumes required, changing out each bottle could be an issue (time/safety)

Here's what ALD Thermal Treatment found regarding *chemical acetylene*:

- Chemical acetylene with DMF solvent is a precisely packaged gas and is ready to use (no solvent variations bottle to bottle)
- Purity is 99.5 percent or better
- The required volume of chemical acetylene is lower than acetone-based acetylene to process the equivalent product
- Weather/outdoor temperature (in upstate Michigan) is not an issue
- Chemical acetylene bottles can be assembled in series or in parallel, while staying under the maximum allowable delivery pressure of 1.03 bar (15 PSI) for piping running inside an industrial building
- Chemical acetylene comes in cluster packs or on a trailer system with bottles connected to a manifold; when it is time to change out the trailer, back-up bottles on the ground are used while the trailer is being removed and a new trailer installed; the backup bottle on the ground can then be re-charged with the DMF acetylene from the new trailer
- When the used trailer is returned, a credit is issued for the volume(s) of unused gas left in the bottles
- Back-up bottles on the ground can be re-charged repeatedly without concern of introducing contaminants
- One-line-hook-up and very easy change-out of the cluster pack or trailer, with no changing of individual bottles



**Figure 6** Load of input sun gears ready for processing.

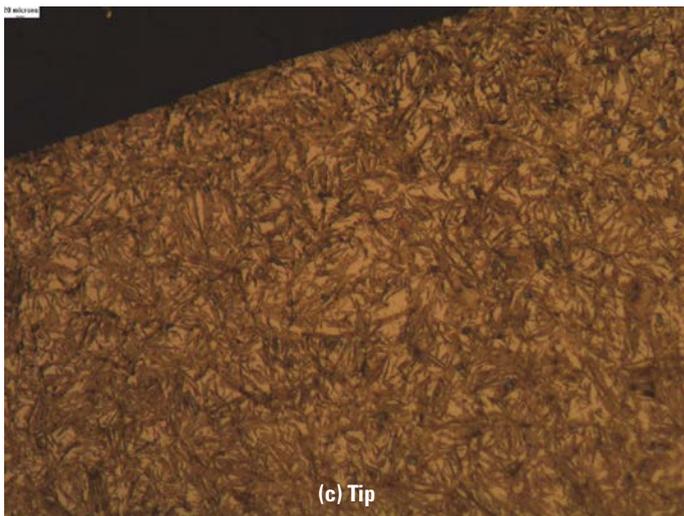
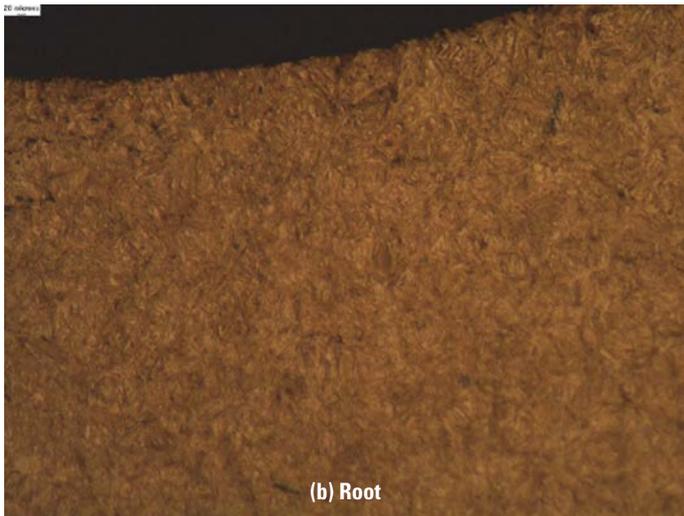
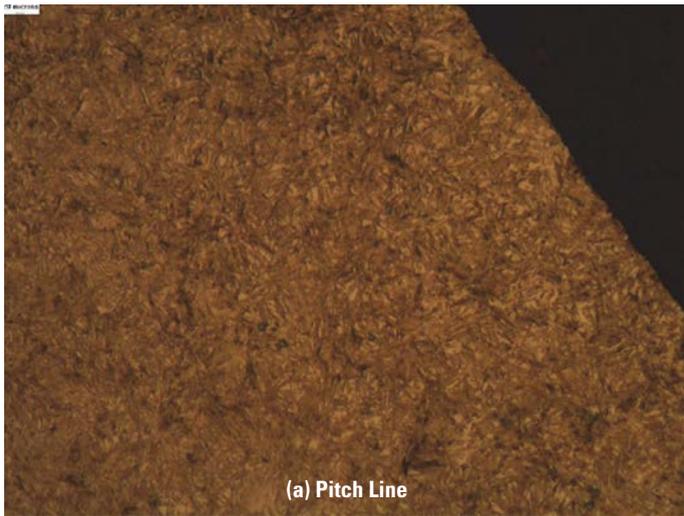


Figure 7 Sun gear microstructures at 500x.

- Maintaining flow rate is not an issue, given that the acetylene is in gaseous form; there is no concern over changing concentrations, volume or flow rates

**Application example.** Production loads of input sun gears (Fig. 6) of SAE 5120M material are low-pressure vacuum carburized with DMF acetylene to achieve a total case depth of 0.3–0.5 mm (0.012”–0.020”) at the pitch line, while achieving a surface hardness of 58–62 HRC. Bainite, excessive amounts of retained austenite and excessive carbide formation are to be avoided in the root, active flank and tip (Fig. 7).

**Lessons Learned**

- Chemical acetylene with DMF solvent provides extended equipment uptime productivity with dramatically simplified downtime, increased safety and simplicity of operation while producing superior metallurgical results. The bottom line is that the consistency of gear quality is positively impacted.
- While there are many choices for hydrocarbon, gases with low-pressure carburizing, and although very special circumstances may necessitate an alternative choice, chemical acetylene and acetylene mixtures are now clearly become viable choices, and are the hydrocarbon of choice. ⚙️

Author and lecturer **Daniel H. Herring**— “The Heat Treat Doctor”— has penned over 500 published papers and four books; the most recent is Vacuum Heat Treatment. Herring completed his undergraduate work at the University of Illinois in 1971, moving on to gain a post-graduate degree in 1974 at Chicago’s Illinois Institute of Technology (IIT). An active member of the engineering, materials and metallurgical community, Herring’s credentials include a research associate professorship at the Illinois Institute of Technology/Thermal Processing Technology Center, and consulting technical editor and monthly columnist for Industrial Heating magazine. Prior to forming The Herring Group(specializing/consulting in for solving heat treating problems in industry and heat treat and metallurgical offering services) in 1995, Herring spent over 25 working for several furnace equipment manufacturers, where he held key positions in metallurgy, engineering, international marketing, sales, research and development, and new product and business development. He is an active member of a number of technical societies, which include ASM International, APMI International, SAE International, SME and AGMA, and is a member of the American Gas Association (AGA) “Hall of Flame.”



**Robert Peters** is senior vice president for business development at ALD Own and Operate. He possesses 40-plus years of manufacturing experience, particularly in such areas as machining (tool-and-die; CNC Programming); electroplating (chrome, cadmium, copper, nickel and anodizing types 1, 2 and 3);heat treatment (LPC, nitriding, plasma carburizing, brazing), and Research and Development. Peters also serves on committees for both SAE (Society of Automotive Engineers) and AMEC, the London-based, international engineering consultancy and project management services company.



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