Final Technical Report

Agency:	US Department of Energy
Organization Element:	Office of Energy Efficiency and Renewable Energy Golden Field Office
Award Number:	DE-EE0003474
Project Title:	Novel Steels for High Temperature Carburizing
Project Period:	08/16/2010 through 04/30/2012
Recipient Organization:	Caterpillar, Inc. Attn: Tammy Anderson 14009 Old Galena Road Mossville, IL 61552
Partners:	None
Principal Investigator:	Marvin McKimpson (309) 578-5189 mckimpson_marv@Cat.com
Date of Report:	July 27, 2012

Acknowledgment:

This report is based upon work supported by the U. S. Department of Energy under Award No. DE-EE0003474.

Disclaimer:

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government, nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. Any findings, opinions, and conclusions or recommendations expressed in this report are those of the authors and do not necessarily reflect those of the United States Government or any agency thereof.

Table of Contents

List of Acronyms

NETL	National Energy Technology Laboratory
RCS	Round cornered square
TBtu	Trillion British thermal units
USDOE	United States Department of Energy

List of Figures

List of Tables

List of Appendices

Executive Summary

This program was undertaken to develop a microalloy-modified grade of standard carburizing steel that can successfully exploit the high temperature carburizing capabilities of current commercial low pressure (i.e. “vacuum”) carburizing systems. Such steels can lower the amount of energy required for commercial carburizing operations by reducing the time required for deep-case carburizing operations. The specific technical objective of the work was to demonstrate a carburizing steel composition capable of maintaining a prior austenite grain size no larger than ASTM grain size number 5 after exposure to simulated carburizing conditions of 1050^{o}C for 8 hr.[1] Such thermal exposure should be adequate for producing carburized case depths up to about 2 mm.

Such carburizing steels are expected to be attractive for use across a wide range of industries, including the petroleum, chemical, forest products, automotive, mining and industrial equipment industries. They have potential for reducing energy usage during low pressure carburizing by more than 25%, as well as reducing cycle times and process costs substantially. They also have potential for reducing greenhouse gas emissions from existing low pressure carburizing furnaces by more than 25%. High temperature carburizing can be done in most modern low pressure carburizing systems with no additional capital investment. Accordingly, implementing this technology on carburizing furnaces will provide a return on investment significantly greater than 10%. If disseminated throughout the domestic carburizing community, the technology has potential for saving on the order of 23 to 34 trillion BTU/year in industrial energy usage.

Under the program, two compositions of microalloyed, coarsening-resistant low alloy carburizing steels were developed, produced and evaluated. After vacuum annealing at 1050^{o}C for 8 hrs and high pressure gas quenching, both steels exhibited a prior austenite ASTM grain size number of 5.0 or finer. For comparison, a control alloy of similar composition but without the microalloy additions exhibited a duplex prior austenite grain size with grains ranging from ASTM grain size 3 down to ASTM grain size 1 after similar processing and thermal exposure. These results confirm the potential for using microalloy additions of Ti, B, Nb, Al, rare earths and/or N for austenite grain size control in Cr-Mo (i.e. 4000-series) low alloy carburizing steels. They also demonstrate that these microalloy additions will not compromise the processability of the steel; all three materials produced under the program could be hot worked readily using normal steel processing protocols.

To fully realize the technical and commercial potential of these steels, there is a need to continue development work using larger-scale heats. These larger-scale heats are needed to provide adequate material for fatigue testing of quenched and tempered alloys, to conduct more complete investigations of potential alloy chemistries and to provide additional material for processing studies. It will also be beneficial to carefully review intellectual property issues associated with this family of steels, since existing Japanese patent literature suggests that significant microstructural and/or process characterization work may be needed on new materials to confirm that these materials fall outside existing patent claims.

Introduction

This program was undertaken to develop a microalloy-modified grade of standard carburizing steel which can successfully exploit the high temperature carburizing capabilities of current commercial low pressure (i.e. “vacuum”) carburizing systems. Such steels can lower the amount of energy required for commercial carburizing operations by reducing the time required for deep-case carburizing operations. The specific technical objective of the work was to demonstrate a carburizing steel composition capable of maintaining a prior austenite grain size no larger than ASTM grain size number 5 after exposure to simulated carburizing conditions of 1050^{o}C for 8 hr.[1] Such thermal exposure should be adequate for producing carburized case depths up to about 2 mm.

Such carburizing steels are expected to be attractive for use across a wide range of industries, including the petroleum, chemical, forest products, automotive, mining and industrial equipment industries. They have potential for reducing energy usage during low pressure carburizing by more than 25%, as well as reducing cycle times and process costs substantially. They also have potential for reducing greenhouse gas emissions from existing low pressure carburizing furnaces by more than 25%. High temperature carburizing can be done in most modern low pressure carburizing systems with no additional capital investment. Accordingly, implementing this technology on carburizing furnaces will provide a return on investment significantly greater than 10%. If disseminated throughout the domestic carburizing community, the technology has potential for saving on the order of 23 to 34 trillion BTU/year in industrial energy usage.

At present, most commercial gas carburizing operations are done in gas-fired furnaces at 900^{o}C to 950^{o}C. Using higher carburizing temperatures will substantially shorten the time required to achieve a given carburized case depth due to the faster diffusion of carbon in austenite at the higher temperature. As shown in Figure 1, for example, increasing carburizing temperature from 950^{o}C to 1050^{o}C can shorten carburizing cycle times by as much as 60%.[2] When current commercial steels are carburized above 950^{o}C, however, most show excessive austenite grain size coarsening due to either primary or abnormal (i.e. secondary) grain growth. Figure 2, for example, shows the grain growth observed in a commercial SAE 4120 steel vacuum annealed at 1100^{o}C for 10 hrs. The large grain size is obvious. This large grain size degrades both the

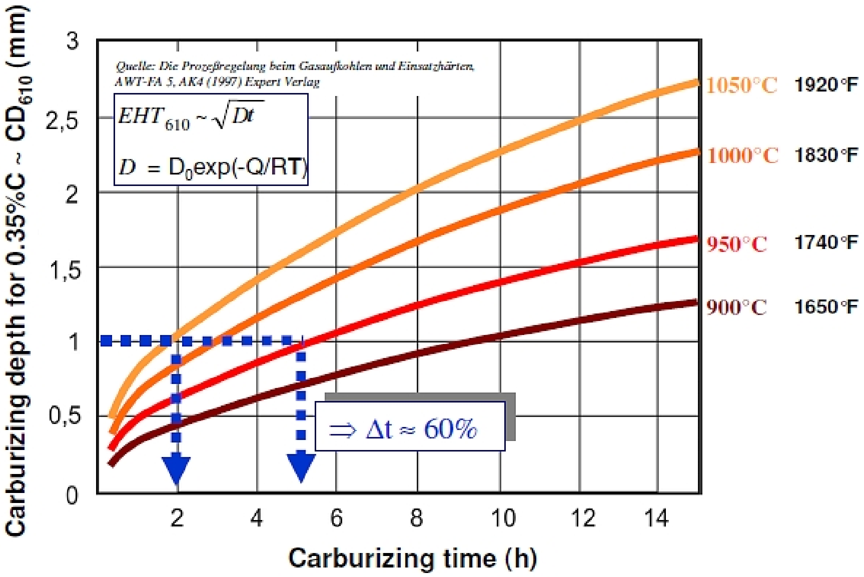


Figure 1. Effect of carburizing temperature on carburizing time.[2]

toughness and fatigue resistance of the final carburized and hardened component. If current commercial steels are deep-case carburized at these higher temperatures, they generally require an additional reheat/hardening operation—and the additional energy usage associated with this reheat operation—in order to attain acceptable mechanical properties.

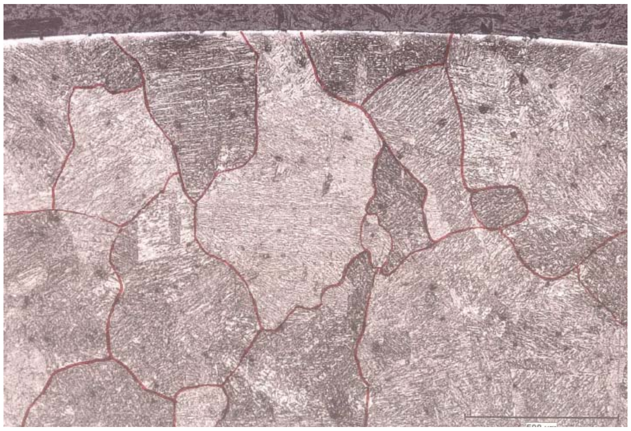


Figure 2. Modified SAE 4120 steel vacuum annealed at 1100^{o}C for 10 hrs. Micron marker is 0.5 mm.

Background

Low pressure (i.e. “vacuum”) carburizing is generally recognized as an emerging heat treat technology with substantial potential for reducing cycle times, reducing energy usage and lowering process cost. The technology was first introduced in the 1970’s to avoid the use of potentially dangerous endothermic carburizing atmospheres containing high concentrations of carbon monoxide and hydrogen. Early furnaces, however, experienced difficulties with sooting, case depth control and carbon potential control. Modern low pressure carburizing systems using acetylene injection have largely overcome these issues and are increasingly used within the industry. In 2000, the North American carburizing market consisted of approximately 4,600 carburizing furnaces. Only about 1% of these (48 units) were low pressure carburizing or plasma carburizing units. Since then, the demand for low pressure carburizing systems has grown rapidly. Although quantitative data on commercial usage of low pressure carburizing technology is difficult to obtain, it has been projected that over 640 units (13% of total North American carburizing furnaces) had been installed by 2010.[3] About three quarters of these units serve the automotive industry, where they are used to produce fuel system, powertrain/transmission, braking, and steering components. The process is also used in the industrial equipment sector for components such as transmission gears, hydraulic cams and bushings. Commercial heat treat shops use low pressure carburizing for a variety of lower-volume components, including some for the biomedical community. A small number of installations also serve the aerospace industry, where they are typically used for components such as braking systems, actuators, planetary gears and shafts.[4]

Low pressure carburizing offers a number of advantages over conventional gas carburizing. The process is carried out in a nearly oxygen-free environment, so there is no intergranular oxidation of the substrate during the carburizing cycle. Part distortion is generally lower than for conventional carburizing systems, and both temperature control and case depth uniformity are generally quite good. The process has a low consumption of carburizing gas (typically acetylene), as well as low gaseous and thermal emissions. Cycle times are generally 15-20% shorter than those for conventional carburizing due to enhanced kinetics at the surface of the part.

The process also has substantial potential for being done at temperatures 100^{o}C to 150^{o}C higher than standard atmosphere carburizing operations. Most commercial gas carburizing operations for steel are currently done in gas-fired furnaces at temperatures of 900^{o}C to 950^{o}C. Depending on required case depth, cycle times may extend up to 25 or 30 hours. Historically, carburization temperatures have been limited by both the temperature capability of the gas-fired furnaces used and the grain-coarsening resistance of commercial steels. Modern electrically-heated low pressure (i.e. “vacuum”) carburizing systems, however, can readily operate at 1100^{o}C or higher, removing many of the equipment barriers associated with higher-temperature carburizing.

Prior Investigations

This research effort was undertaken to determine if microalloy additions could be used to improve the grain coarsening resistance of carburizing steels and therefore remove the major remaining hurdle to higher-temperature, more energy-efficient commercial carburizing operations. A number of prior investigators have explored using elevated levels of nitrogen, niobium, titanium or other microalloying additions to improve the coarsening resistance of steel. The compositions evaluated, however, generally either do not provide the grain coarsening resistance needed for deep-case carburizing at higher carburizing temperatures or involve alloy additions likely to be difficult to implement in commercial steel continuous casting operations. Nakamura, for example, demonstrated that steels containing high levels of both aluminum (up to 0.11 wt%) and nitrogen (up to 0.038 wt%) were able to resist coarsening at 1100^{o}C for 8 hrs.[5] Such steels, however, are likely to be quite challenging—and expensive—to produce using current commercial continuous casting technology.

A substantial amount of work has also been done to explore the use of niobium additions to improve coarsening resistance through the formation of niobium carbonitrides. The bulk of this work, however, suggests that niobium additions alone are likely to be of limited benefit above about 1000^{o}C. Ureshino et.al. reported that Nb additions of 0.05 to 0.08 wt% in steels containing 140 to 200 ppm N were successful in resisting grain coarsening up to 1000^{o}C.[6] Alogab et. al. found that a modified SAE 8620 steel containing 0.1 wt% Nb, 0.03 wt% Ti and 90 ppm N showed significant grain coarsening in 30 to 60 minutes at 1050^{o}C and in less than 30 minutes at 1100^{o}C.[7] Nippon Steel reported work on one 0.2 wt% C carburizing steel containing 0.2 wt% Nb, 0.03 wt% soluble aluminum, and 160 ppm N that maintained an austenite grain size 7.7 after exposure at 1070^{o}C for 5 hours.[8] Klinkenberg reported that 16MnCr5 base steels containing 130 to 190 ppm N, 0.03-0.06 Nb and 0.02 Ti (1 alloy) did resist coarsening up to 1100^{o}C, but only for times up to 3 hrs.[9]

Titanium additions may have greater potential for conferring coarsening resistance for extended periods at 1050^{o}C - 1100^{o}C due to the greater stability of TiC particles compared to Nb carbonitrides. Hashimoto et. al. has reported that a 0.2 wt% C steel (modified JIS SCM420) containing up to 0.16 wt% Ti resisted coarsening at 1050^{o}C for 6 hours, and that similar levels of Ti reduced coarsening of a cold-forged JIS SCR420 steel (similar to SAE 5120) at temperatures up to 1000^{o}C.[10] High Ti levels are a concern for fatigue-critical applications such as gears due to the potential for forming large Ti carbonitrides. Nevertheless, 20CrMnTi steel containing 0.04-0.10 wt% Ti is an established commercial product in China, suggesting that carbonitride issues can be controlled.[11]

Initial Technical Strategy

At the start of the program, it was envisioned that two parallel strategies would be pursued for developing coarsening-resistant carburizing steels. First, a series of alloys would be evaluated containing various nitrogen and titanium levels in order to identify the critical levels of these two alloying elements required to achieve adequate grain coarsening resistance for deep-case carburizing at 1050^{o}C or higher. Second, thermochemical modeling would be used to identify other potential microalloy additions in steel capable of forming stable phases exhibiting a sharp drop in solubility with temperature in the austenite phase field. Such phases are of interest for coarsening-resistant steels because they have the greatest potential for producing the fine array of dispersoid particles generally considered necessary for controlling grain growth, particularly abnormal grain growth.[12] Both strategies were to be explored using a modified SAE 4120 low alloy steel base composition containing nominally 1.2 wt% Cr and 0.4 wt% Mo.

Under the original project plan, sixteen 45-kg heats of experimental steel were to be produced spread over three generations of material. All sixteen of these heats were to be procured from a domestic source. This source was contacted prior to submission of the original project proposal to confirm that they would be willing and able to produce these required heats. After contract award, the source was again contacted, and formal negotiations were initiated for procuring the first heats. In February 2011, however, the supplier reported that they would only provide experimental steels with the understanding that any information provided to them—including target compositions—would not be held in confidence. Such an arrangement was not considered acceptable because it would not preserve potential patent rights for either the prime contractor or for the U.S. Department of Energy.

Strategy Revisions

While these supplier discussions were taking place, work was also underway to finalize compositions for the first experimental alloys. Analyses of compositions published in the English literature and U.S. patent database using the Thermo-Calc thermodynamic analysis software package (Thermo-Calc Software, Inc., McMurray, PA) showed that alloys containing microalloy additions of only Ti and N were not likely to meet program objectives. As recognized in the literature, the solubility of TiN is quite small, even in austenite. Equilibrium solidification of the modified SAE 4120 base alloy composition is such that the final liquid solidifies in contact with austenite, so the alloys to be developed under the program should not be limited by the VERY low solubility of TiN in delta iron. Nevertheless, it is extremely difficult, even under equilibrium solidification conditions, to avoid precipitation of TiN in the liquid phase. Accordingly, the volume fraction of TiN dispersoids that can be formed in the solid state upon cooling from 1300^{o}C to 1100^{o}C is small—much smaller than the volume fraction of AlN expected to be present in the alloys developed by Nakamura that have demonstrated coarsening resistance for 8 hrs at 1100^{o}C.[5] Accordingly, it is not reasonable to expect that Ti and nitrogen additions alone will provide adequate coarsening resistance to meet program objectives; alternative approaches must be used.

The thermodynamic analysis work done to identify alternative stable dispersoid particles for conferring grain coarsening resistance confirmed the high stability of titanium carbonitrides, niobium carbonitrides and boron nitrides, as well as various oxides and sulfides.[*] The published literature suggests that zirconium, tantalum and rare earth nitrides also have high chemical stability, although Thermo-Calc does not contain data for these compounds. No potentially useful phosphides or unique ternary compounds were identified.

Based on these results, two revised microalloying strategies were pursued. The first was to pursue high-nitrogen alloys with microalloy additions to maximize the amount of stable nitride dispersoids present in the material. Discussions with various steelmaking personnel suggested that the maximum level of nitrogen feasible to incorporate into low alloy carburizing steels on a commercial basis was likely to be on the order of 300 ppm. Similarly, the maximum amount of Ti one is likely to be able to use in continuously-cast steels without generating excessive large TiN particles is on the order of 0.02 wt% Ti. Niobium is particularly useful as a microalloy additive, since it forms a NbC-rich phase that is soluble in molten steel but typically begins to

---

[*] The data contained in Thermo-Calc show BN to be more stable than AlN in austenite at the temperatures of interest. Other published data is not entirely consistent with this.

precipitate at ~1300^{o}C. In order to avoid cracking during hot rolling, however, it is desirable to limit Nb addition levels to about 0.06 wt% Nb. Boron levels above those typically used to improve hardenability (i.e. greater than ~ 40 ppm) are also potentially useful for forming BN, but high levels of boron are undesirable because they both generate large constituent particles and substantially lower the solidus temperature of the alloy. Low levels of rare earth additions (~ 0.05 wt%) are also likely to be desirable as long as the sulfur content of the alloy is maintained at an appropriately-low level. Subject to these constraints, the amount of each microalloy addition should be selected so that the atomic fraction of stable nitride and stable carbonitride-forming elements (excluding Al) is slightly lower than that required to combine with all of the nitrogen in the alloy. Furthermore, the aluminum level of the alloy should be chosen so that there is some free aluminum in the steel once (essentially) all the available nitrogen has been combined with the stable nitride-forming elements, stable carbonitride-forming elements and aluminum. This condition minimizes the likelihood of nitrogen gas porosity forming in the alloy during solidification.[*]

The second microalloy strategy was to provide grain coarsening resistance using primarily carbonitride rather than nitride dispersoids. Thermo-Calc simulations of various Ti-Nb-N-C steels showed that two largely-immiscible carbonitride phases typically form during solidification—one based primarily on TiN and one based primarily on NbC. Subsequent literature investigations confirmed that this is generally observed in low alloy steels.[13,14] Accordingly, one can also produce a coarsening-resistant steel using high titanium levels (e.g. up to ~0.15 wt% Ti) coupled with elevated Nb and low (as low as practical) nitrogen. In this case, the Nb is beneficial because it both increases the stability and volume fraction of the mixed Ti-Nb carbonitride phase. Keeping the N as low as possible minimizes the volume fraction of TiN-based compounds in the steel, reducing the risk of large, cuboid inclusions.

Experimental Steel Heats

These two microalloying strategies were largely developed by the time the initially-envisioned steel supplier determined that they could not commit to maintaining confidentially of the experimental steels produced under the program. Accordingly, as efforts were initiated to identify an alternate supplier for experimental steel heats, a strong emphasis was placed on identifying potential sources capable of processing the high-nitrogen steels required under the first microalloying strategy. Several sources with small-scale melting facilities were considered, including national laboratories, and two domestic metal producers. One of the domestic metal producers was eventually selected as the preferred alternative, primarily because it had capabilities for vacuum melting of 45 kg (100 lb) steel heats, had in-house capabilities for hot rolling these heats down to 32 mm round-cornered square bars, and is not currently a commercial producer of low alloy carburizing steels. Discussions with this producer were initiated in January 2011 and an agreement covering production of experimental steel heats was signed on 12 April 2011.

---

[*] As an aside, it should also be noted that residual AlN formed in the alloy is also likely to contribute to improved grain coarsening resistance of the alloy. Despite what is commonly stated in the literature, Thermo-Calc simulation results suggest that at high AlN levels, a portion of the AlN will, in fact, remain undissolved at 1100^{o}C as suggested by US patent 3155549.

Later in April, two experimental heats were ordered from the producer to confirm the company's ability to produce the required microalloy steels. The first of these heats was a high-nitrogen alloy with microalloy additions of Ti, Nb, and B. The second was a control alloy of the base Cr-Mo low alloy steel with no microalloy additions. The heats were processed down to round cornered square (RCS) bars in June 2011, and chemical analysis results on the two heats were received in July 2011. The macroalloy contents of both steels (C, Mn, Cr, Mo, etc.) matched target values quite well. The levels of critical microalloy additions, however, were outside of allowable limits. The supplier then remade both heats at their expense and processed them down to nominally 32 mm RCS bars. Chemical analyses of the remade bars, however, showed that they, too, failed to meet chemistry requirements for several critical microalloy additions. At this point, attempts to produce the required experimental steels at this metal producer were abandoned.

Three other steel producers were then contacted to see if any of these organizations might be able to produce the materials required under the project. All three organizations declined, saying that they were unable to undertake toll work at that time. The USDOE National Energy Technology Laboratory (NETL) facility in Albany OR, however, expressed a willingness to produce a limited number of steel heats for the program. This laboratory has experience with a wide range of ferrous and nickel-base alloys—including a number of high-nitrogen steels, capabilities for vacuum melting both 45 kg and 7 kg steel heats, and facilities for homogenization and hot rolling of ingots.

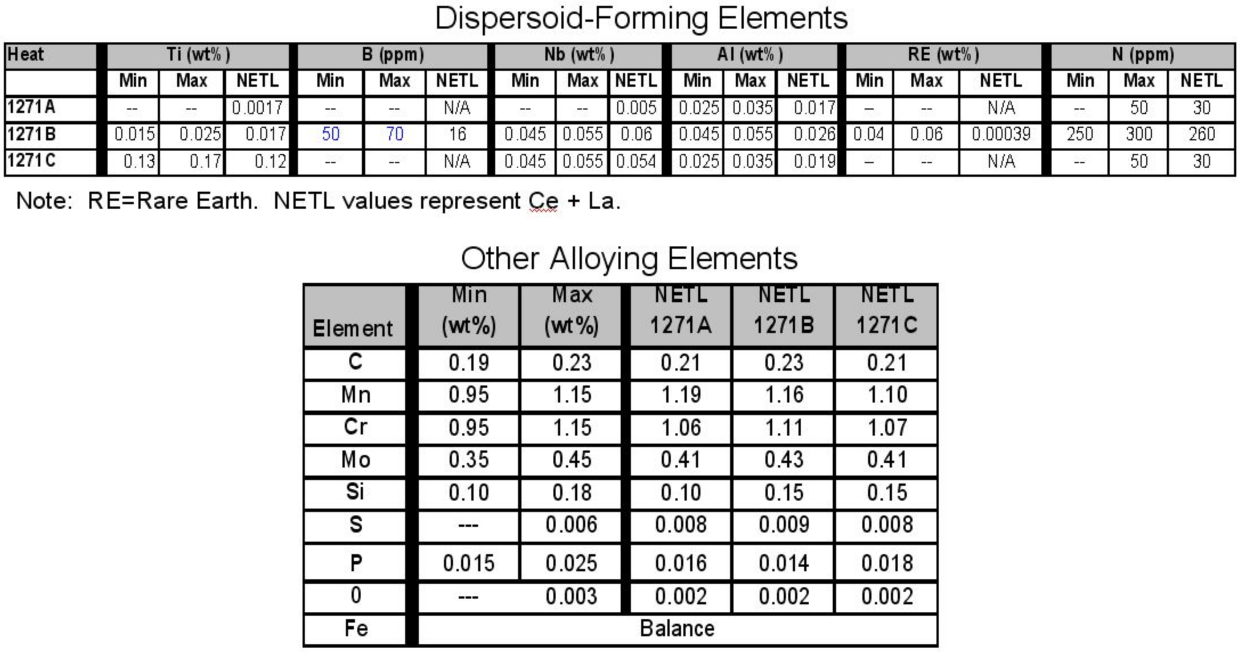
Although NETL is generally not structured to produce toll heats for industrial clients, the laboratory agreed to produce and hot work three 7-kg heats of material for the program. An agreement covering production of these materials was executed with this laboratory on 26 September 2011. The three compositions chosen for these heats were one high-nitrogen alloy, one high-titanium alloy and one microalloy-free alloy to serve as a control. The three alloys were cast in November 2011. Due to furnace issues at NETL, however, it was not possible to hot work the alloys until early January 2012. At that point, the three ingots were processed down to hot rolled slabs nominally 90 mm wide x 285 mm long by 15 mm thick.

When these three hot rolled slabs were being produced, it was envisioned that these three slabs would be evaluated and then one or more larger-scale (nominally 45 kg) heats would be produced and evaluated based on the results of these smaller-scale heats. As evaluation of the three 7-kg heats was nearing completion, however, it was learned that NETL-Albany site would not, in fact, be able to produce larger-scale heats in support of the program. Although the laboratory has the necessary facilities and technical expertise to produce the materials, it was determined by NETL-Albany site personnel that the laboratory would be unable to undertake toll work of this type at the present time. This situation was reviewed with the U.S Department of Energy. All agreed it would not be feasible to locate an alternative supplier for larger-scale heats, procure the necessary steels and evaluate these steels within the constraints of the current program. Accordingly, it was jointly agreed that the program would be terminated without production and evaluation of any larger-scale steel heats.

Results and Discussion

Target and actual compositions of the three heats produced at NETL are summarized in Figure 3. Alloy 1271A is the baseline control with no microalloy additions, Alloy 1271B is the high-nitrogen material and 1271C is the high-titanium alloy. Alloy 1271A, the control, met chemistry targets nearly exactly. Alloy 1271B showed a generally-acceptable chemistry, although levels of B, Al and rare earths—all key microalloying elements—were lower than target values. This material also showed some evidence of residual gas porosity after casting. Alloy 1271C matched its target chemistry quite well. The chemistries of all three alloys matched target values much more closely than the steels previously cast by previous suppliers and were judged acceptable for the program.

The hot working schedule for the three materials is shown in Figure 4. Note that this hot working schedule is important for two reasons. First, it affects both the size and number of dispersoid particles in each steel, thereby influencing the ability of these dispersoids to resist austenite grain coarsening. Second, it also has a strong effect on the final austenite grain size of the as-worked steel. The finer this starting grain size, the easier it will be to maintain an ASTM grain size number of 5 or finer during high temperature carburizing operations. After hot rolling, each slab was sectioned as shown in Figure 5.



Dispersoid-Forming Elements

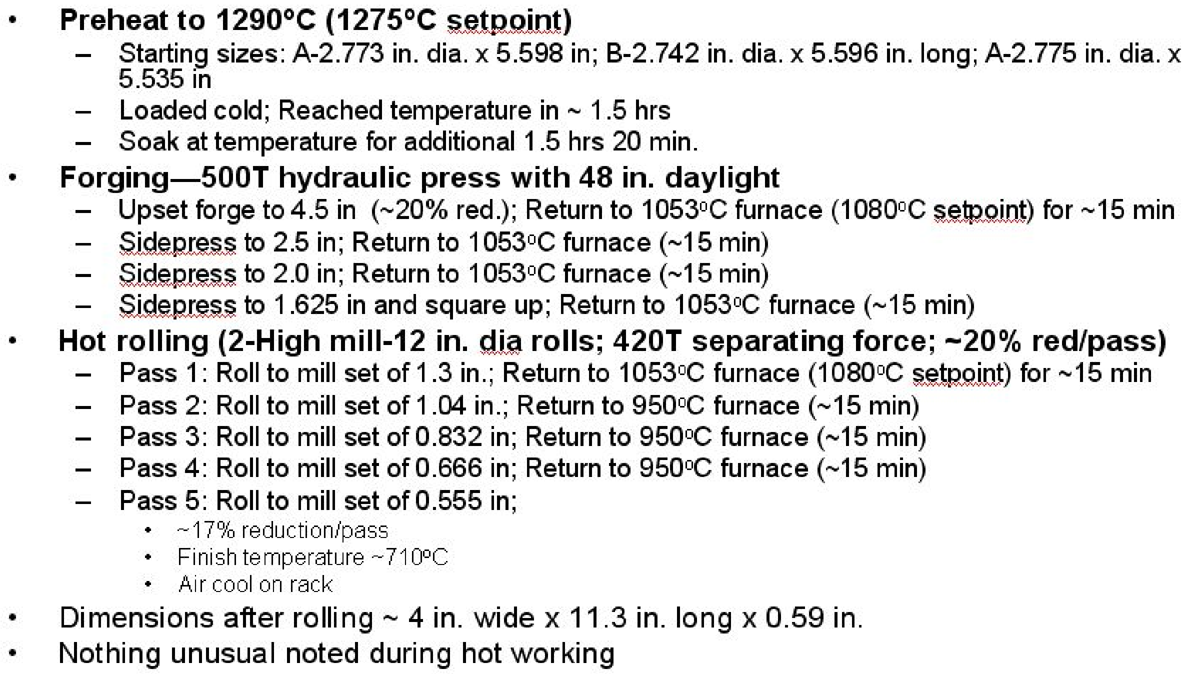
Heat	Ti (wt%)			B (ppm)			Nb (wt%)			Al (wt%)			RE (wt%)			N (ppm)		
	Min	Max	NETL	Min	Max	NETL	Min	Max	NETL	Min	Max	NETL	Min	Max	NETL	Min	Max	NETL
1271A	--	--	0.0017	--	--	N/A	--	--	0.005	0.025	0.035	0.017	–	--	N/A	--	50	30
1271B	0.015	0.025	0.017	50	70	16	0.045	0.055	0.06	0.045	0.055	0.026	0.04	0.06	0.00039	250	300	260
1271C	0.13	0.17	0.12	--	--	N/A	0.045	0.055	0.054	0.025	0.035	0.019	–	--	N/A	--	50	30

Note: RE=Rare Earth. NETL values represent Ce + La.

Other Alloying Elements

Element	Min (wt%)	Max (wt%)	NETL 1271A	NETL 1271B	NETL 1271C
C	0.19	0.23	0.21	0.23	0.21
Mn	0.95	1.15	1.19	1.16	1.10
Cr	0.95	1.15	1.06	1.11	1.07
Mo	0.35	0.45	0.41	0.43	0.41
Si	0.10	0.18	0.10	0.15	0.15
S	---	0.006	0.008	0.009	0.008
P	0.015	0.025	0.016	0.014	0.018
0	---	0.003	0.002	0.002	0.002
Fe	Balance				

Figure 3. Target and actual compositions of experimental alloys produced under the program. "Min" and "Max" represent the target compositions ranges for each alloying element. Actual alloy chemistries provided by NETL.



- **Preheat to 1290°C (1275°C setpoint)**
  - Starting sizes: A-2.773 in. dia. x 5.598 in; B-2.742 in. dia. x 5.596 in. long; A-2.775 in. dia. x 5.535 in
  - Loaded cold; Reached temperature in ~ 1.5 hrs
  - Soak at temperature for additional 1.5 hrs 20 min.
- **Forging—500T hydraulic press with 48 in. daylight**
  - Upset forge to 4.5 in (~20% red.); Return to 1053^{o}C furnace (1080^{o}C setpoint) for ~15 min
  - Sidepress to 2.5 in; Return to 1053^{o}C furnace (~15 min)
  - Sidepress to 2.0 in; Return to 1053^{o}C furnace (~15 min)
  - Sidepress to 1.625 in and square up; Return to 1053^{o}C furnace (~15 min)
- **Hot rolling (2-High mill-12 in. dia rolls; 420T separating force; ~20% red/pass)**
  - Pass 1: Roll to mill set of 1.3 in.; Return to 1053^{o}C furnace (1080^{o}C setpoint) for ~15 min
  - Pass 2: Roll to mill set of 1.04 in.; Return to 950^{o}C furnace (~15 min)
  - Pass 3: Roll to mill set of 0.832 in; Return to 950^{o}C furnace (~15 min)
  - Pass 4: Roll to mill set of 0.666 in; Return to 950^{o}C furnace (~15 min)
  - Pass 5: Roll to mill set of 0.555 in;
    - ~17% reduction/pass
    - Finish temperature ~710^{o}C
    - Air cool on rack
- Dimensions after rolling ~ 4 in. wide x 11.3 in. long x 0.59 in.
- Nothing unusual noted during hot working

Figure 4. Hot working schedule used for experimental ingots processed at NETL in January 2012. Values are reported in mixed (English and SI) units to reflect the units actually used for characterizing the quantity reported.

Grain Size and Charpy Impact Results

Sets of triplicate microstructure coupons and Charpy specimens were vacuum annealed for 8 hrs at 900^{o}C, 950^{o}C, 1000^{o}C, 1050^{o}C and 1100^{o}C. The materials were then cooled to 840^{o}C for 30 minutes, gas-quenched in high pressure helium, and tempered at 150^{o}C for 1 hr. One set of triplicate microstructure coupons and Charpy specimens of each alloy was also annealed at 900^{o}C for 1 hr, cooled to 840^{o}C for 30 min, gas-quenched an tempered at 150^{o}C for 1 hr. to serve as a control. The gas quench used for all samples generated a cooling rate intermediate between that of water and oil, and was sufficient to produce a martensitic structure in all materials. The microstructure coupons were then given an additional temper at 300^{o}C for 3 hours, polished and etched using a picral-based etch to reveal prior austenite grain boundaries.[*] Prior austenite grain size was determined by matching the observed grain size with standard ASTM grain size templates. An attempt was made to measure this grain size using automated image analysis, but the amount of manual image editing required to produce reliable grain size numbers—particularly at the finer grain sizes—was found to be prohibitive.

---

[*] This additional temper, as well as the minimum phosphorus level called out for each alloy, was needed to facilitate etching of prior austenite grain boundaries for the grain size measurements.

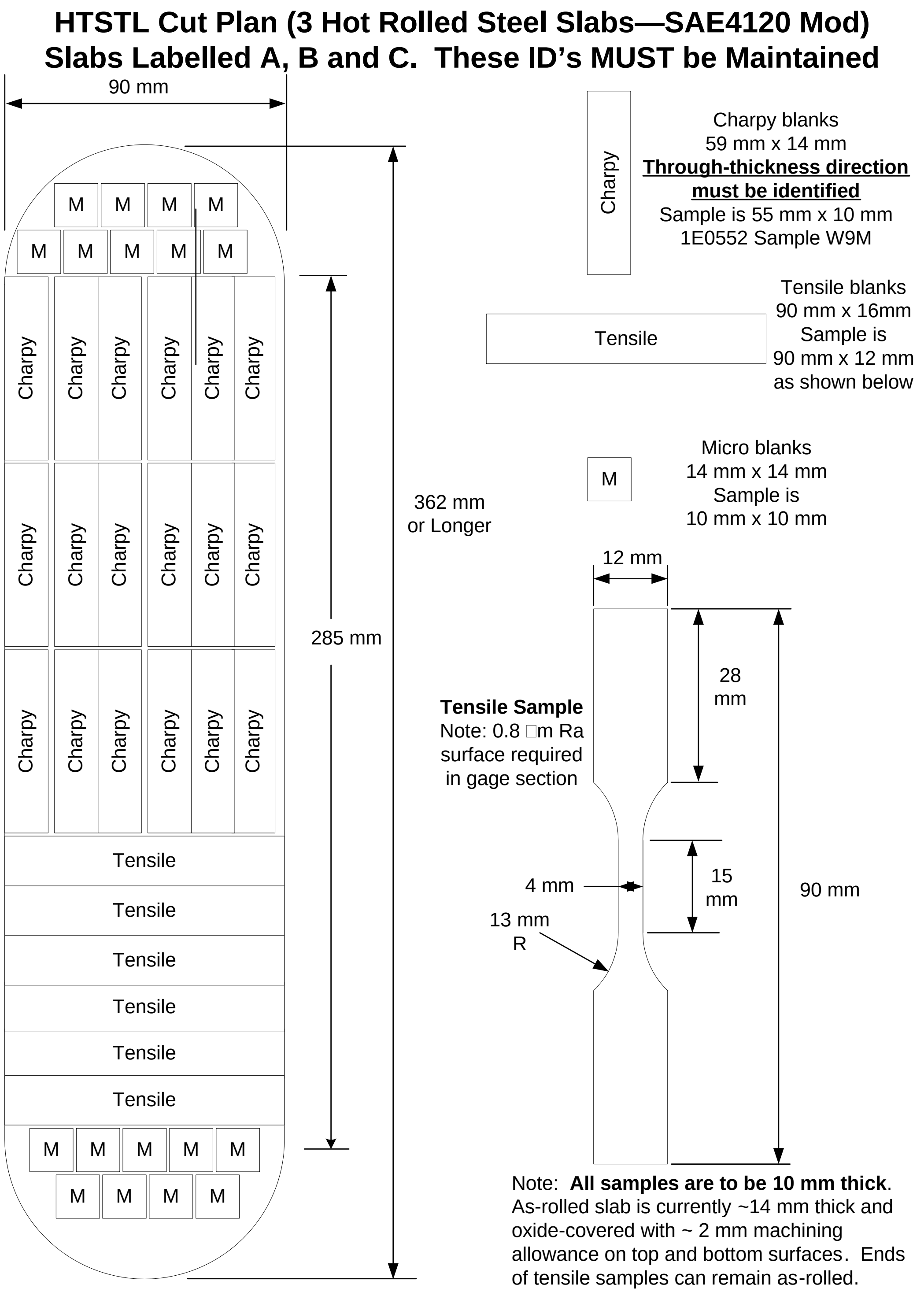
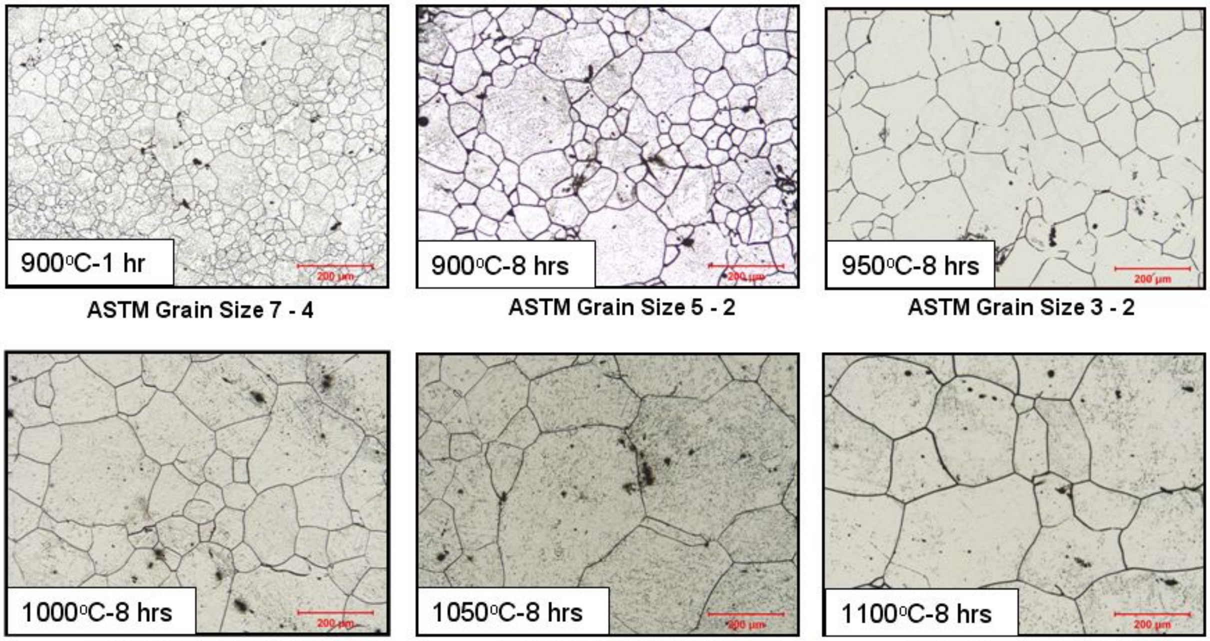


Figure 5. Cut plan used for sectioning of the three experimental billets hot worked at NETL.

After quenching and tempering, the Charpy coupons were finish-machined, the required notch was cut in each sample using electrodischarge machining, and the samples were given a 16-hr bakeout to eliminate any potential for hydrogen embrittlement. Each coupon was then impact-tested at room temperature.

The prior austenite grain sizes observed in the three materials are shown in Figures 6, 7 and 8. As shown in Figure 6, Alloy 1271A, the microalloy-free control exhibited a duplex microstructure with ASTM grain size numbers ranging from 5 down to 2 after 8 hours at only 900^{o}C. In contrast, both Alloys 1271B and Alloy 1271C exhibited grain sizes smaller than ASTM grain size number 5 after being held at 1050^{o}C for 8 hrs. Both Alloys 1271B and 1271C exhibited duplex grain structures after annealing at 1100^{o}C. Alloy 1271C, however, appeared slightly more resistant to grain coarsening than Alloy 1271B, since it exhibited a maximum ASTM grain size number of only 4 after the 1100^{o}C exposure. Both Alloy 1271B and Alloy 1271C did contain occasional angular titanium carbonitride particles. Alloy 1271C also contained a small, gray clustered phase. Both of these phases are shown in Figure 9. Energy-dispersive spectroscopy suggested this phase to be a complex Ti-Fe carbosulfide, probably one similar to the $Ti_4C_2S_2$ predicted from Thermo-Calc analysis.

Charpy impact data obtained on the various materials are summarized in Figure 10. Each bar represents the average of the three Charpy impact samples processed at the indicated condition. Not surprisingly, Alloy 1271A, the microalloy-free control, showed higher impact toughness than either experimental steel at all conditions tested. The toughnesses of Alloys 1271B and

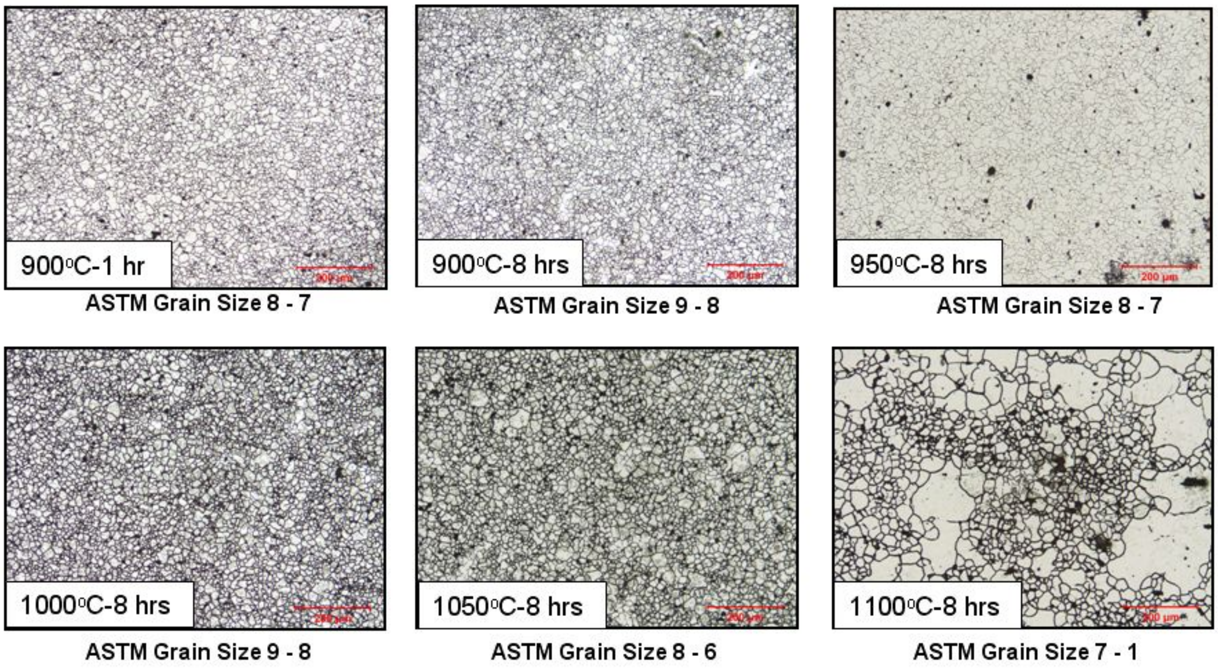


ASTM Grain Size 7 - 4 | ASTM Grain Size 5 - 2 | ASTM Grain Size 3 - 2

ASTM Grain Size 3 - 0 | ASTM Grain Size 3 - 1 | ASTM Grain Size 3 - 1

Note: first grain size number indicates finest grain size and second indicates largest grain size

Figure 6. Grain size observed in Alloy 1271A as a function of thermal exposure conditions.



ASTM Grain Size 8 - 7

ASTM Grain Size 9 - 8

ASTM Grain Size 8 - 7

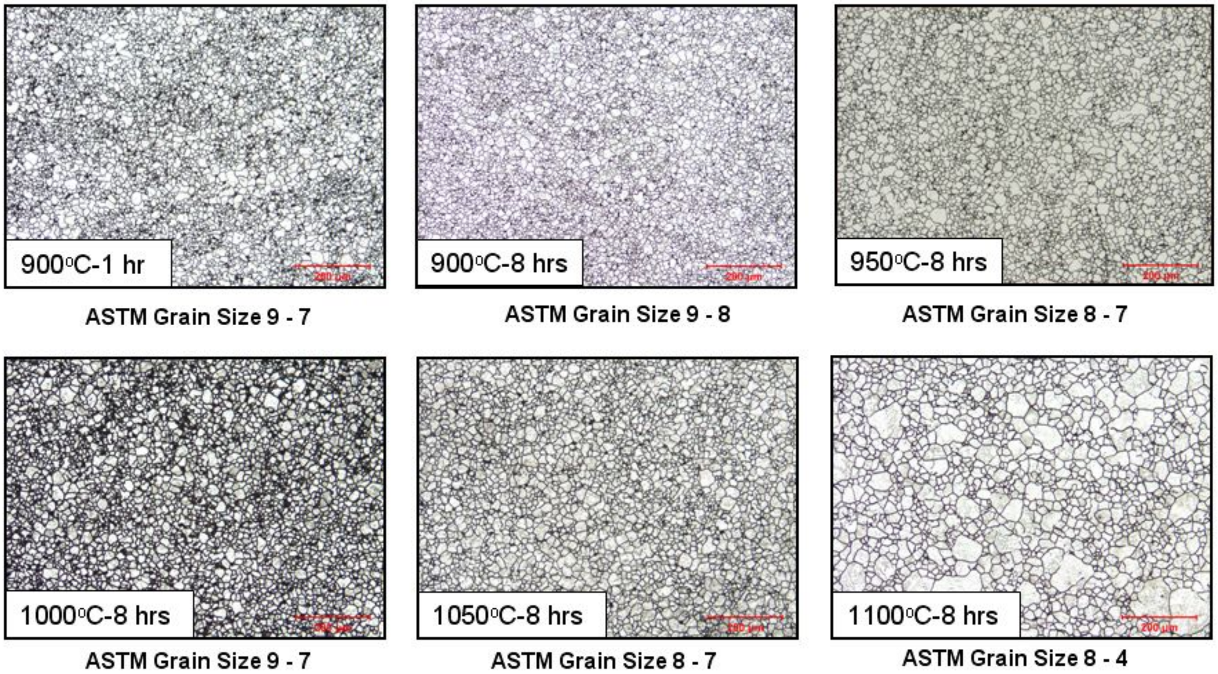
ASTM Grain Size 9 - 8

ASTM Grain Size 8 - 6

ASTM Grain Size 7 - 1

Note: first grain size number indicates finest grain size and second indicates largest grain size

Figure 7. Grain size observed in Alloy 1271B as a function of thermal exposure conditions.



ASTM Grain Size 9 - 7

ASTM Grain Size 9 - 8

ASTM Grain Size 8 - 7

ASTM Grain Size 9 - 7

ASTM Grain Size 8 - 7

ASTM Grain Size 8 - 4

Note: first grain size number indicates finest grain size and second indicates largest grain size

Figure 8. Grain size observed in Alloy 1271C as a function of thermal exposure conditions.

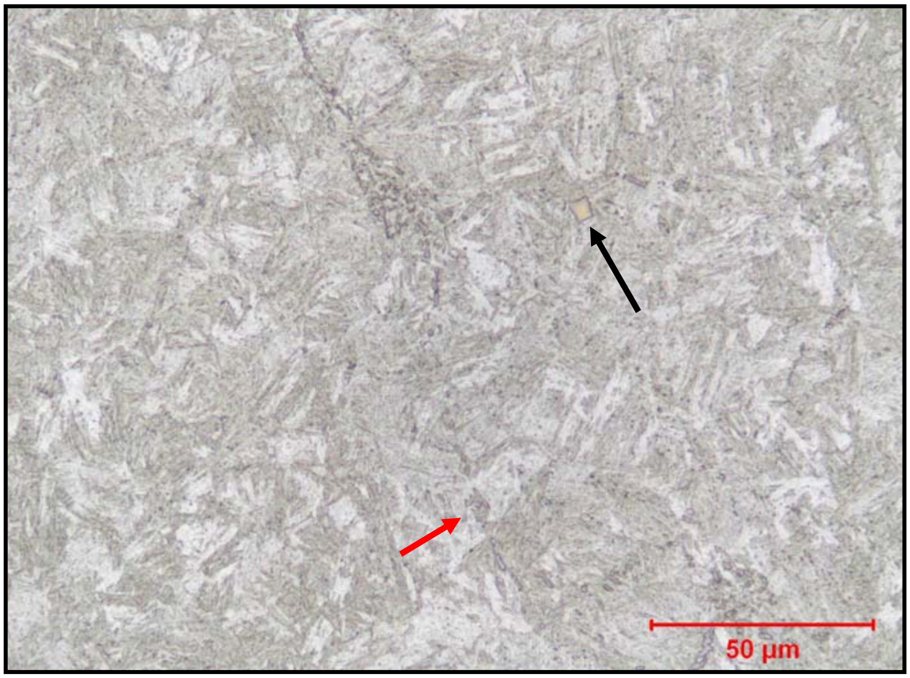


Figure 9. Titanium-rich phases observed in Alloy 1271C. The cuboid particle indicated by the black arrow is a nitrogen-rich titanium carbonitride particle. The lighter-gray particles indicated by the red arrow are complex titanium carbosulfides.

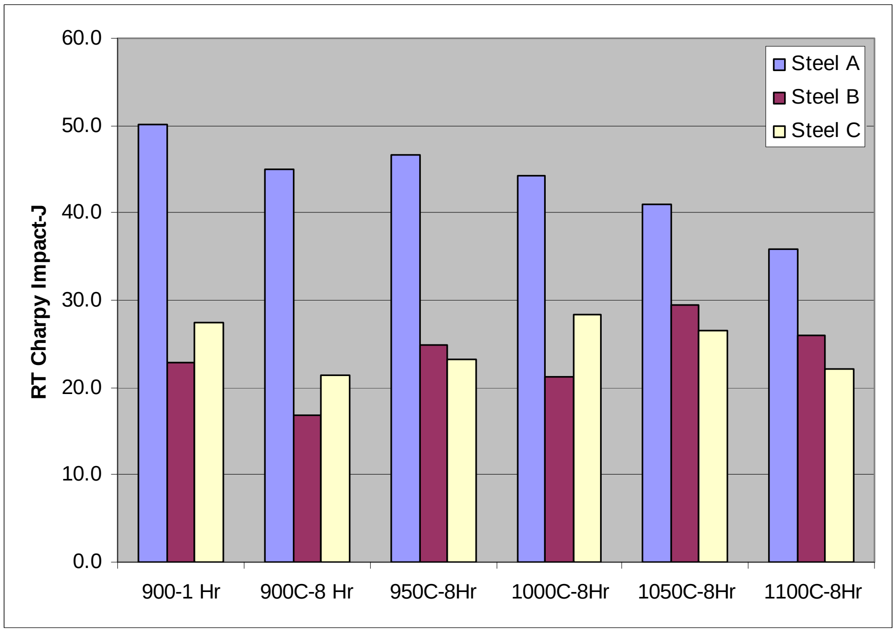


Figure 10. Room temperature Charpy impact values observed in each of the quenched and tempered experimental alloys as a function of prior thermal exposure. Alloys A, B and C refer to Alloys 1271A, 1271B and 1271C, respectively.

Alloy 1271C were comparable, although the Alloy 1271B data showed slightly more scatter. This additional scatter may be due to the residual gas porosity observed in the material. Several of the Alloy 1271B Charpy fracture surfaces showed features strongly suggestive of incompletely-healed gas porosity in the material.

Tensile Results

These metallographic and impact toughness results confirmed that both Alloys 1271B and 1271C exhibited sufficient grain coarsening resistance to maintain a prior austenite grain size of no larger than 5 after vacuum annealing at 1050°C for 8 hrs. Accordingly, a set of triplicate tensile bars of each alloy was then vacuum annealed for 8 hrs at 1050°C, cooled to 840°C for 30 minutes, gas-quenched in high pressure helium, and tempered at 150°C for 1 hr using the same protocol as was used for the original microstructure and Charpy coupons. An additional triplicate set of tensile coupons was also vacuum annealed at 900°C for 1 hr, cooled to 840°C for 30 min, gas-quenched and tempered at 150°C for 1 hr. to serve as a control. All six sets of bars were then tensile-tested in accordance with standard practices.

The results obtained are shown in Table 1. The results obtained on all three materials were generally similar, confirming that the microalloy additions to Alloys 1271B and 1271C did not compromise the tensile strength of the base low alloy quenched and tempered steel. Several of the 1271B bars did show unusually low elongations to failure. As with the Charpy specimens, this was probably due to residual gas porosity in these alloys after casting.

Alloy Potential

These results indicate the excellent potential for using microalloy additions to produce low alloy steels capable of being carburized for 8 hrs at 1050°C or higher without exhibiting excessive austenite grain growth. Of the two alloys evaluated, Alloy 1271C, the high-titanium steel, exhibited slightly better coarsening resistance than Alloy 1271B, the high-nitrogen steel. It is not clear, however, whether this improved resistance arises from the innate superiority of this alloy system or from the fact that the 1271B heat produced under this program had undesirably-low levels of B, Al and rare earth elements. Higher levels of these elements would have increased the volume fraction of stable nitrides present in the alloy at 1100°C, and may have increased its coarsening resistance.

Table 1. Tensile properties observed in experimental alloys after thermal exposure. Each value represents the average of triplicate measurements.

Alloy	Thermal Exposure	Tensile Strength (MPa)	Yield Strength (MPa)	Strain to Failure (%)
1271A	1050°C-8 Hrs	1464	1112	18.3
1271B	1050°C-8 Hrs	1460	1216	8.0
1271C	1050°C-8 Hrs	1408	1099	20.0
1271A	900°C-1 Hr	1455	1134	22.3
1271B	900°C-1 Hr	1483	1218	8.7
1271C	900°C-1 Hr	1433	1161	19.7

Both alloy systems appear to have significant potential for optimization. The target levels of Ti, B, Nb, rare earths and nitrogen in Alloy 1271B all represented “best guesses” of reasonable limits for this alloy in continuously-cast commercial alloys. Higher levels of these elements would likely confer greater grain coarsening resistance. If these higher levels can be consistently achieved in standard commercial practice without causing nitrogen porosity or other processing difficulties, the resulting steels are likely to have even better coarsening resistance than the alloy evaluated under this program. Similarly, the grain coarsening resistance of the Alloy 1271C material is determined primarily by the levels of Ti and Nb. If these can be increased, the coarsening resistance of the steel can probably also be increased.

As suggested above, there is also substantial potential for optimizing the thermomechanical processing schedules used for the two materials. The schedule used for these ingots was based on information taken from the literature and was subject to all of the constraints inherent in batch processing of small ingots. Although all three alloys in this study were processed using the same hot working schedule, there is also a strong probability that the optimum practices for generating a fine, stable dispersoid population of nitrides and carbonitrides as required for the Alloy 1271B material may, in fact, be different from that required to produce a fine, stable dispersoid population of carbides as required for the Alloy 1271C material.

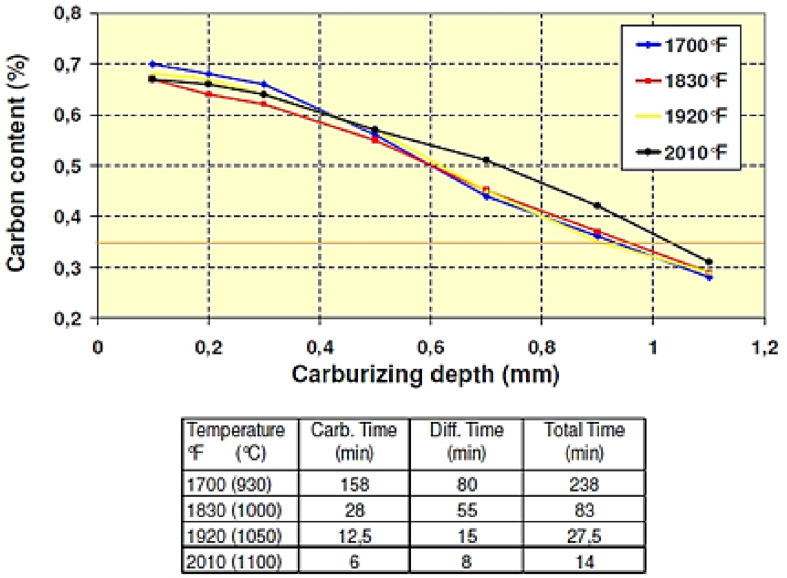
Benefits Assessment

It is generally agreed that increasing the temperature of steel low pressure carburizing operations will result in a significant reduction in process cycle time. Figure 11, for example, shows data taken from a 2008 ALD Low Pressure Carburizing Symposium presentation by Dr. K. Loeser.[2] By increasing carburizing temperature from 930°C to 1100°C, one can reduce total cycle time (carburizing time + diffusion time) for development of a 1 mm case depth from 238 minutes to 14 minutes—a reduction of almost 95%. This reduction in cycle time will result in a substantial reduction in energy usage during carburizing. Energy savings accrue from two things: 1) replacement of conventional furnace gas carburizing operations with low pressure carburizing, and 2) reductions in furnace cycle times for high temperature vacuum carburizing operations. The technology also has potential for reduced greenhouse gas emissions, particularly compared to conventional low pressure carburizing.

Energy Savings

Consider the scenario of a heat treat shop that needs to add new carburizing furnace capacity for deep-case carburizing of steel components. The shop might consider two options—conventional gas-fired carburizing furnaces using an endothermic gas atmosphere or a low pressure carburizing system. Required capacity could be achieved by either installing four new pit furnaces or one low pressure carburizing system with two large treatment chambers serviced by one set of ancillary wash, pre-treatment and quench modules. Further assume that the low pressure carburizing system, like most modern systems, is an electrically-heated system that can be used equally-well for carburizing at conventional temperatures (i.e. 900°C-950°C) or at higher temperatures—e.g. 1050°C to 1100 °C.

Relative energy usage for the conventional gas-fired furnace vs. the conventional-temperature low pressure carburizing furnace operated at conventional carburizing temperatures (900°C to 950°C) is shown in Table 2. Energy usage for the pit furnaces was estimated based on actual industrial production experience with carburizing cycles, burnout cycles and conditioning runs. Energy usage for the low pressure carburizing system was based on a vendor-supplied quote and back-up spreadsheet with estimated power, acetylene, nitrogen and water usage for both the treatment chambers and modules as a function of cycle parameters and furnace loading. Energy content of both the endothermic gas



Temperature °F (°C)	Carb. Time (min)	Diff. Time (min)	Total Time (min)
1700 (930)	158	80	238
1830 (1000)	28	55	83
1920 (1050)	12.5	15	27.5
2010 (1100)	6	8	14

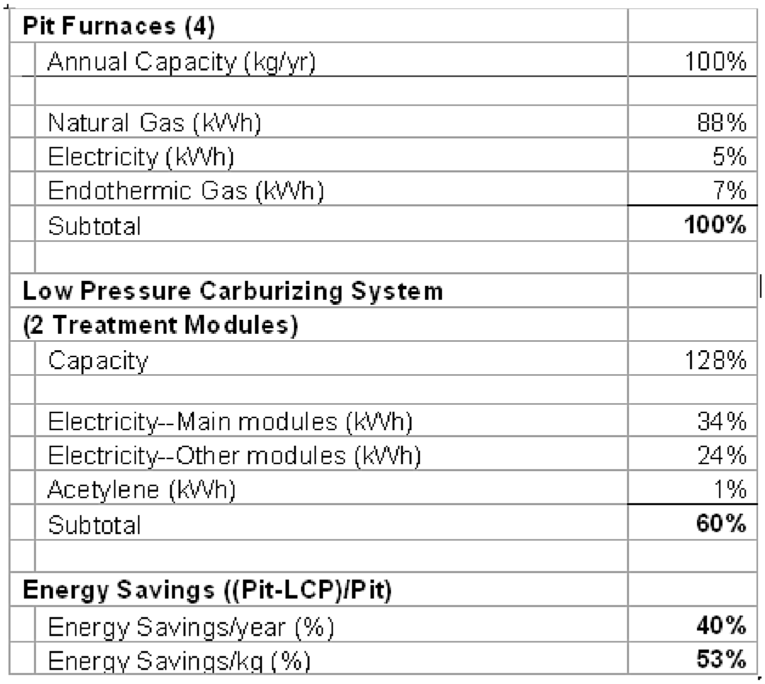
Figure 11. Effect of carburizing temperature on cycle time. (SAE 5115; 12 mbar acetylene; CD=1 mm)[2]

(conventional furnace) and the acetylene (low pressure carburizing system) was calculated as feedstock energy. For convenience, all values were converted to kWh. Note that the low pressure carburizing system—even at conventional carburizing temperatures—has potential for generating 40% or more in energy savings.[*]

High temperature carburizing will further increase these energy savings. Increasing temperature to 1050^{o}C increases the time and energy needed to heat the workload, but also dramatically shortens the hold time required for the cycle. The vendor-supplied spreadsheet mentioned above can be used to estimate these effects. The difference in heat-up energy can be found by linearly extrapolating spreadsheet values to the desired processing temperature. The change in hold time as a function of temperature can be obtained from Figure 11, and the energy difference associated with this change can be estimated from the vendor spreadsheet.[†] Power for the controls and pumps required to operate the carburizing system will vary linearly with the total cycle time (heat-up + hold) of the furnace. Acetylene usage will be similar at the two temperatures.

Using these assumptions, one can calculate total furnace power requirements for low pressure carburizing of material to a given case depth at two different temperatures. Table 3 summarizes the results obtained for low pressure carburizing of a steel to a case depth of 1.5 mm at 950^{o}C and 1050^{o}C. Carburizing the material at the higher temperature can save 28% of the energy required for the vacuum carburizing operation.

Table 2. Energy usage--carburizing furnace options.



Pit Furnaces (4)	
Annual Capacity (kg/yr)	100%
Natural Gas (kWh)	88%
Electricity (kWh)	5%
Endothermic Gas (kWh)	7%
Subtotal	**100%**
Low Pressure Carburizing System	
(2 Treatment Modules)	
Capacity	128%
Electricity--Main modules (kWh)	34%
Electricity--Other modules (kWh)	24%
Acetylene (kWh)	1%
Subtotal	**60%**
Energy Savings ((Pit-LCP)/Pit)	
Energy Savings/year (%)	**40%**
Energy Savings/kg (%)	**53%**

Note that neither the results shown in Table 2 nor Table 3 include any allowances for elimination of subsequent direct hardening operations. If steel treatment practices can be developed that retain sufficiently fine austenite grain sizes during high temperature carburizing, it is very reasonable to expect that these follow-on reheat operations can be eliminated. Furnace hardening operations are generally considered to require 25%

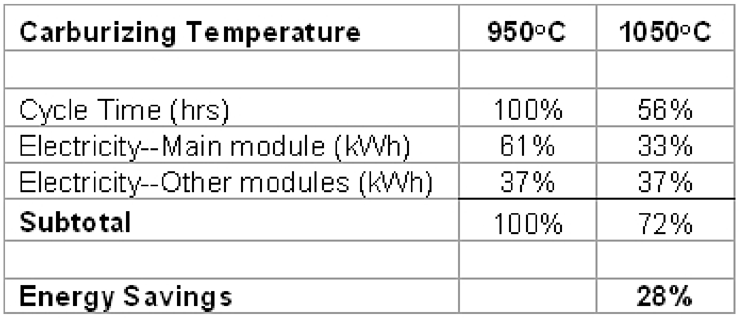
---

[*] For comparison, Appendix C of Ref. 17 estimates that case hardening in a vertical pit furnace requires 1.00 million BTU/ton and hardening in a vacuum furnace requires 0.44 million BTU/ton, corresponding to an energy savings of 56%. This is value is similar, but slightly larger than that estimated above. As an aside, it is interesting that Ref. 17 also estimates that box furnaces require 3.03 million BTU/ton of steel processed. Other types of hardening furnaces have energy requirements between 0.44 and 3.03 million BTU/ton.

[†] This approach does involve several assumptions. It is possible that energy usage/time during the hold period is overestimated due to ambiguities in the spreadsheet. Similarly, heat losses due to the higher processing temperature may be underestimated. Both effects are anticipated to be fairly small.

to 50% of the energy needed for carburizing operations, so elimination of these hardening operations can further increase the energy savings associated with high temperature low pressure carburizing.

Table 3. Effect of carburizing temperature on energy usage during carburizing.



Carburizing Temperature	**950°C**	**1050°C**
Cycle Time (hrs)	100%	56%
Electricity--Main module (kWh)	61%	33%
Electricity--Other modules (kWh)	37%	37%
Subtotal	100%	72%
Energy Savings		**28%**

At the start of the program, it was estimated that total domestic energy savings enabled by high temperature low pressure carburizing would be on the order of 20-30 trillion BTU/yr, or about 5% of the total energy consumed by the domestic heat treating industry. This estimate was developed as follows: In 2004, it was reported that the domestic heat treating industry consumed 458 trillion BTU of energy per year.[15] Allowing for a 20% increase in gross domestic product (GDP) between 2004 and 2008, the heat treating industry consumed about 550 trillion BTU of energy in 2008. Although detailed statistics are not available, carburizing operations probably consume 20% to 30% of this total, or about 110 to 165 trillion BTU/year.[*] As illustrated above, high temperature low pressure carburizing may consume as little as 60% x 75% = 45% of the energy required for conventional gas carburizing at conventional temperatures. Accordingly, if all carburizing installations were converted to high temperature low pressure carburizing operations, total energy savings would be 60 to 90 trillion BTU/year. If only a third of the carburizing installations are converted to high temperature low pressure carburizing operations, total energy savings would be about 20 to 30 trillion BTU, similar to estimates contained in a recent Technical Final Report prepared under a grant funded by the\U.S. Department of Energy.[16]

Data released since the start of the program allow these data to be updated slightly. U.S. Census Bureau data released in 2005 showed the total value of product shipments for the metal treating industry (NAICS code 332811) to be $3,373,790,000 in 2004. Similar data released in 2010 and 2012 showed the total value of shipments to be $5,198,793,000 in 2008 (just before the economic slowdown of several years ago), and $4,802,648,000 in 2010. All of these values are reported in currency dollars. Using the 2008 data and adjusting these values to constant dollars based on the Consumer Price Index, this corresponds to an increase of 39% in real sales. Assuming heat treat energy usage scales linearly with product shipments, this would correspond to a 2008 energy usage of 620 trillion BTU for heat treatment operations, about 13% more than estimated in the original proposal. Accordingly, projected energy savings for the technology

---

[*] Data contained in Ref. 17 confirm the reasonableness of this estimate. This report estimates that the total process energy usage for domestic heat treating operations in 1992 was 252 trillion Btu (TBtu). Of this amount, 37.98 TBtu was used for machine case hardening of industrial machinery (SIC 35) and 30.55 was used for direct hardening and quenching of components for industrial machinery. Accordingly ~ 55% of the total energy used for direct + case hardening was used for case hardening. Assuming that 55% of the 24.84 TBtu used for endothermic atmosphere generation was also used for case hardening, the total energy used for case hardening would be ~ 51.6 TBtu or 20% of the total process heat energy used for heat treating. (Note that this value may be a slight overestimate because the case hardening category used also includes some energy used for case hardening processes other than carburizing. Nevertheless, it provides a useful benchmark.)

would also increase by 13%, raising them to 23-34 trillion BTU/yr. Essentially all of the energy saved would be electrical energy.

Greenhouse Gases

High temperature low pressure carburizing also has long-term potential for substantial reductions in greenhouse gas emissions. Conventional atmosphere carburizing furnaces are generally gas-fired. Greenhouse gas emissions from them arise primarily through combustion of the natural gas used to fire the furnace and produce the endothermic carburizing atmosphere. Low pressure carburizing furnaces, in contrast, use electricity to heat the furnace and run the various pumps required to operate the system. Most electricity in the United States is currently generated from fossil fuels. Accordingly, burning 1 kWh of natural gas generates significantly less greenhouse gas emissions than generating 1 kWh of electricity. The low pressure carburizing furnace system shown in Table 3 uses less total energy than pit furnaces of similar capacity, but will be responsible for more greenhouse gas emissions. Assuming 1 kWh of electricity is associated with emission of 0.68 kg of CO_2, the low pressure carburizing system called out in Table 3 will actually have 13% more greenhouse gas emissions than the four pit furnaces of similar capacity.

Even with current electrical generating technology, however, greenhouse gas emissions from high temperature carburizing systems will be significantly more favorable than those from conventional low pressure systems. Assuming that the energy savings associated with these systems is at least 25%, the savings in greenhouse gas emissions will also be at least 25%. In this case, greenhouse gas emissions from the low pressure system will, in fact, be less than those from a conventional gas-fired atmosphere carburizing furnace by about 12%. In the future, if greenhouse gas emissions associated with electricity generation are reduced through clean coal technology, increased use of nuclear power, wind energy or other means, the greenhouse gas comparisons between the two technologies will look much more favorable. If greenhouse-gas-free sources of electricity are developed, both conventional and high temperature low pressure carburizing systems will be essentially free of greenhouse gas emissions.

Commercialization

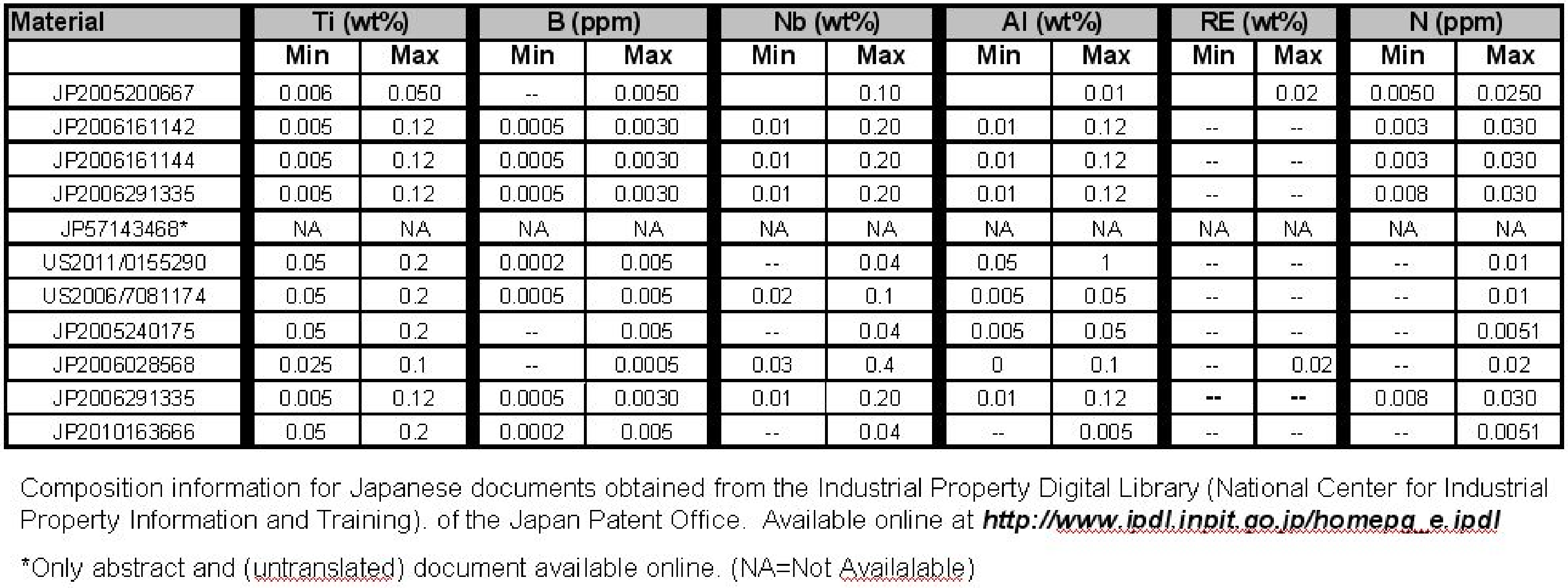
At the start of the program, it was envisioned that the steels being developed under the program would be commercialized as a joint effort between Caterpillar, the prime contractor, and a steelmaking partner organization. As described above, this partnership did not develop as anticipated. The anticipated partner chose not to participate due to concerns about intellectual property, and other potential partners contacted chose not to participate.

The commercial value and energy-saving potential for these high temperature carburizing steels remains unchanged from what was envisioned at the start of the program. The steels are anticipated to be of greatest interest to the automotive, industrial and toll processing sectors of the low pressure carburizing market, segments which probably account for more than 90% of the total market.[4] It will offer these markets both increased productivity and reduced cost through shorter cycle times and lower energy usage. The specific SAE 4120-Modified composition explored under this program is likely to be of particular interest to the industrial sector for applications such as on-highway trucks, marine engines, electrical generator sets, construction equipment and mining equipment. The technology is particularly suitable for such markets because of the high surface hardness and deep case depths required for many of these applications.

The experiences of the prime contractor under this program, however, suggest that the process of commercialization for these steels may be challenging. Caterpillar, the prime contractor under the current program, is not well-positioned to independently commercialize these steels due to the challenges it has experienced in melting and processing experimental steel heats. In prior years, Caterpillar has successfully developed, patented and commercialized a number of steels customized for particular applications. When that work was done, however, there were substantially more options for obtaining small-scale heats of experimental steels than there appear to be at present.

Patentability and intellectual property issues will also need to be examined carefully. Based on the review of U.S. patents and published English-language literature that was done at the start of the program, there appeared to be significant opportunities for developing and patenting coarsening-resistant carburizing steels based on either high-nitrogen/low-titanium compositions or low-nitrogen/high-titanium compositions. Both approaches appear to have significant potential for generating coarsening-resistant steels free of excessive numbers of large TiN or Ti(C,N) cuboids. Accordingly, development work proceeded along these lines under the program, and culminated in Alloys 1271B and 1271C as described above. Invention disclosures covering both compositions were prepared and submitted to USDOE as required under the program. Patent searches resulting from these invention disclosures indentified several documents—particularly in the Japanese patent literature—dealing with somewhat similar materials. A summary of the Ti, B, Nb, Al, rare earth and N contents called out in these documents is shown in Table 4. Abstracts of the documents, as well as additional comments about the claims contained in these documents, are contained in the Appendix. Careful review of the global patent literature, including the documents referenced in Table 4, may be required in order to determine how new generations of coarsening-resistant alloys similar to those explored under this program can be commercialized most effectively.

Table 4. Composition data for various coarsening-resistant steel alloys compiled from the patent literature.



Material	Ti (wt%)		B (ppm)		Nb (wt%)		Al (wt%)		RE (wt%)		N (ppm)	
	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max
JP2005200667	0.006	0.050	--	0.0050		0.10		0.01		0.02	0.0050	0.0250
JP2006161142	0.005	0.12	0.0005	0.0030	0.01	0.20	0.01	0.12	--	--	0.003	0.030
JP2006161144	0.005	0.12	0.0005	0.0030	0.01	0.20	0.01	0.12	--	--	0.003	0.030
JP2006291335	0.005	0.12	0.0005	0.0030	0.01	0.20	0.01	0.12	--	--	0.008	0.030
JP57143468*	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
US2011/0155290	0.05	0.2	0.0002	0.005	--	0.04	0.05	1	--	--	--	0.01
US2006/7081174	0.05	0.2	0.0005	0.005	0.02	0.1	0.005	0.05	--	--	--	0.01
JP2005240175	0.05	0.2	--	0.005	--	0.04	0.005	0.05	--	--	--	0.0051
JP2006028568	0.025	0.1	--	0.0005	0.03	0.4	0	0.1	--	0.02	--	0.02
JP2006291335	0.005	0.12	0.0005	0.0030	0.01	0.20	0.01	0.12	--	--	0.008	0.030
JP2010163666	0.05	0.2	0.0002	0.005	--	0.04	--	0.005	--	--	--	0.0051

Composition information for Japanese documents obtained from the Industrial Property Digital Library (National Center for Industrial Property Information and Training). of the Japan Patent Office. Available online at ***http://www.ipdl.inpit.go.jp/homepg_e.ipdl***

*Only abstract and (untranslated) document available online. (NA=Not Availalable)

Accomplishments

Under this program, two compositions of microalloyed, coarsening-resistant low alloy carburizing steels were developed, produced and evaluated. After vacuum annealing at 1050^{o}C for 8 hrs and high pressure gas quenching, both steels exhibited a prior austenite ASTM grain size number of 5.0 or finer. For comparison, a control alloy of similar composition but without the microalloy additions exhibited a duplex prior austenite grain size with grains ranging from ASTM grain size 3 down to ASTM grain size 1 after similar processing and thermal exposure. These results confirm the potential for using microalloy additions of Ti, B, Nb, Al, rare earths and/or N for austenite grain size control in Cr-Mo (i.e. 4000-series) low alloy carburizing steels. Invention disclosures covering the compositions of the coarsening-resistant alloys have been filed.

Thermochemical modeling using Thermo-Calc has shown that vanadium has little value as a microalloy addition for improved austenite grain coarsening resistance at 1050^{o}C – 1100^{o}C due to the high solubility of VN and VC in this temperature range. Thermo-Calc results also indicate that AlN—despite some of the comments made in the literature—is surprisingly useful as a grain-boundary-pinning additive in this temperature range. Aluminum nitride does begin to dissolve in austenite at temperatures below 1050^{o}C as is commonly reported in the literature. If the volume fraction of aluminum nitride is relatively high, however, a significant amount of material remains undissolved at 1100^{o}C. Even at fairly low titanium levels, TiN and nitrogen-rich Ti(C,N) begin to precipitate in the liquid during casting and—at least in the austenite phase field—show little change in solid solubility with temperature. Boron nitride shows similar—or slightly greater—stability than AlN, but B additions cause a substantial reduction in the solidus temperature of the alloy. Niobium additions are particularly useful for grain size control because Nb readily forms a carbide that can dissolve significant amount of both Ti and N and NbC-based phases generally precipitate below the solidus of the alloy. For carburizing steels, the level of Nb additions appears to be limited primarily by concerns about hot cracking during processing.

Experimental hot working of the three experimental alloys produced under the program showed that microalloy additions of Ti, B, Al, and rare earth elements (at the levels evaluated under the program) did not compromise the processability of the SAE 4120-Modified low alloy steel matrix. In general, the 7 kg heats of steel processed at NETL—Albany Site could be hot worked readily using normal steel processing protocols. The hot working schedule used for the three alloys was more carefully defined and controlled that might typically be used for a standard carbon steel. This, however, was driven by the need for controlled thermomechanical processing in order to produce a fine grain size and controlled dispersoid population in the as-rolled material. It was NOT driven by a need to control processing within a very tight window in order to prevent cracking or other process defects during hot working. Alloy 1271B did appear to have some porosity, presumably nitrogen gas porosity, after solidification. It is not clear whether this porosity was due to an inherent propensity for gas porosity in the target composition at the cooling rate used for casting or whether it was due to the specific chemistry (e.g. the low Al content) of this particular heat.

The program has also more clearly defined the issues which must be addressed in order to successfully commercialize coarsening-resistant low alloy steels for high temperature carburizing. The commercializing organization must, of course, have ready access to small-scale melting facilities for both material development and application evaluation. It must also have a well-defined “pipeline” for developing application data for initial commercial opportunities. There must also be a clear understanding of how intellectual property associated with the materials can be protected in commercial markets.

Conclusions

Microalloy additions of Ti, B, Nb, Al, rare earths and/or N can be used successfully for improved austenite grain size control in Cr-Mo (i.e. 4000-series) low alloy carburizing steels. After vacuum annealing at 1050^{o}C for 8 hrs and high pressure gas quenching, steels containing commercially-feasible levels of these additives exhibited a prior austenite ASTM grain size number of 5.0 or finer. For comparison, a control alloy of similar composition but without the microalloy additions exhibited a duplex prior austenite grain size with grains ranging from ASTM grain size 3 down to ASTM grain size 1 after similar processing and thermal exposure. Note that 1050^{o}C for 8 hours is similar to the thermal exposure required for carburizing a commercial low alloy steel to a depth of 2 mm.

Microalloy additions of dispersoid-forming elements did lower room temperature Charpy impact strength of the Cr-Mo low alloy steels evaluated under the program. Charpy impact values for the two materials evaluated ranged from just under 20 J to nearly 30 J for materials gas-quenched from 840^{o}C and tempered at 150^{o}C for 1 hr. Impact toughness of the materials was nearly independent of thermal exposure for conditions ranging from 1 hr at 900^{o}C to 8 hrs at 1100^{o}C. Tensile tests run on vacuum-annealed, quenched and tempered coupons confirmed that the microalloy additions did not compromise the tensile strength of the base low alloy steel.

If microalloy-modified low alloy carburizing steels can be commercialized successfully, these steels have potential for saving 23-34 trillion BTU/yr. Since these alloys are most suitable for use in electrically-heated low pressure carburizing furnaces, essentially all of the energy saved will be in the form of electrical energy. These estimates are based on an assumption that a third of current domestic carburizing capacity will be converted to high temperature low pressure carburizing operations. If the energy- and cost-savings associated with this technology are large enough to trigger additional conversion from conventional furnace carburizing to high temperature low pressure carburizing, energy savings will be somewhat greater.

With current electrical generating technology, greenhouse gas emissions from high temperature low pressure carburizing operations are likely to be at least as great as from existing conventional gas carburizing furnaces. If greenhouse-gas-free sources of electricity are developed, however, both conventional and high temperature low pressure carburizing systems will be essentially free of greenhouse gas emissions.

Recommendations

The work conducted under this program has clearly demonstrated the potential for using microalloy-modified low alloy steels for high temperature carburizing, as well as for product applications requiring very fine grained steels. To fully realize the technical and commercial potential of these steels, it is recommended that additional development work be carried out on these materials using larger-scale heats. Substantial valuable information was learned using the 7-kg heats produced under the program at NETL-Albany Site. Additional, larger-scale heats, however, will provide material for fatigue testing of quenched and tempered alloys (something that was not possible to do under the current program), as well as a much more complete investigation of potential alloy chemistries. It will also provide additional material for processing studies. As noted previously, controlled thermomechanical processing of these microalloy-modified steels after solidification will probably be essential for optimizing as-rolled grain size and grain coarsening resistance. Carefully controlled melt processing will probably also be needed to allow maximum titanium levels while avoiding potentially-catastrophic large TiN-based cuboid inclusions. Both require heat sizes substantially larger than 7 kg. Larger heat sizes will also provide additional material for applications development trials.

If this additional development work is undertaken in accordance with the Stage-Gate development process, the near-term objective must be to accumulate the information required to complete Stage 3—Concept Development. Stage 3 has five required deliverables:

- Test results of all relevant experimental and simulation work demonstrating technology performance, energy benefits, economic benefits and market attractiveness,
- Modeling or other results demonstrating scalability to commercial operations,
- Performance and test results that can be verified by end-users,
- Commercial/partner agreements as appropriate for commercializing the technology, and
- Updated technology specifications and plans for Stage 4 completion.

At the end of Stage 3, the technology is to be ready for pilot-scale commercial production and field tests by end users. For the high temperature low pressure carburizing steels being developed under this program, this means that the steels must be ready for production of small-scale commercial heats (~ 100T or larger) and trials by user organizations.

In parallel with efforts to produce and evaluate additional larger-scale heats, there is also a need to take a careful look at intellectual properties associated with this family of steels. Accordingly, it is recommended that a detailed patent review be undertaken for these materials. The existing Japanese literature also suggests that significant material and/or process characterization work (including transmission electron microscopy characterization of dispersoid populations) may be needed on new materials in order to determine if these materials do or do not fall outside existing patent claims.

The work conducted under this program has also highlighted an opportunity for additional domestic laboratory and/or pilot-scale steelmaking facilities within the United States. Technical progress on this program was significantly impacted by challenges associated with obtaining small-scale heats of experimental steels. Admittedly, some of these challenges may have been driven by a significant market pull for low alloy steels that can be readily processed at higher temperatures and/or to very fine grain sizes. It is recommended that the U.S. Department of Energy and/or other interested parties continue to consider potential innovative approaches to address this situation.

References Cited

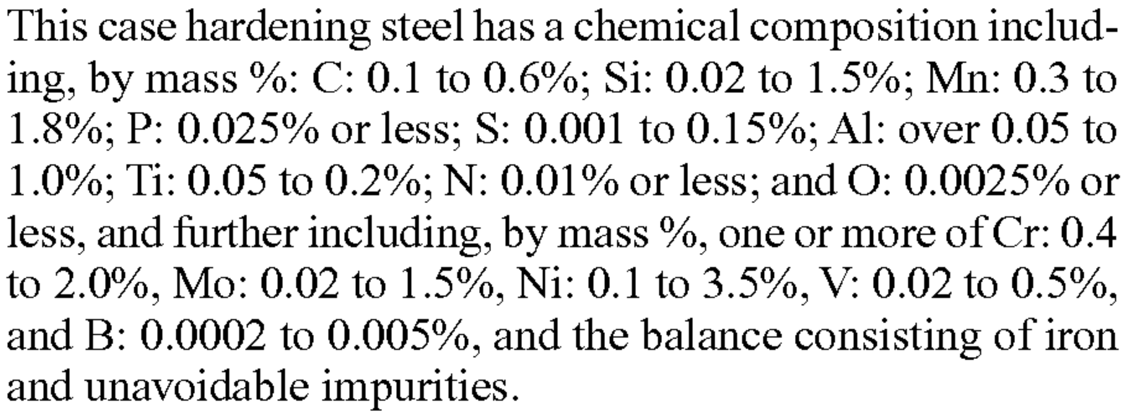
1. ASTM International, "E112-10: Standard Test Methods for Determining Average Grain Size", West Conshohocken, PA, 2010.
2. K. Loeser, "Meeting the Challenges of LPC" (presentation), Vacuum Carburizing Symposium, Dearborn MI, 23-24 Sept. 2008.
3. F. Otto and D. Herring, "Gear Heat Treatment—Part 2", Heat Treating Progress, July/August 2002. Available online at *http://www.mtvac.com/pdfs/gear_heat_treatment2.pdf* .
4. "Vacuum Carburizing", Midwest Thermal-Vac Website (*www.mtvac.com*). Accessed 9 July 2009.
5. Nakamura, H. "Steel for High Temperature Cementation", US Patent 3155549. 1964.
6. Y. Ureshino, O. Nakano, J. Fukuda and T. Fujiwara, "Development of New Alloy Steel for High Temperature Low Pressure Carburizing", SAE paper 2002-01-2000. (2002).
7. K. A. Alogab, D. K. Matlock, J. G. Speer and H. J. Kleebe, "The Influence of Niobium Microalloying on Austenite Grain Growth Coarsening Behavior of Ti-Modified SAE 8620 Steel", ISIJ International, Vol. 47 (2007). Pp. 307-316.
8. M. Kubota and T. Ochi, "Development of Anti-coarsening Extra-fine Steel for Carburizing", Nippon Steel Technical Report 88, July 2003. pp. 81-86.
9. C. Klinkenberg, "Niobium in Microalloyed Structural and Engineering Steels", Material Science Forum, Vol. 539-43 (2007). Pp. 539-543.
10. K. Hashimoto, T. Tanaka, H. Nishimori and K. Hiraoka, "Grain Growth Property of Ti-modified Carburizing Steels", SAE paper 2005-01-0985. (2005).
11. P. Zhao, Personal Communication, Caterpillar, Inc., Peoria IL, June 2009.
12. F. Humphreys and M. Hatherly, *Recrystallization and Related Annealing Phenomena*, 2nd Ed., Elsevier, New York, 2004.
13. K. Frisk, "Thermodynamic modeling of multicomponent cubic Nb, Ti and V carbides/carbonitrides", *Computer Coupling of Phase Diagrams and Thermochemistry*, 32 (2008). 326-337.
14. K. Banerjee et. al., "Nonisothermal Austenite Grain Growth Kinetics in a Microalloyed X80 Linepipe Steel, *Met. and Mat. Trans. A*, vol. 41A, Dec 2010. p. 3161-3172.
15. "Supporting Industries—Industry of the Future Fiscal Year 2004 Annual Report". Industrial Technologies Program, Energy Efficiency and Renewable Energy, USDOE. Available online at *http://www1.eere.energy.gov/industry/about/pdfs/supporting_industries_fy2004_4.pdf* .
16. D. Apelian, "Materials and Process Design for High-Temperature Carburizing: Integrating Processing and Performance", Final Technical Report--DOE Contract FC36-01ID14207. July 2007.
17. D. Gerhardt and J. Bluestein, "1992 Industrial Process Heat Energy Analysis—Final Report", Gas Research Institute Report No. GRI-96/0353. September 1996. (Prepared by Energy and Environmental Analysis, Inc., Arlington VA.)

Appendix 1

Various patent documents relating to
coarsening-resistant steels for
high temperature carburizing.

Type:	US Patent Application
Number:	US 2011/0155290
Title:	Case Hardening Steel, Carburized Component, and Manufacturing Method of Case Hardening Steel
Inventor(s) & Assignee:	Kei Miyanishi et. al.
Date:	June 30, 2011 (Publ. Date)

Abstract:



This case hardening steel has a chemical composition including, by mass %: C: 0.1 to 0.6%; Si: 0.02 to 1.5%; Mn: 0.3 to 1.8%; P: 0.025% or less; S: 0.001 to 0.15%; Al: over 0.05 to 1.0%; Ti: 0.05 to 0.2%; N: 0.01% or less; and O: 0.0025% or less, and further including, by mass %, one or more of Cr: 0.4 to 2.0%, Mo: 0.02 to 1.5%, Ni: 0.1 to 3.5%, V: 0.02 to 0.5%, and B: 0.0002 to 0.005%, and the balance consisting of iron and unavoidable impurities.

Additional Comments:

- Composition of steel further comprises less than 0.04 mass% Nb (Claim 2)
- The volume fraction of bainite after hot rolling is 30% or less, and the grain size after hot rolling is 8 to 11 as defined by JIS G0552. (Claims 3 and 4)
- The maximum diameter of Ti-based precipitates in a cross-section along any longitudinal direction is 40 μm or less. (Claim 5)
- Includes heating the steel to 1150°C or higher for 10 minutes or longer before hot rolling into wire rod or bar and the finishing temperature after hot rolling is 1000°C to 840°C. After hot rolling, the bar is cooled from 800°C to 500C at a rate of 1°C or less. (Claims 7, 9 and 10)

Type:	US Patent
Number:	7,081,174
Title:	Process for Producing Steel Products Having Improved Grain Size Properties and Machinability
Inventor(s) & Assignee:	Ryoji Hayashi and Makoto Iguchi (Sanyo Special Steel Co. Ltd.)
Date:	July 25, 2006

Abstract:

Disclosed is a production process of a steel product for induction hardening and a steel product for carburizing, having improved grain size properties and machinability. This production process comprises the steps of: providing an ingot or bloom comprising a steel comprising, by weight, carbon (C): 0.10 to 0.45% or 0.25 to 0.70%, silicon (Si): 0.03 to 1.0%, manganese (Mn): 0.2 to 2.0%, titanium (Ti): 0.05 to 0.2%, aluminum (Al): 0.005 to 0.05%, and nitrogen (N): not more than 0.01% with the balance consisting of iron (Fe) and unavoidable impurities; and subjecting the steel ingot or bloom to a series of hot working steps including the step of rolling the steel ingot or bloom into a semi-finished steel product, the step of rolling the semi-finished steel product into a steel bar or wire rod, and the step of forging the steel bar or wire rod into a product. In the above series of hot working steps, the steel is given a thermal history in which said steel is at least once heated to 1,250° C. or above, is cooled to room temperature, and is then reheated to a temperature range of 800 to 1,100° C.

Additional Comments:

- After reheating, steel is cooled from 800C to 500C at a cooling rate no more than 5C/s so that hardness is not more than 100 HRB. (Claim 1)
- Steel may also contain various levels of B, Cr, Ni, Mo, V, Nb (0.02-0.10 wt%), Pb, Bi, S and/or Ca. (Claims 2, 3 and 4)
- After hot working, the steel shall contain not more than 10,000 Ti-bearing compounds/μm^2. After carburizing, the steel shall contain not less than 50 Ti-bearing compounds/μm^2. (Claim 5)
- Patent also covers a similar steel for induction hardening that contains 0.25 – 0.70 wt% C. (Claim 7)

Type:	Japanese Patent Publication
Number:	JP2005240175A
Title:	Case Hardening Steel Having Excellent Coarse Grain Preventing Property on Carburizing and Fatigue Property, and its Production Method
Inventor(s) & Assignee:	Ochi Tatsuro et. al. (Nippon Steel)
Date:	August 9, 2005 (Publication)

Abstract:

PROBLEM TO BE SOLVED: To provide case hardening steel in which the generation of coarse grains can be stably suppressed in a carburizing quenching stage, the generation of strain and bending after the carburizing quenching can be prevented, further, the generation of coarse grains can be prevented even in high temperature carburizing, and sufficient strength properties such as rolling fatigue strength can be obtained, and to provide its production method.

SOLUTION: Steel in which 0.05 to 0.2% Ti and the other specified components are comprised in specified ranges, the content of N is limited to <0.0051%, or further, <0.04% Nb is comprised, the precipitation amount of AlN after hot rolling is limited to ≤0.01%, or further, the structural fraction of bainite after the hot rolling is limited to ≤30%, or further, the ferrite crystal grain size number after the hot rolling is controlled to No. 8 to 11 prescribed in JIS G0552, or further, in the cross-section in the longitudinal direction in the matrix after the hot rolling, the maximum diameter of Ti based precipitates by the statics of the extremes measured under the following conditions is controlled to ≤40 μm is produced.

Additional Comments:

- Content appears somewhat similar to application US 2011/0155290, although the N content is lower and this publication includes a restriction on AlN.
- Claimed chemical composition includes limits for C, Si, Mn, S, Al, Ti, Cr, Mo, Ni, V, B, P and Nb (< 0.04%) (Claims 1 and 2)
- Steel is held at 1150°C for 10 minutes or more before hot rolling into wire rod or steel bar, finishing at 1000 to 840°C, and cooling from 800°C to 500°C at a rate of 1°C or less. (Claims 6, 8 and 9)

Type:	Japanese Patent Publication
Number:	2006-028568
Title:	Steel for High Temperature Carburizing and its Production Method
Inventor(s) & Assignee:	Hatano Hitoshi et. al. (Kobe Steel Ltd.)
Date:	February 2, 2006 (Publication)

Abstract:

PROBLEM TO BE SOLVED: To provide a steel for high temperature carburizing in which the coarsening of crystal grains is prevented even at high carburizing temperature exceeding 1,000°C, and mechanical properties are hard to be deteriorated, and to provide a useful method for producing the steel for high temperature carburizing.
SOLUTION: This steel for high temperature carburizing contains 0.13 to 0.40% C, 0.030 to 0.40% Nb and 0.025 to <0.10% Ti. In the steel, carbides and/or carbonitrides satisfying the inequality [Ti]/[Nb]≥0.05 (wherein [Ti] and [Nb] denote each content (mass%) of Ti and N in the carbides and/or carbonitrides) exist by ≥2.0×107 pieces/mm2.

Additional Comments:

- In addition, to Ti and Nb, limits are specified for Si, Mn, Al, S, P, O, Ni, Cu, Cr, Mo, B, V, Zr, Hf, Ta, Ca, Mg, rare earths and N. (Claims 1, 2, 4, 5, 6, 7 and 8)
- N is specified to be below 0.02wt% and such that [Ti]-47.9[N]/14>=0.0050. (Claim 2)
- Steel contains < 10 particles/mm^2 of particles => 8 μm (Claim 3)
- Steel is heated to a temperature T (in ^{o}C) above 1250^{o}C and held for a time t (in hrs) as given by:
  $(T+273)^2$ x [log(t)+20] >= $4.64x10^7$
  before hot or cold forging. (Claims 9 and 10)
- Steel is cooled from the solidus to 1200C at a cooling rate of >=10^{o}C/minute (Claim 11)

Type:	Japanese Patent Publication
Number:	2006-291335
Title:	Steel for Case Hardening Having Excellent High Temperature Carburizing Characteristic and Workability
Inventor(s) & Assignee:	Murakami Toshio (Kobe Steel Ltd.)
Date:	October 26, 2006

Abstract:

PROBLEM TO BE SOLVED: To provide a steel for case hardening having an excellent crystal grain coarsening prevention effect exceeding the conventional level while suppressing the trouble due to addition of a large amount of Nb and Ti to be added for the purpose of preventing the crystal grain coarsening during high temperature carburizing and suppressing lowering of workability and cutting performance after forging. SOLUTION: The contents of C, Si, and Mn which are basic elements of steel products are specified and Al, Nb, Ti, V, and N are incorporated as special elements therein to make the steel exhibit the crystal grain coarsening prevention effect due to carbonitrides of Al, Nb, and Ti and to generate carbonitrides of V on a suitable amount of V. The case hardening steel having accelerated ferrite transformation, improved workability and excellent workability and hardening properties in combination is thereby obtained.

Additional Comments:

- Composition limits are claimed for C, Si, Mn, S, N (0.008 – 0.030 wt%), Al, Nb (0.01-0.20 wt%), Ti (0.005 – 0.12 wt%), V, Cr, Cu, Ni, Mo, B, Pb, Bi, Ca, Mg, Te, Zr. (Claims 1-7)

Type:	Japanese Patent Publication
Number:	2010-163666
Title:	Case Hardening Steel Having Excellent Coarse Grain Preventing Property on Carburizing and Fatigue Property, and Production Method Thereof
Inventor(s) & Assignee:	Ozawa Shuji et. al. (Nippon Steel Corp.)
Date:	July 27, 2010 (Publication Date)

Abstract:

PROBLEM TO BE SOLVED: To provide case hardening steel in which the generation of coarse grains can be stably suppressed in a carburizing and hardening process, the occurrence of strain and bending after the carburizing and hardening can be prevented, further, the generation of coarse grains can be prevented even in high temperature carburizing, and sufficient strength properties such as rolling fatigue strength can be obtained, and to provide a production method thereof.
SOLUTION: The case hardening steel is characterized in that it contains 0.05 to 0.2% Ti and the other specified components in specified ranges, the content of Al is limited to <0.005% and the content of N is limited to <0.0051%, the precipitation amount of AlN after hot rolling is suppressed, or further, the structural fraction of bainite after the hot rolling is limited to ≤30%, or further, the ferrite crystal grain size number after the hot rolling is controlled to No. 8 to 11 prescribed in JIS G0552, or further, in the cross-section in the longitudinal direction in the matrix after the hot rolling, the maximum diameter of Ti based precipitates by the statics of extremes measured under the following conditions is controlled to ≤40 μm.

Additional Comments:

- Publication appears somewhat similar to JP2005-2400175
- Composition limits are called out for C, Si, Mn, S, Al (less than 0.005 wt%) Ti (0.05 – 0.20 wt%), N (<0.0051 wt%), P, O, Cr, Mo, Ni, V, B, Zr, Mg, and Nb (<0.04 wt%). (Claims 1, 2 and 3)
- Material contains <= 30 mole% bainite and a ferritic grain size of 8 – 11 as specified by JIS G0552. (Claims 4 and 5)
- Maximum diameter of Ti-bearing particles is <= 40 mm in a longitudinal direction after hot rolling. (Claim 6).
- Steel is held at 1150°C for 10 minutes or more before hot rolling into wire rod or steel bar, finishing at 1000 °C to 840°C, and cooling from 800°C to 500°C at a rate of 1°C or less. (Claims 7, 8 and 9)

Type:	Japanese Patent Publication
Number:	2005-200667
Title:	Steel for High Temperature Carburizing, and Manufacturing Method Therefor
Inventor(s):	Hatano Hitoshi et. al. (Kobe Steel Ltd.)
Date:	July 28, 2005

Abstract:

PROBLEM TO BE SOLVED: To provide carburizing steel in which grain coarsening can be prevented even at a carburizing temperature exceeding 1,050°C and mechanical properties are hardly deteriorated, and also to provide a manufacturing method therefor. SOLUTION: The carburizing steel has a composition consisting of, by mass, 0.10 to 0.30% C, 0.05 to 0.80% Si, 0.3 to 2.2% Mn, 0.006 to 0.050% Ti, 0.0050 to 0.0250% N, <0.010% Al, ≤0.10% S, ≤0.030% P, ≤0.0030% O and the balance substantially Fe, wherein the number of Ti-containing nitrides with 10 to 250 nm grain size present in this steel is set to $\geq 2\times 10^4$ pieces/mm2.

Additional Comments:

- Composition limits specified for C, Si, Mn, Ti (0.006 – 0.05 wt%), N (0.005 – 0.025 wt%), Al (<0.010 wt%), S, P, O, Ni, Cu, Cr, Mo, B, V, Nb (<= 0.10 wt%), Ca, Mg, Zr, and rare earth elements (Claims 1, 3, 4 and 5)
- [Ti]/[N] <= 3.4 (Claim 2)
- Steel shall be cooled from the solidus to 1200^{o}C at 10^{o}C/minute or faster.

Type:	Japanese Patent Publication
Number:	2006-161142
Title:	Case-Hardening Rolled Bar Steel Having Excellent High Temperature Carburizing Property
Inventor(s) & Assignee:	Murakami Toshio et. al. (Kobe Steel Ltd.)
Date:	June 22, 2006

Abstract:

PROBLEM TO BE SOLVED: To provide a case-hardening rolled bar steel which can exhibit excellent grain coarsening prevention effect even when subjected to carburizing at a temperature higher than before in order to perform carburizing or carbo-nitriding treatment in a shorter period of time when the case-hardening rolled bar steel is used as a stock for bar-shaped machine parts such as a pulley for a CVT requiring carburizing depth.

SOLUTION: The case-hardening rolled bar steel having excellent grain coarsening prevention properties in high temperature carburizing is composed of a steel in which the contents of C, Si, Mn or the like are specified, and the contents of N, Al, Nb and Ti are also specified, and the number of precipitates is $\leq 1.0\times10^{12}$ pieces/m^2, the precipitates being formed in such a manner that two or more of the carbides, nitrides and carbonitrides with the diameter of the equivalent circle of $\geq$100 nm and comprising at least one element selected from Al, Nb and Ti are stuck or compounded.

Additional Comments:

- Composition limits are called out for C, Si, Mn, S, Cr, N (0.003 – 0.03 wt%), Al (0.01-0.12 wt%), Nb (0.01-0.20 wt%), Ti (0.005-0.12 wt%), Cu, Ni, Mo, B, Pb, Bi, Mg, Ca, Te, rare earth elements, Zr and V (Claims 1, 2, 3, 4, 5, 6 and 7)

Type:	Japanese Patent Publication
Number:	2006-161144
Title:	Carburizing Rolled Steel Having Excellent High Temperature Carburizing Property and Hot Forgeability
Inventor(s) & Assignee:	Murakami Toshio et. al. (Kobe Steel Ltd.)
Date:	June 22, 2006

Abstract:

PROBLEM TO BE SOLVED: To provide a carburizing rolled steel which can exhibit excellent grain coarsening prevention effect and also has low hot deformation resistance and excellent hot forgeability even when subjected to carburizing at a temperature higher than before in order to perform carburizing or carbo-nitriding treatment in a shorter period of time when the carburizing rolled steel is used as a stock for bar-shaped machine parts such as a pulley for a CVT requiring carburizing depth and excellent hot forgeability.
SOLUTION: The carburizing rolled steel having excellent high temperature carburizing properties and hot forgeability is composed of a rolled steel in which the contents of C, Si, Mn or the like are specified and the contents of N, Al, Nb and Ti are also specified, and regarding its microstructure, the area ratio of ferrite+pearlite is ≥90%, and also, the ferrite grain size number is ≤11.

Additional Comments:

- Publication contains limits on C, Si, Mn, S, Cr, N (0.003 – 0.030 wt%), Al (0.01 – 0.12 wt%), Nb (0.01 – 0,20 wt%), Ti (0.005-0.12 wt%), Cu, Ni, Mo, B, Pb, Bi, Mg, Ca, Te, rare earth elements, Zr and V. (Claim 1, 2, 3, 4, 5, 6, 7)
- Alloy shall contain dispersoid particles with a diameter of 15-100 nm and a number density of more than 1 x 10^7 particles/mm^2.

Type:	Japanese Patent Publication
Number:	2006-291335
Title:	Steel for Case Hardening Having Excellent High Temperature Carburizing Charcteristic and Workability
Inventor(s) & Assignee:	Murakami Toshio et. al. (Kobe Steel Ltd.)
Date:	October 26,2006

Abstract:

PROBLEM TO BE SOLVED: To provide a steel for case hardening having an excellent crystal grain coarsening prevention effect exceeding the conventional level while suppressing the trouble due to addition of a large amount of Nb and Ti to be added for the purpose of preventing the crystal grain coarsening during high temperature carburizing and suppressing lowering of workability and cutting performance after forging.
SOLUTION: The contents of C, Si, and Mn which are basic elements of steel products are specified and Al, Nb, Ti, V, and N are incorporated as special elements therein to make the steel exhibit the crystal grain coarsening prevention effect due to carbonitrides of Al, Nb, and Ti and to generate carbonitrides of V on a suitable amount of V. The case hardening steel having accelerated ferrite transformation, improved workability and excellent workability and hardening properties in combination is thereby obtained.

Additional Comments:

- Publication contains limits on C, Si, Mn, S, Cr, N (0.008 – 0.030 wt%), Al (0.01 – 0.12 wt%), Nb (0.01 – 0.20 wt%), Ti (0.005-0.12 wt%), Cu, Ni, Mo, B, Pb, Bi, Mg, Ca, Te, Zr and V. (Claim 1, 2, 3, 4, 5, 6, 7)

Type:	Japanese Patent Publication
Number:	S57-143468
Title:	High Speed Tool Steel
Inventor(s):	Fukui Shoichi (Daido Steel Co. Ltd)
Date:	September 4, 1982

Abstract:

PURPOSE: To enhance the durability, toughness, wear resistance, etc. of the resulting titled steel by providing a specified composition contg. C, Si, Mn, Cr, Mo, W, V and ≥1 kind of REM to prevent the coarsening and segregation of carbide.
CONSTITUTION: This high-speed tool steel has a composition consisting of 0.35W 1.5% C, 0.1W2.0% Si, 0.1W1.5% Mn, 2.0W10.0% Cr, 0.5W12.0% Mo, 0.5W23.0% W, 0.5W5.0% V, 0.005W0.60% in total of ≥1 kind of REM and the balance Fe with inevitable impurities while satisfying the relation of 2Mo+W=1.5W30.0%. The composition may further contain 1.0W20.0% Co and/or one or more among 0.25W1.0% Cu, 0.001W0.050% B, ≤2.0% Ti, ≤2.0% Zr, ≤2.0% Hf, ≤2.0% Y, ≤2.0% Sc and ≤0.30% N.

Additional Comments:

- Only abstract is available